The effect of physical ageing on the properties of poly(ethylene terephthalate)

A. Aref-Azar, F. Biddlestone, J. N. Hay* and R. N. Haward
The Centre for Materials Science, and The Department of Chemistry, The University of Birmingham, Birmingham B15 2TT, UK
(*Received* 15 *October* 1982)

Physical ageing rates of poly(ethylene terephthalate) have been measured, and ageing is interpreted to be associated with the conventional glass formation process, which occurs at a more rapid rate at higher temperatures. Ageing is accompanied by a marked change in mechanical properties, increased tensile yield stress and drawing stress, more localized yielding of the polymer and a marked decrease in impact strength. The fracture results have been attributed to the increased yield stress and a change in contribution of plane stress and plane strain conditions in the samples. Fracture surfaces show evidence of mixed modes of fracture.

Keywords Poly(ethylene terephthalate); physical ageing; differential scanning calorimetry; mechanical properties; fracture; glass transition

INTRODUCTION

Glassy polymers are known[1] to change their physical and mechanical properties with time when stored at temperatures close to but below their glass transition temperatures, T_g. Perhaps the best-documented effect that occurs under these conditions is the reduction in the rate of creep, but many other changes occur, including decreases in enthalpy, volume and impact strength[2-7] and changes in the distribution of rotational isomers[8-10]. Particular interest attaches to the relationship between changes in structure that occur during ageing and the several consequent changes in physical properties, as these can throw an important light on polymer structure–property relationships in general. This applies particularly to embrittlement, especially of polycarbonate, which accompanies physical ageing and for which many explanations have been advanced[2-6,11-15]. There has been some discussion on the role of internal stresses but we have recently shown that these occur when sudden cooling is employed and, although physical ageing can eliminate them (and hence cause embrittlement), this is not a general feature of physical ageing[16]. Nevertheless, in spite of a large volume of work, especially with polycarbonate, some confusion still exists and it has proved very difficult to separate embrittlement due to the simple increase in yield stress[13,14,16] from those due to plastic strain localization wholly or partly associated with strain softening[5,17].

At room temperature, poly(ethylene terephthalate) (PET) readily changes from tough to brittle fracture and in particular shows substantial changes in properties during physical ageing[7,11,12]. It was therefore decided to study changes in the physical properties that accompany physical ageing and the corresponding structural alterations that occur. A few results from other polymers have been included for comparative purposes[18].

EXPERIMENTAL

Commercial PET (sample A) was used as supplied (commercial-grade Grilene, Emser Werke AG, Switzerland). It had a viscosity average molecular weight* of $3 \times 10^4 \mathrm{g\,mol^{-1}}$. Amorphous (1 mm thick) sheets were moulded at 550K and $30 \mathrm{MN\,m^{-2}}$ pressure for 2 min followed by quenching in ice–water. Sheets 2 and 3 mm thick could not be prepared in this way since they crystallized on quenching. These were used as injected-moulded plaques as supplied by the manufacturer.

Samples were stress relieved above the glass transition temperature but below the temperature of onset of crystallization. All these samples were amorphous as determined by d.s.c. and density measurements.

A second sample of PET (sample B) was also used as supplied (an amorphous isotropic film, ICI Petrochemical and Plastics Division). Its viscosity average molecular weight was $1.6 \times 10^4 \mathrm{g\,mol^{-1}}$.

A Perkin–Elmer differential scanning calorimeter, Model 2, was used for the thermal analyses of the polymers. Its use has been extensively described elsewhere[9]. It was interfaced to a Scanning Autozero and a Tetronix Programmable Calculator to improve the accuracy of the determinations. The calorimeter's thermal response was calibrated for the heat of fusion of indium ($28.4 \mathrm{J\,g^{-1}}$) and the temperature from the melting point of zone-refined diphenyl-benzoic acid and stearic acid.

Tensile tests were made on an Instron TT-BM tensometer using standard dumbbell-shaped specimens, BS

---

* To whom communications should be addressed

* Derived from the intrinsic viscosity $\eta' = 0.98 \mathrm{dl\,g^{-1}}$ and using $\eta = 2.1 \times 10^{-4} (\bar{M}_v)^{0.82}$ in 1:1 mixture (by volume) of 1,1,2,2-tetrachloroethane/phenol.

0032-3861/83/101245-07$03.00
© 1983 Butterworth & Co. (Publishers) Ltd.

2782, cut from moulded PET sheets. Impact measurements were made on a Monsanto Charpy Impact Machine using 3 mm thick specimens, 6.35 mm × 50 mm, notched to a depth of 1.7 mm and with various notch tip radii.

Draw ratios were determined in tensile tests from the deformation of metal grids evaporated directly onto the specimen surface through a copper gauze of mesh size 64 μm square. Measurements were made under load on specimens viewed directly with a microscope tensometer, as described previously[19].

