

Influence of morphology and surface preparation on the weatherability of polypropylene

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Regions within injection moulded polypropylene bars having different morphologies have been exposed by milling away material from the surface then illuminating them with ultraviolet radiation (u.v.) for periods of up to 18 weeks. The crystal morphology prior to u.v. exposure was determined using X-ray diffraction. The effects of the u.v. were investigated using tensile tests and differential scanning calorimetry. Examples of bars broken in the tensile tests were examined in the scanning electron microscope. When tensile tests were conducted on samples that were exposed for a short while to u.v. after removing the surface, cracks formed that followed the machining marks and failure occurred at a fairly low extension. Some of the ductility was restored if the machine marks were polished away before conducting the u.v. exposure. The results appeared to be insensitive to surface finish at longer exposure times. The severity of the damage caused by photo-oxidation increases as the crystallinity increases.

1. Introduction

When a semicrystalline polymer suffers chemical attack it generally degrades much more rapidly in the non-crystalline phase than in the crystal phase. Preferential swelling and/or dissolution of the non-crystal phase when exposed to an aggressive liquid can lead to etching, and this has been exploited in the microscopy of semicrystalline polymers [1–4]. Photochemical degradation, as suffered during outdoor exposure, is also believed to be concentrated in the non-crystalline regions [5]. There are several reasons for this. Oxygen required for the photo-degradation can diffuse fairly freely through the non-crystalline fraction, but does not penetrate readily into the crystals. This naturally restricts reaction preferentially to the non-crystal phase, though it leaves open the possibility of reaction at the crystal surface. In the case of a folded-chain lamellar crystal, distortion of the bonds near the fold surface may enhance the likelihood of reaction here. If there are defects on the molecules they will be excluded from the crystals; chemical reaction will occur preferentially at the defects, again leading to degradation in the non-crystal phase.

When semicrystalline polymers are injection moulded they form a layer structure in which different morphologies form at different depths [6–26]. Equiaxed spherulites generally form in the interior (core), whereas near the surface there is significant preferred orientation and, usually, different crystallinity. In polypropylene it is usually observed that there is a surface skin between 0.1 and 0.3 mm thick; properties such as density probably vary significantly

through the depth of the skin, though most measurements reported in the literature do not discriminate within the skin. There is then an *intermediate* layer in which the morphology is generally similar to the core, but contains some orientation. It is therefore to be expected that the material at different locations within a moulding will have different sensitivity to degradative attack. The studies reported here were instigated to attempt to verify this. An investigation into the effect of machining on the weatherability of polypropylene was conducted as a necessary prerequisite to the interpretation of the results relating to morphology. Photo-oxidation was performed indoors using ultraviolet (u.v.) irradiation.

2. Experimental procedure

2.1. Materials and sample preparation

Samples were made from polypropylene (ICI GXE35) in the form of injection moulded bars measuring approximately $190 \times 12.7 \times 3.2$ mm using a tool with an end-gated cavity. The material was fed into the mould cavity through a tab gate that left a witness mark in the surface formed at the fixed plate, allowing identification of the back–front of the moulding. The samples were moulded in a single batch; several mouldings were rejected at the beginning of the production run to ensure the machine had reached equilibrium before collecting samples for testing. The injection pressure used was 107 MPa, and the temperatures were: barrel, 200 °C (both zones); nozzle, 200 °C; mould, 40 °C.

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Some of the bars were exposed to the u.v. source as-moulded. The skin layer in these bars was approximately 0.25 mm thick. From other studies [27] it is known that under the conditions used in the work reported here, degradation occurs overwhelmingly in a region near to the surface less than 0.5 mm thick, and that even within this region it is biased strongly towards the surface. Thus, in the as-moulded bars, photo-oxidative degradation occurs mainly in the skin. To investigate the degradation of the core material it was exposed by milling away material from the surface prior to exposure to the u.v. source. Milling was performed with a single point cutter using a fly cutting action. This left a fairly smooth surface, but it lacked the gloss of the as-moulded surface. It was anticipated that this might provide flaws that would initiate cracks, and in some cases the surfaces were polished to restore a gloss that was visually comparable to that of the as-moulded surfaces.

The following types of sample were prepared:

1. bars with 0.2 mm removed from both surfaces;
2. bars with 0.2 mm removed from both surfaces, then polished;
3. bars with 0.6 mm removed from both surfaces; and
4. bars with 1.2 mm removed from one surface.