RESULTS AND DISCUSSION

Measurement of physical ageing The glass transition of physically aged specimens exhibited a marked endothermic process, as measured by d.s.c. (see *Figure 1*). This, although an artifact of the rates of heating and cooling, was a convenient way of characterizing the extent of ageing. The excess enthalpy, ΔH_t, which has developed after an ageing period t, was measured as outlined by Savill and Richardson[20] from the difference in enthalpy between a standard quenched glass and the aged glass between two fixed temperatures, below and above the transition region.

The maximum enthalpy change, ΔH_∞, is then

$$\Delta H_\infty = \Delta C_p \Delta T \qquad (1)$$

corresponding to equilibrium being achieved at the ageing temperature. ΔC_p is the difference in specific heat between quenched glass and the liquid at T_g, and

$$\Delta T = T_g - T_A$$

T_g being defined with respect to the standard quenched glass.

The extent of ageing, i.e. $\Delta H_t / \Delta C_p \Delta T$, was then observed to increase logarithmically with the ageing period t (see *Figure 2*), from which it was possible to define a relaxation time for the ageing process[21]. Over the limited temperature range studied, $\Delta T \simeq 40$K, a single Arrhenius relationship was found to describe the ageing process and an activation energy of 650 ± 100 kJ mol^{-1} was observed. This was close to the value observed for the glass formation process, as determined by the rate dependence of the quenched glass transition temperature, T_g.

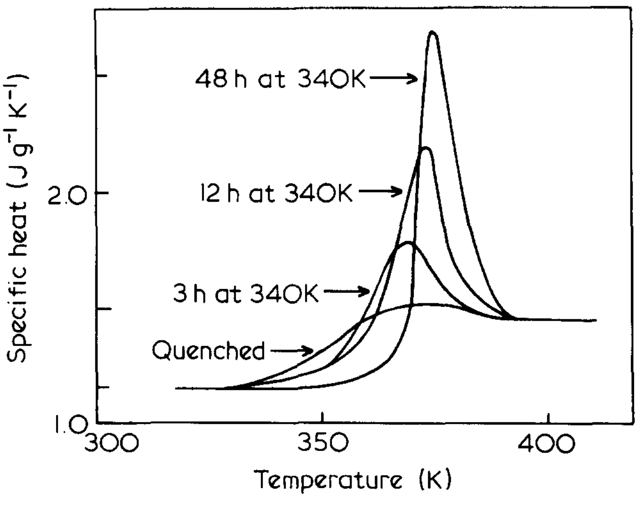


Figure 1 Endothermic ageing peaks in PET

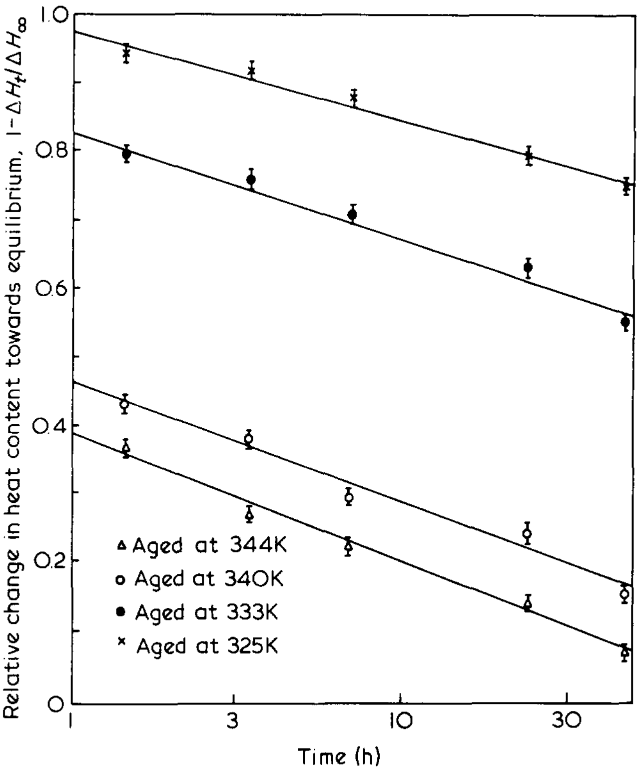


Figure 2 The relative change in ageing enthalpy towards equilibrium with time (sample A)

These very simple relationships adequately describe the ageing process and enabled PET specimens to be aged to fixed extents at intermediate temperatures.

Measurement of mechanical properties

As previously noted, the effect of physical ageing on the stress–strain curves is substantial[7,11,12] and PET behaved in an analogous fashion to that observed with polycarbonate (PC) and poly(vinyl chloride) (PVC), as shown in *Figure 3*. The most marked effect was that of increasing the yield stress (σ_y) from about 40 to 60 MN m^{-2}, and increasing the rate of fall of the stress on yielding. This latter point will be dealt with later. The increased yield stress is substantially greater than the changes observed with PC[2,5]. The drawing stress, although also increasing with ageing, did not increase as much as the yield stress.

With the higher strain-rate experiments, there was a momentary decrease in stress immediately after yielding due to a localized heating in the shear bands formed initially. This has also been observed with PVC and PC[22], and as observed previously the size of the effect increased with length of the testpiece and strain rate. Eventually brittle fracture occurred above a length of 20 cm owing to thermal runaway. Specimens which did not fracture but exhibited these thermal effects displayed a marked thinning of the specimen along the direction of the initial shear bands, which persisted in the specimen after further yielding and fracture.

In spite of the increased yield and draw stresses, the draw ratio of aged PET did not increase over that of the quenched material, being 3.35 ± 0.18 for both quenched and highly aged polymers. Ageing also had a minimal

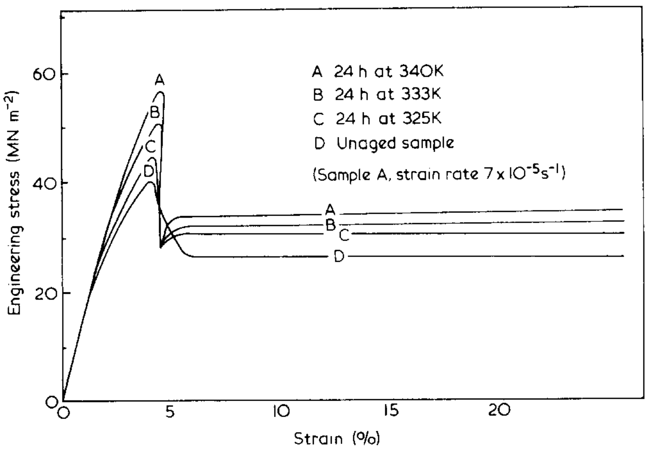


Figure 3 **The effect of ageing on engineering stress–strain curves**

effect on the tensile modulus (see *Figure 4*); this was unexpected and is under further investigation.

Yield stresses are dependent on temperature and strain rate. The effect of temperature can be seen in *Figure 5* for annealed and quenched PET. Nominally the yield stress falls close to zero at the glass transition temperature, but measured in this way the value of T_g is higher for the aged material. This, however, is consistent with *Figure 1* and indeed with any other measurement in which the material is heated and then reflects the slower thermal response of aged specimens. The thermodynamically measured T_g, defined by equating the enthalpy of the glass and the liquid, i.e.

$$H_{g,T_g} = H_{l,T_g} \tag{2}$$

does in fact decrease progressively with ageing period until at equilibrium

$$\Delta H_{\infty} = \Delta C_p \Delta T \tag{3}$$

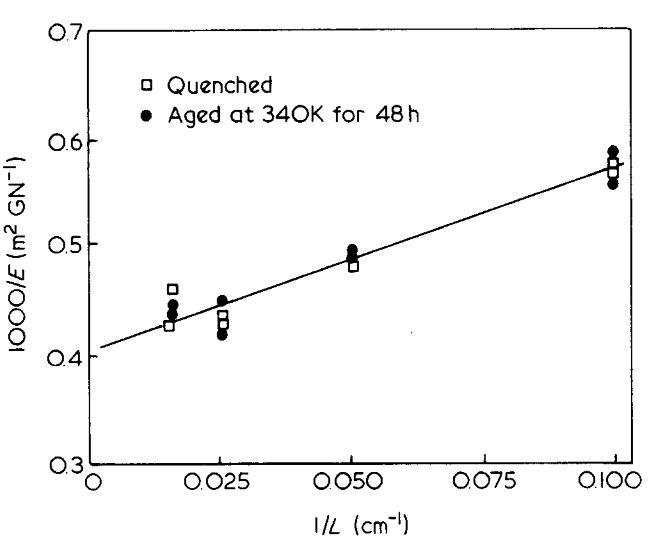


Figure 4 **Reciprocal of the measured Young's modulus plotted against reciprocal specimen length. (This method allows extrapolation of the modulus to infinite specimen length to correct for clamping errors. Ageing showed no measurable effect.) Young's modulus for quenched and aged specimens is 2.5 GN m^{-2}**

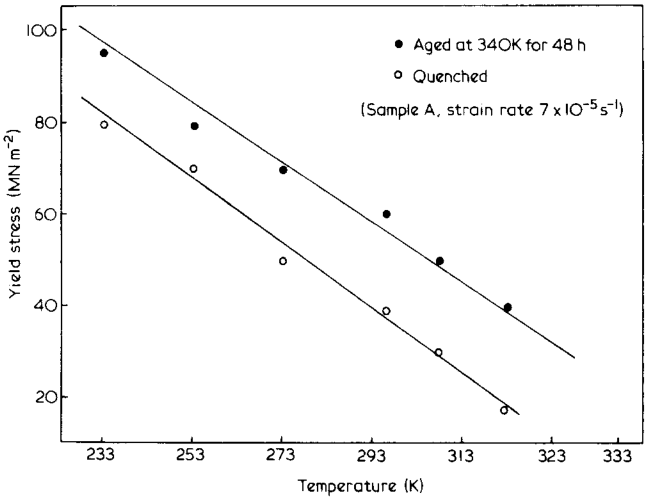


Figure 5 **The effect of temperature on yield stress for quenched and aged PET**

when the thermodynamic transition temperature is equal to the ageing temperature.