Thus in samples 1 and 2 the new surface was located within the skin, near to the boundary with the intermediate layer; and in samples 3 and 4 the new surfaces were located in the core material. Sample 3 contained only core material. Sample 4 was the same thickness as sample 3, but retained one skin surface. Sample 4 had an imbalanced residual stress distribution after removal of the surface layer [28,29] and became curved.

2.2. Photo-oxidation conditions

Fluorescent tubes type *UVA-340* (Q-Panel Co.) were used as the u.v. radiation source. The tubes used were chosen because their output in the u.v. matched the spectrum of solar radiation at the Earth's surface fairly closely. The supplier's own data show that the match is extremely close in the wavelength range below 360 nm, down to the cut-off at approximately 290 nm [30]. This has been confirmed by measurements of the spectral output of the UVA-340 tubes made using a Bentham Instruments spectroradiometer based on a double grating monochromator [31].

The tubes were approximately 1.2 m long, with fairly uniform output over the central metre. They were used in pairs spaced closely together. The intensity used was approximately 1.7 W m^{-2} in the wavelength range 290–320 nm, i.e. the total radiation below 320 nm wavelength. This is roughly half of the midsummer intensity at noon in Jeddah, Saudi Arabia, which has a quite severe climate [32,33]. The daily dose for samples exposed in the laboratory under these conditions is therefore approximately 41 W h m^{-2} compared to the daily u.v. dose within this wavelength range in Jeddah in midsummer of 20 W h m^{-2} .

The exposures were conducted in a constant temperature room set at 30°C ; the temperature fluctuated less than $\pm 1^\circ\text{C}$, and for the tests reported here the temperature was between 29.9 and 30.5°C . In most cases the bars were placed on an open frame, with the face containing the tab gate facing downwards and the upper surface facing the u.v. source. Some exposures were conducted with the bars loaded in uniaxial tension ($\sim 10 \text{ MN m}^{-2}$) using dead weight loading [27].

2.3. Mechanical testing

Samples were subjected to a tensile test after chosen periods of conditioning. Tests were conducted at 50 mm min^{-1} crosshead speed. The bars were tested to fracture, and the fracture surfaces retained for microscopical examination. Four samples were tested for each set of exposure conditions.

2.4. Surface morphology and fractography

Samples were cut away about 5–10 mm below the fracture surface for examination in the scanning electron microscope (SEM). They were mounted on an SEM stub and gold-coated to minimize problems with radiation damage and charging [4]. The original surfaces of the moulding were examined in addition to the fracture surface, especially near the intersection with the fracture surface.

2.5. Crystal characterization

The crystal characteristics of the material at the different depths exposed by milling were investigated prior to u.v. exposure by wide angle X-ray diffraction in a diffractometer (Philips PW1730) using CuK_α radiation.

Differential scanning calorimeter (DSC) studies were performed on a Mettler-Toledo FP90 system using the FP85 DSC cell. Samples were prepared by milling away a depth of 0.2 mm from the surface of the test bar. Approximately 5 mg of material was used for each run. Thermograms were recorded first using a heating rate of $13^\circ\text{C min}^{-1}$, then while cooling at $13^\circ\text{C min}^{-1}$, and finally while reheating at $13^\circ\text{C min}^{-1}$.

3. Results

3.1. Initial crystal morphology

Diffractometer traces are given in Fig. 1 for samples for which the surface on which the X-ray beam impinged was (a) the as-moulded surface, (b) the surface exposed by milling away 0.2 mm, and (c) the surface exposed by milling away 0.6 mm. The differences between the three traces are partly the result of different molecular orientation at different depths [26,34], and partly because of different crystallinities at different depths and of the presence of different fractions of different phases. The monoclinic (α -phase) dominates, but a significant fraction of hexagonal β -phase is indicated by the (300) reflection appearing at

approximately $2\theta = 16.1^\circ$ in the traces for the as-moulded surface and the one for 0.2 mm removal.