The effect of strain rate on yield stress is shown in *Figure 6*. The dependence changes with extent of ageing. If the activation volume for the yielding process can be equated to the Eyring volume, v, i.e.

$$v = 4kT \frac{\partial \ln \dot{\Sigma}}{\partial \sigma_y} \tag{4}$$

then the activation volume increases with ageing extent. This, of course, has been reported previously by Brady and Yeh[23] for PC and polystyrene (PS).

It has been reported previously that the endothermic process observed in the d.s.c. measurement of the glass transition on aged specimens is removed entirely after yielding[1,8]. There were some difficulties in confirming this result with fully extended material due to the occurrence of crystallization. However, by removing material from an incipient neck it was possible to confirm that at least 90% of the endothermic process had been eliminated. This increased yield stress indicates that the mechanical work

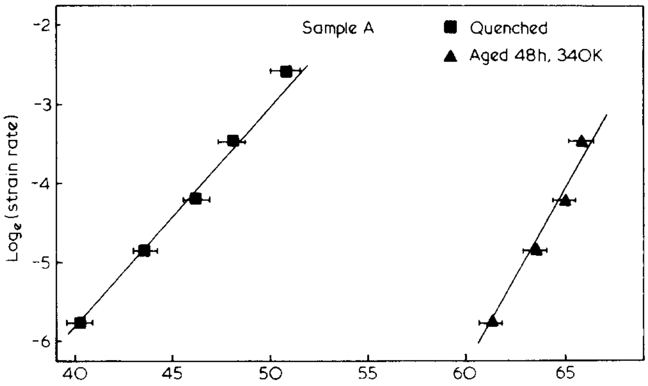


Figure 6 **The effect of strain rate on yield stress of quenched and aged PET**

required to deform the specimen increases with ageing but at the end of the deformation the material produced has the same enthalpy. Accordingly some of this additional work is used in increasing the enthalpy. Consistent with this, the yield stress increased linearly with ΔH_t and independently of the ageing temperature (see *Figure 7*). However, in comparing the two energies separately, the additional mechanical work required to deform aged rather than quenched specimen is then

$$\Delta E_w = (\sigma_a - \sigma_q)(\Delta - 1)/A\rho \tag{5}$$

in which σ_a andσ_q are the drawing stresses of aged and quenched material respectively, Δ the draw ratio, ρ the material density and A the cross-sectional area of the specimen prior to the test.

ΔH_t and ΔE_w are plotted against one another in *Figure 8*, for PET and other polymers, PVC and PC. Most of the data fall close to the same dependence through the origin with a slope 0.22 ± 0.02.

The additional mechanical work required to deform aged specimens is then four to five times the enthalpy of ageing. However, recent work with an i.r. camera showed that most of the mechanical work in deforming quenched specimens appeared as heat in the necking region[24]. Accordingly, aged specimens should exhibit different heat loss behaviour.

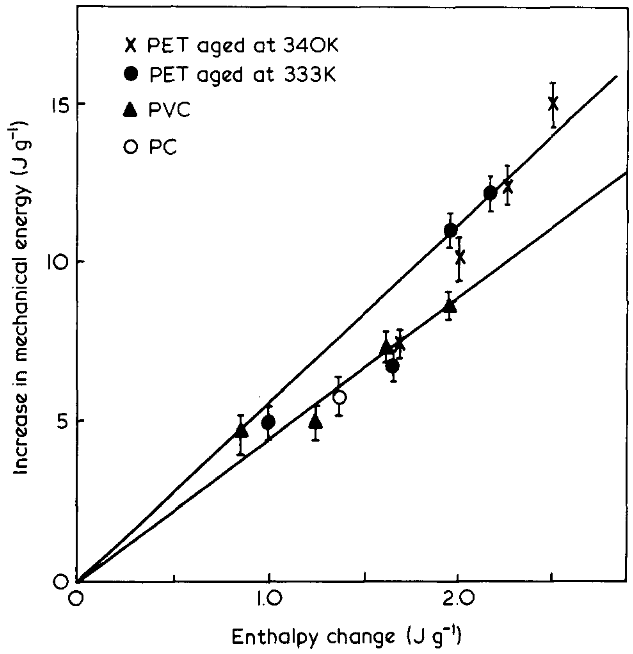


Figure 8 The relation between increased mechanical energy to deform aged and quenched specimens and the enthalpy changes on ageing

CONCLUSIONS

In tensile experiments, the rate of fall in engineering stress after yield with strain increases progressively with ageing. This has been observed in other thermoplastic materials[5, 11, 25, 26] and attributed to a greater localization of plastic strain[27]. However, with PET this effect is particularly marked but is observably due to geometric changes in the specimen in yielding, as can be seen in the change in neck formation. With PET, the effect is particularly marked. It would be logical to ascribe the increased fall in stress with the aged material to the elimination of structure formed during physical ageing and producing the higher yield stress. However, the concept of a fall in yield stress associated with plastic yield is not supported by experiments in plane strain compression where similar elimination of the ageing endotherms occurs without geometric change. In both cases crystallization occurs during yielding to a similar extent, and although it is a complication, it is not believed to alter these conclusions. *Figure 9* clearly shows the diffuse shear bands formed prior to yielding in a quenched specimen as well as the more sharply defined neck with an aged specimen.

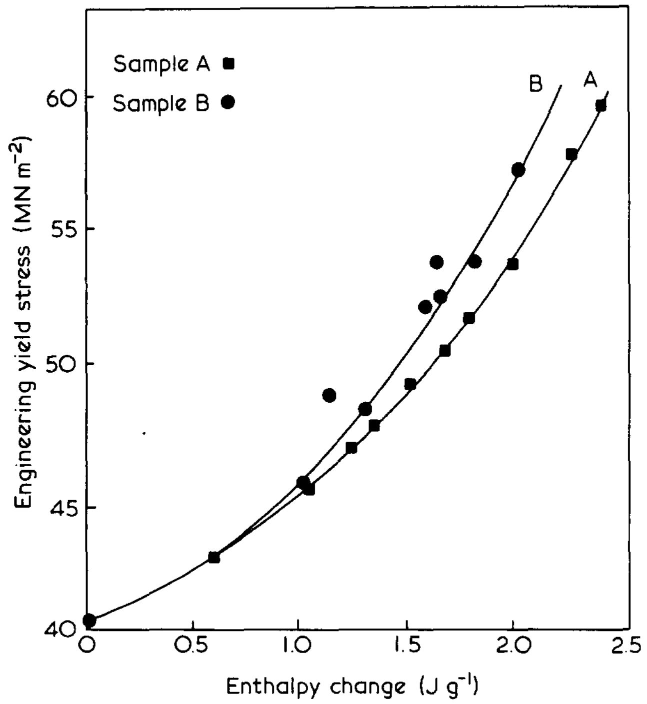


Figure 7 The variation of the yield stress with enthalpy changes on ageing

Coates and Ward[28] have measured neck profiles in linear polyethylene (PE) and related these to the strain-hardening behaviour and the strain rate sensitivity of the material. The increased apparent activation volume of aged specimens accordingly appears to be dominant in determining the neck profile, since plane strain compression indicates that aged and quenched specimens have the same strain-hardening characteristics.

Single edge-notched test pieces drawn in tension, and four-point loaded specimens of the Charpy type of PC fail by the formation of a craze at the tip of a triangular plastic zone which generates into a crack[21, 27] if it is not swamped by the development of the plastic zone. Similar plastic zones are observed with PET[29]. Most of the plastic deformation occurs in this zone and is therefore a major element in the impact energy of the specimen. On fracture, the size of the deformation zone can be observed on the fracture surface, and the site of the initiating craze is displaced from the notch surface by an amount related to the zone size (see *Figure 10*). There is a correlation between impact strength and the position of the craze site on the fracture surfaces.