The most important morphological characteristic in studies of weathering is probably the crystallinity, f_c , and this has been determined from the diffractometer traces using the method of Weidinger and Hermans [35]. This method lacks the rigour of that of Ruland [36, 37], as conceded by the authors [35], but is claimed by them to give results that are remarkably consistent and generally in agreement with those obtained by Ruland's procedure. It has the advantage of being relatively rapid in execution, whereas the Ruland method is not very practicable if measurements are required from a large number of samples. The present measurements have confirmed that the method gives very good reproducibility and reveals trends in crystallinity that are consistent with other measurements. Further discussion of the application of this method in studies of degradation of polypropylene will be given elsewhere [38].

The β -phase index, B , was calculated according to Turner-Jones *et al.* [39]. There are reservations about the quantitative interpretation of this parameter, but it has been evaluated as a qualitative guide to β -phase content.

The results obtained for both f_c and B are shown in Table I. The crystallinity increases progressively as the distance from the surface increases. The greatest concentration of the β -phase is at the second level (0.2 mm). There is no evidence for the presence of any β -phase at 0.6 mm depth.

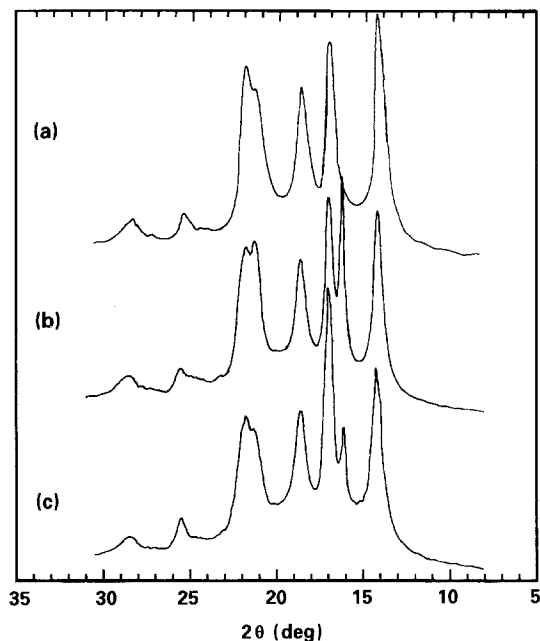


Figure 1 X-ray diffractometer traces from unexposed bars: (a) with 0.6 mm removed, (b) with 0.2 mm removed, and (c) as-moulded.

TABLE I Fractional crystallinity, f_c , and β -index, B

Depth (mm)	f_c	B
As-moulded surface	0.470	0.16
0.2	0.500	0.30
0.6	0.525	0.00

3.2. Mechanical tests

The results of the mechanical tests are summarized in Table II. Fig. 2 contains plots of the tensile strength results for bars that were exposed (i) as-moulded; (ii) with 0.2 mm removed from both sides; and (iii) with 0.6 mm removed from both sides. Each datum is the average for four tests. The unexposed samples all necked and then displayed a high degree of cold drawing. The gauge length of the bars was approximately 100 mm, so the drawing was in the range 400–600%. The tests were conducted in a room with no temperature control, and some of the variation in maximum

TABLE II Results of the mechanical tests

Sample	Maximum stress (MN m ⁻²)	Elongation (mm)
After zero exposure		
As-moulded	35.1 ± 0.3	527.0 ± 36
-0.2 mm: B ^a	36.5 ± 0.1	652.0 ± 22
-0.2 mm: B, P ^b	33.8 ± 0.3	455.0 ± 22
-0.6 mm: B	37.4 ± 1.1	649.0 ± 29
-1.2 mm: S ^c	32.1 ± 0.2	575.0 ± 30
After three weeks exposure		
As-moulded	36.1 ± 0.7	377.0 ± 63
-0.2 mm: B	37.9 ± 0.6	19.9 ± 2
-0.2 mm: B, P	34.7 ± 0.4	445.0 ± 10
-0.6 mm: B	38.4 ± 0.2	14.6 ± 1
After six weeks exposure		
As-moulded	32.9 ± 2.6	8.5 ± 1.2
-0.2 mm: B	21.7 ± 1.6	5.0 ± 0.1
-0.6 mm: B	17.9 ± 0.1	4.0 ± 0.1
-1.2 mm: S	16.2 ± 0.7	4.4 ± 0.2
After 12 weeks exposure		
As-moulded	26.7 ± 0.2	11.1 ± 0.3
-0.2 mm: B	25.5 ± 0.6	8.8 ± 0.4
-0.6 mm: B	18.8 ± 0.6	6.1 ± 0.6
After 18 weeks exposure		
As-moulded	24.8 ± 0.1	9.7 ± 0.1
-0.2 mm: B	21.0 ± 0.3	8.4 ± 0.3
-0.6 mm: B	13.8 ± 0.1	5.9 ± 0.1

^a B, material removed from both sides.