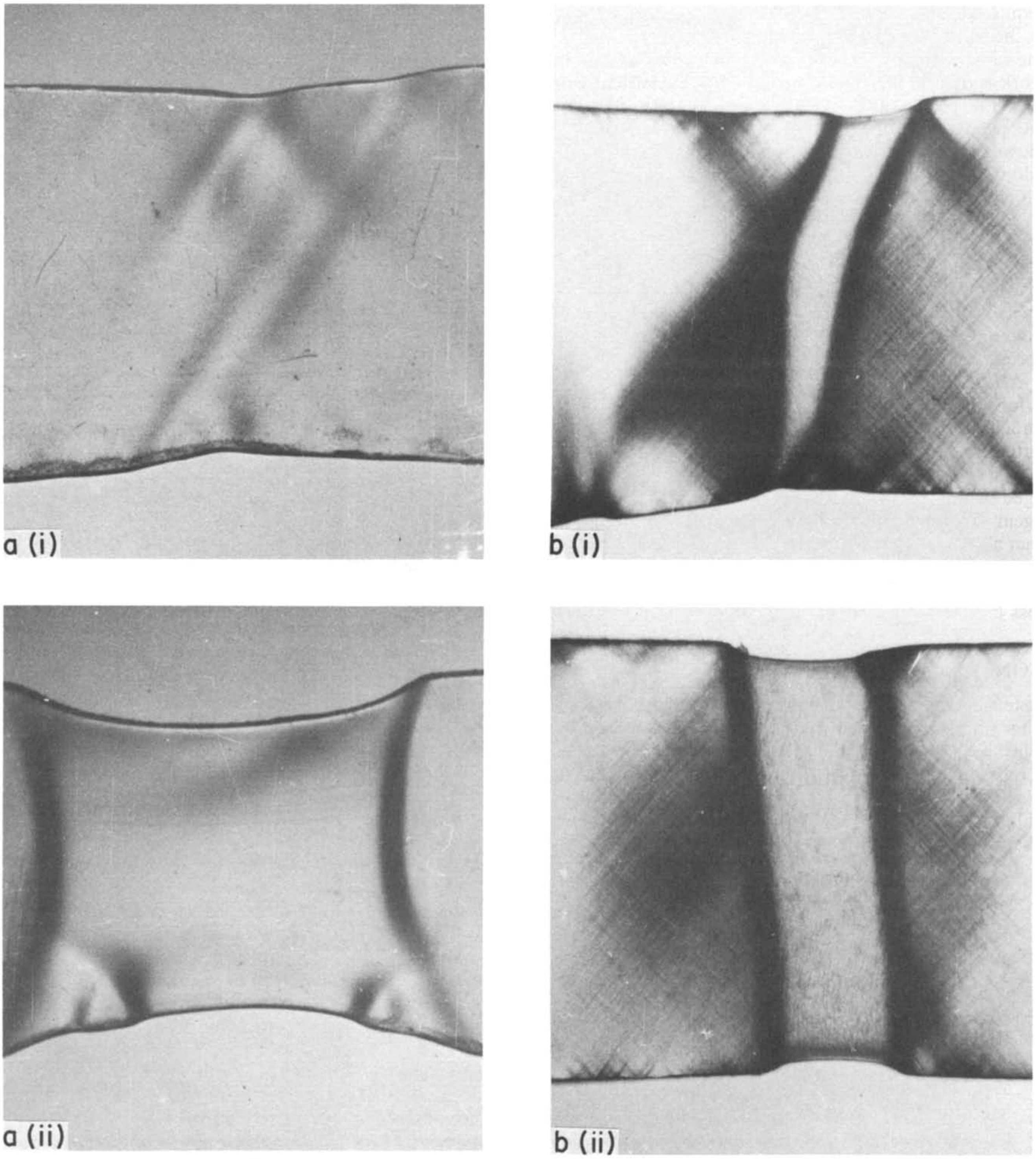
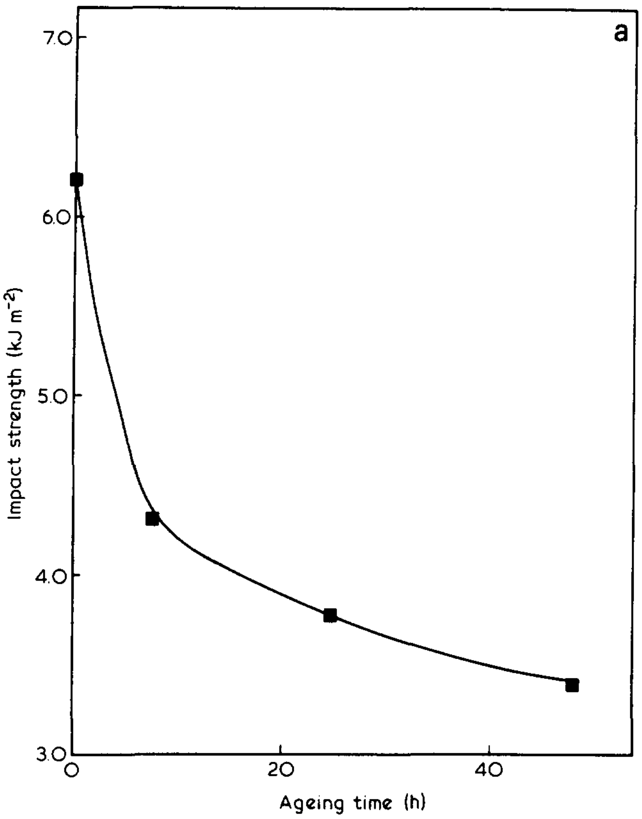


Figure 9 Shear band formation on yielding in tensile tests: (a) quenched PET, (i) as initially formed and (ii) neck propagation; (b) aged PET (48 h, 340K), (i) as initially formed and (ii) neck propagation

Measured impact strength decreased with extent of ageing, sample thickness and notch tip radius, and at the same time the site of the initial craze moves towards the notch tip surface.

With PET, Charpy impact samples fractured in a brittle fashion or with a mixture of the two modes. However, unlike PC, they were not observed to fail in a totally ductile mode, i.e. by deforming and tearing plastically through the deformed material for the notch surface[16,19,27]. Ductile fractures of this type could be observed in a slow bending test or Charpy impact test on notched specimens with large notch tip radii and with quenched material (see *Figure 11*). However, there was considerable variation in the impact strength and characteristics of the fracture surface, such as to suggest that PET is close to the brittle–ductile transition.



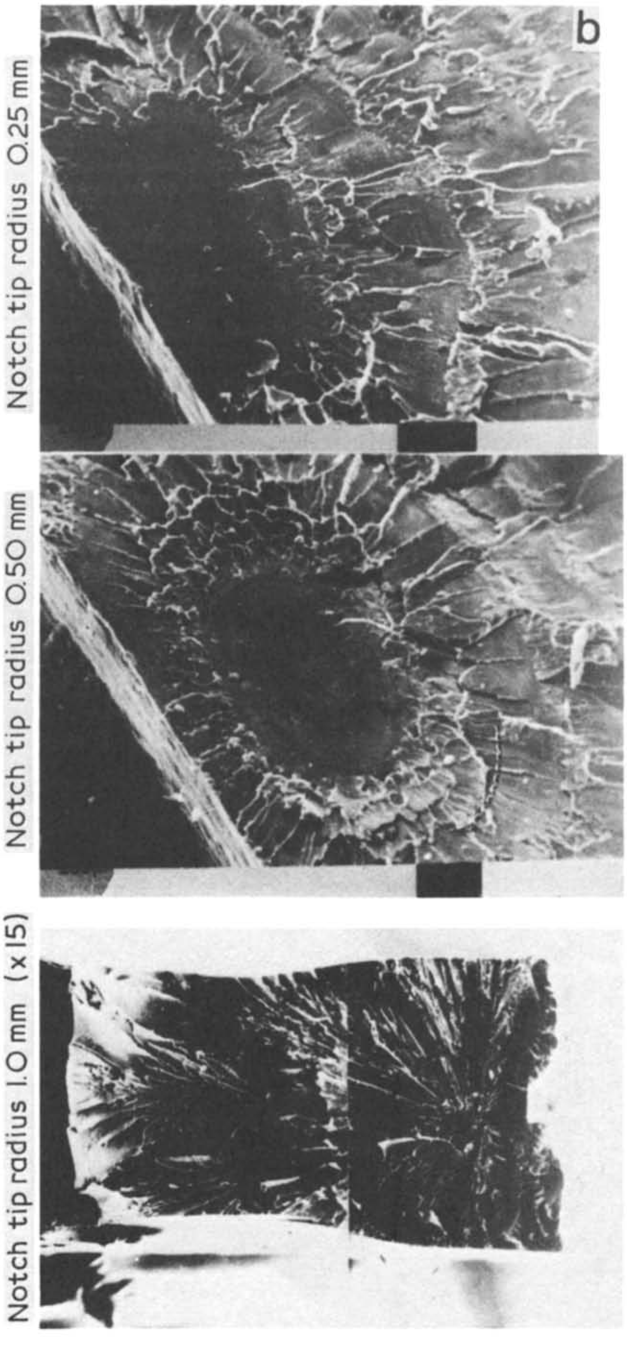
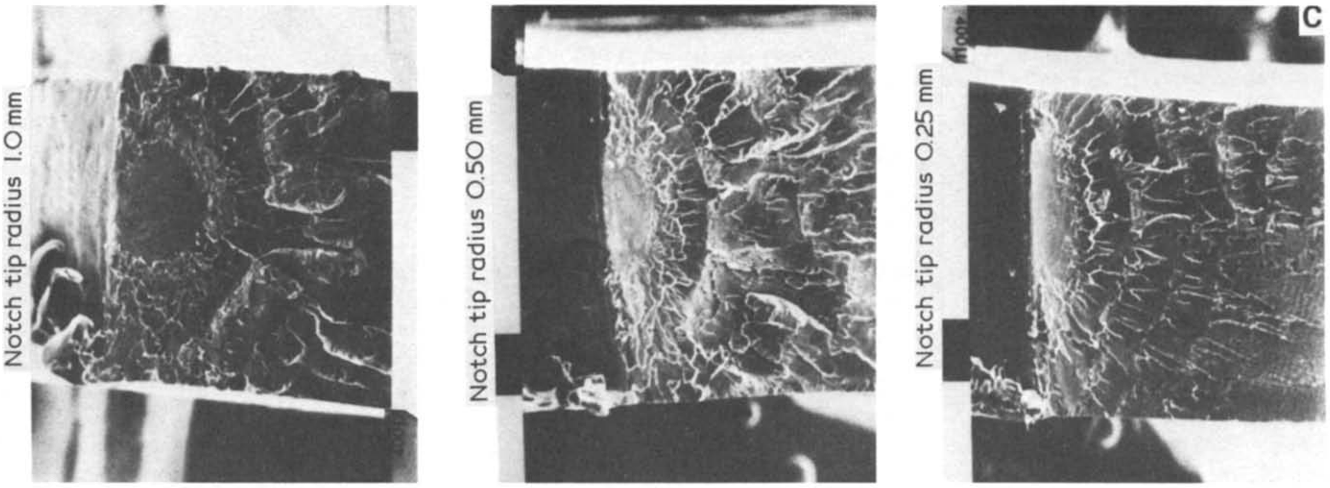


Figure 10 Fracture surfaces of 2 mm thick PET specimens: (a) impact strength changes with ageing; (b) variation of craze site with notch tip radius (quenched PET); (c) variation of craze site with notch tip radius (aged PET)