^b P, polished after milling.

^c S, material removed from one side only.

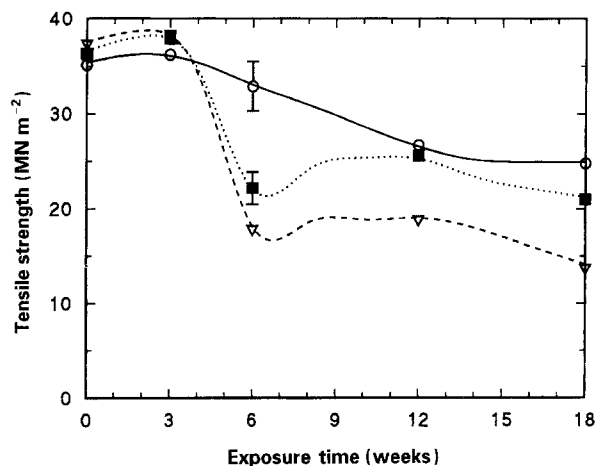


Figure 2 Tensile strength of bars exposed for various times. Results are presented for (O) as-moulded bars, (■) bars from which 0.2 mm was removed from both sides, and (∇) bars from which 0.6 mm was removed from both sides.

stress levels (about $\pm 2 \text{ MN m}^{-2}$) can be attributed to the sensitivity of polypropylene to temperature. Thus there is no evidence that in the unexposed state the strength of the bars is affected by machining away layers of different thickness. The variation in elongation may not be significant either.

After three weeks exposure samples with milled surfaces broke without drawing, whereas the as-moulded samples and those in which the milled surface was polished prior to exposure displayed cold drawing. There did not appear to be a significant variation in the maximum stress recorded in samples exposed for three weeks, and the values covered a similar range to those obtained with unexposed bars.

After six, 12 and 18 weeks exposure all samples broke without drawing, and the elongation in each case was less than any of the values measured at lower exposure times. The maximum stress of the samples exposed for six weeks in the as-moulded state appears to have dropped; more significant perhaps is the large increase in sample-to-sample variability, indicating that an unstable condition is developing. Samples from which layers were removed all displayed a large fall in the maximum stress. Curiously, there appeared to be a slight recovery of the maximum stress recorded with milled samples exposed for 12 weeks, though the as-moulded samples showed further deterioration. The maximum stress recorded with bars exposed for 18 weeks in the as-moulded state and with 0.2 and 0.6 mm removed, respectively, was less than that obtained with similar bars exposed for (all) shorter times.

A bar that had 0.6 mm removed from both faces and was then exposed to u.v. while under 10 MNm^{-2} uniaxial tension, broke during the fifth week of exposure. As-moulded bars exposed under the same conditions (stress and u.v. intensity) broke after seven weeks.

3.3. Scanning electron microscopy

3.3.1. Unexposed surfaces

The milled surfaces showed clear witness of the machining operation (Fig. 3). Fig. 4 shows for comparison a surface prepared using the same conditions, but using a worn tool. It is evident that it is important to work only with a properly sharpened tool.

3.3.2. Surfaces exposed to u.v. for three weeks

The samples exposed to u.v. for three weeks in the as-moulded state formed necks and proceeded to draw when tensile tested. Fig. 5a shows the region near to the neck (see also Fig. 5b). The average elongation to break was somewhat less than that obtained with unexposed bars, but there is evidence of significant deterioration. There is an axial split (see Fig. 5a) and considerable surface damage near to the corner. Fig. 5c shows the area near to the corner on the exposed face; a pattern of cracks has formed in the