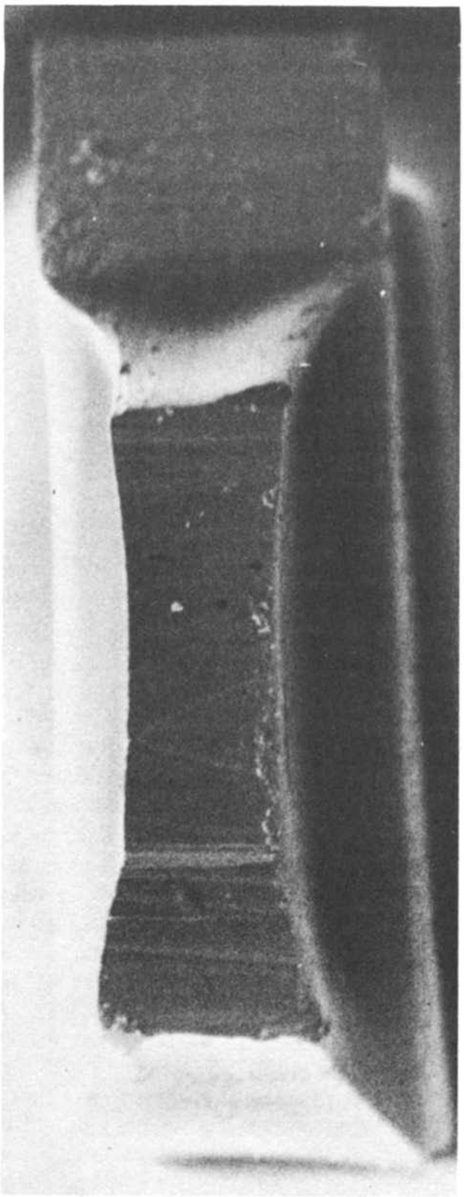


Figure 11 **Fracture surface of 2 mm thick PET specimen: slow ductile fracture**

REFERENCES

1 Struik, L. C. E. 'Physical Ageing of Amorphous Polymers and Other Materials', Elsevier, New York and Amsterdam, 1978
2 Golden, J. H., Hammant, B. L. and Hazell, E. A. *J. Appl. Polym. Sci.* 1967, **11**, 1571
3 Illers, K. H. *Makromol. Chem.* 1969, **1**, 127
4 Allen, G., Morley, D. C. W. and Williams, J. *J. Mater. Sci.* 1973, **8**, 1449
5 Adams, G., Cross, A. and Haward, R. N. *J. Mater. Sci.* 1975, **10**, 1582
6 Wyzgoski, M. G. and Yeh, G. S. Y. *Int. J. Polym. Mater.* 1974, **3**, 149
7 Mininni, R. M., Moore, R. S., Flick, J. R. and Petrie, S. E. B. *J. Makromol. Sci., Phys. B* 1973, **8**, 343
8 Koenig, J. Z. and Antoon, M. K. *J. Polym. Sci., Phys.* 1977, **15**, 1329
9 Aref-Azar, A. A. and Hay, J. N. *Polymer* 1982, **23**, 1129
10 Ito, E., Yamamoto, K. and Koboyashi, Y. *Polymer* 1978, **19**, 39
11 Petrie, S. E. B. 'Polymeric Materials', Am. Soc. Metals, 1975, p. 55
12 Petrie, S. E. B., Benidetto, A. T. and Milt, J. *Polym. Eng. Sci.* 1978, **18**, 1200
13 Parvin, M. and Williams, J. G. *Int. J. Fracture* 1975, **11**, 963
14 Newmann, L. V. and Williams, J. G. *Polym. Eng. Sci.* 1980, **20**, 572
15 Pitman, G. L., Wood, I. M. and Duckett, D. A. *J. Mater. Sci.* 1978, **13**, 2092
16 Zurimendi, J. A., Biddlestone, F., Hay, J. N. and Haward, R. N. *J. Mater. Sci.* 1982, **17**, 199
17 Kramer, E. J. *J. Macromol. Sci.-Phys.* 1974, **B10**, 191
18 Conix, A. *Makromol. Chem.* 1958, **26**, 226
19 Walker, N., Hay, J. N. and Haward, R. N. *J. Mater. Sci.* 1979, **14**, 1085
20 Savill, N. G. and Richardson, M. G. *Br. Polym. J.* 1979, **11**, 123
21 Hirai, N. and Eyring, H. *J. Appl. Phys.* 1958, **29**, 810; *J. Polym. Sci.* 1959, **37**, 51
22 Cross, A. and Haward, R. N. *J. Polym. Sci., Phys.* 1973, **11**, 2423
23 Brady, T. E. and Yeh, G. S. Y. *J. Appl. Phys.* 1971, **42**, 4623
24 Maher, J. H., Hay, J. N. and Haward, R. N. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 2169
25 Bowden, P. B. *Phil. Mag.* 1970, **22**, 455
26 Bowden, P. B. and Raha, S. *Phil. Mag.* 1970, **22**, 413
27 Mills, N. J. *J. Mater. Sci.* 1976, **11**, 363
28 Coates, P. D. and Ward, I. M. *J. Mater. Sci.* 1980, **15**, 2897
29 Ishikawa, M., Nasisawa, I. and Ogawa, H. *J. Polym. Sci., Phys.* 1977, **15**, 1791