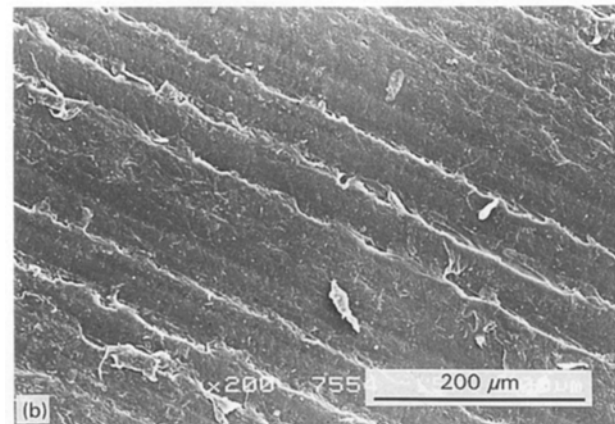
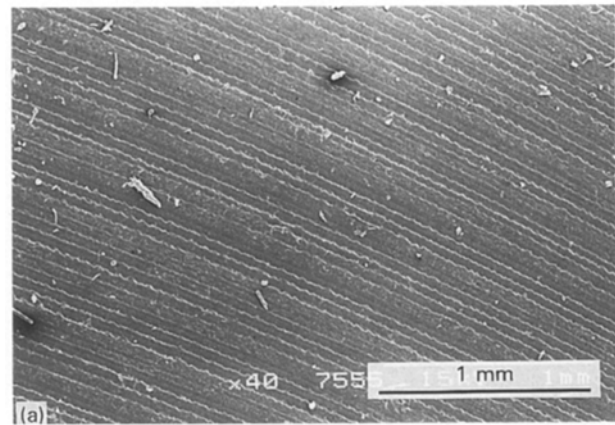


Figure 3 Surface of polypropylene bar after milling away the moulded surface. (a) low magnification, (b) intermediate magnification.

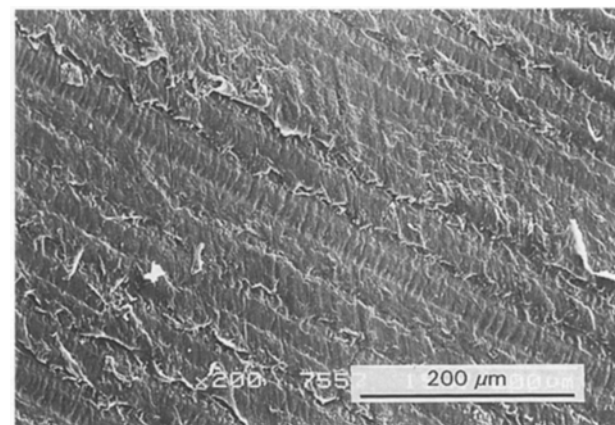


Figure 4 Surface of polypropylene bar after milling away the moulded surface using a worn tool.

surface. The appearance of the corner near to the unexposed face was similar (Fig. 5d).

Fig. 6 shows the surface of a bar that had 0.2 mm removed from both faces, was exposed to u.v. for three weeks, then tested in uniaxial tension. At low magnification (Fig. 6a) the machine marks are more prominent than in the sample inspected prior to u.v. exposure, and at intermediate magnification it was evident that there were deep fractures following the machine marks. At high magnification it appears that a brittle surface is present that has broken to reveal a ductile

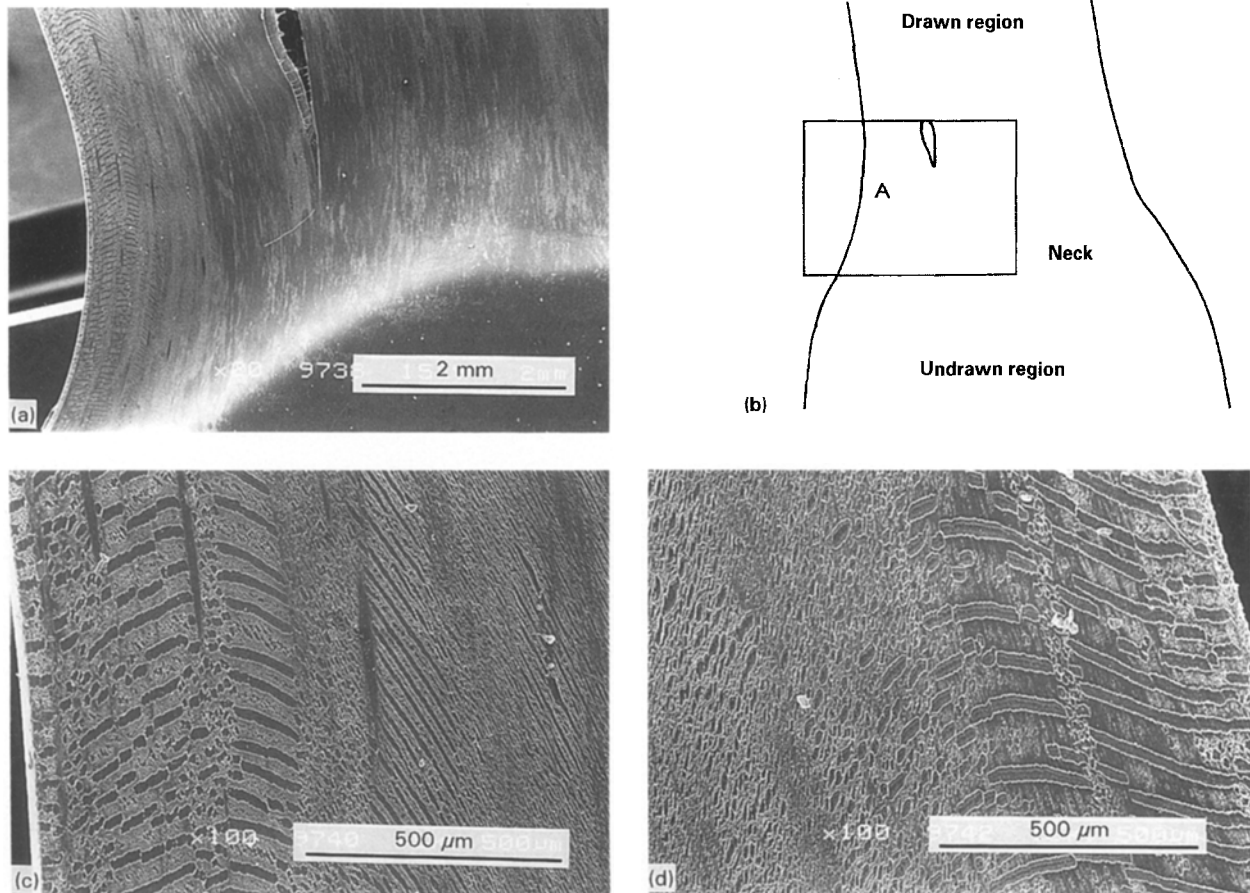


Figure 5 Polypropylene bar tensile tested after three weeks of u.v. exposure. (a) General view of the exposed face, showing an axial split near the top-centre; (b) schematic of the necked region of the bar showing the area imaged in (a); (c) magnified view of region A in figure (b); (d) view of the corresponding corner on the unexposed face.

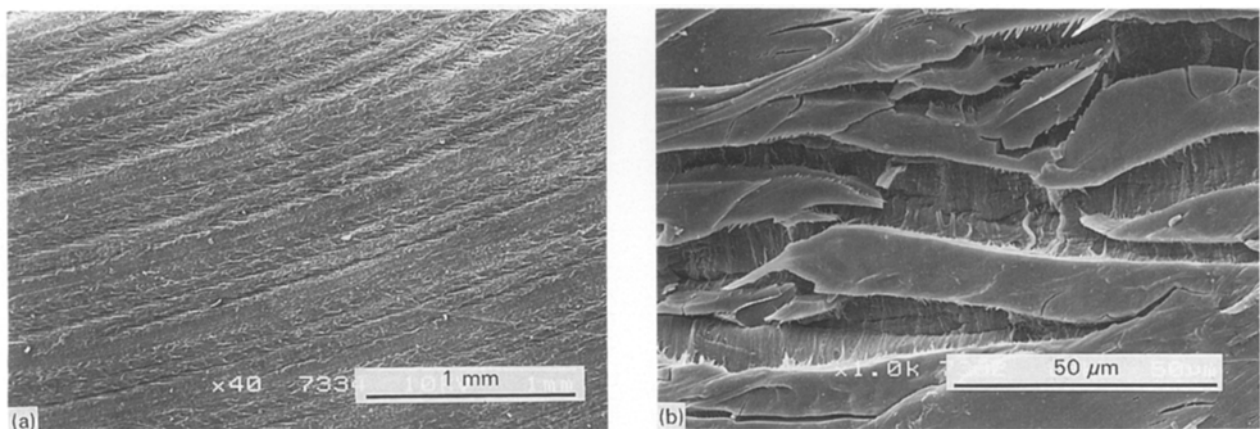


Figure 6 Exposed surface of bar from which 0.2 mm had been removed prior to three weeks u.v. irradiation: images recorded after uniaxial tensile test. (a) low magnification, (b) high magnification.

interior (Fig. 6b). The surface that faced away from the u.v. source showed essentially the same features (Fig. 7). Inspection of the fracture surface revealed that fracture had probably initiated at the surface that faced away from the u.v. source (Fig. 8a). When a region of the fracture surface about 0.4 mm in from the unexposed surface was viewed at high magnification it revealed a pattern of undulations and fissures with a period of $\sim 0.5 \mu\text{m}$ lying approximately parallel to the moulded surface, and a less prominent pattern of striations with a period $\sim 0.3 \mu\text{m}$ lying approximately

normal to the moulded surface (Fig. 8b). An interpretation cannot be offered for these markings, but it is notable that they are located in a region that should be almost isotropic in the as-moulded state. If the markings relate to the lamellar structure of the material, then it is clear that a very significant reordering must have taken place during the deformation and fracture of the bar.

Fig. 9 shows the exposed surface of a bar that was polished after milling to a depth of 0.2 mm, then exposed to u.v. for three weeks and finally tested in

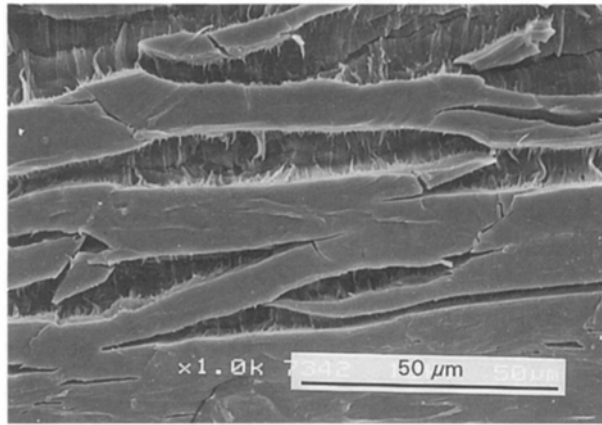


Figure 7 The other surface of the bar shown in Fig. 6.

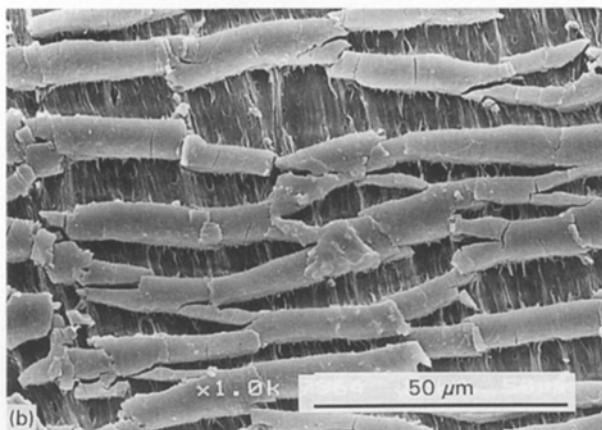
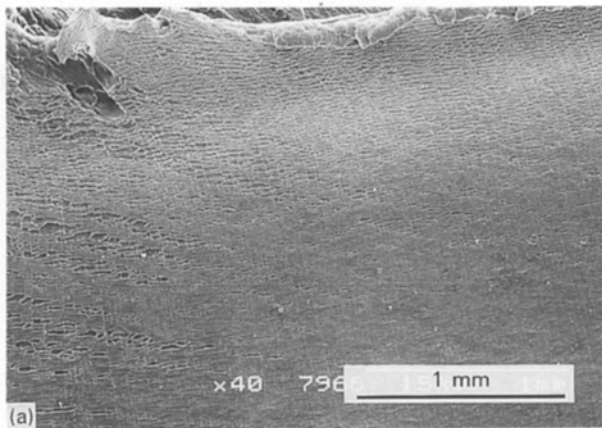


Figure 8 (a) Part of the fracture surface of the bar shown in Figs 6 and 7. The surface shown in Fig. 7 is at the top. (b) High magnification image from the centre of (a).

uniaxial tension. There is very little evidence of the machining operation, though at high magnification (Fig. 9b) the local damage is seen to be rather similar to that in Fig. 6b. The unexposed surface contained a hybrid pattern. Fissures lying perpendicular to the bar axis were found over the whole surface, but in addition witness marks revealing the pattern of machine marks that had been polished away became visible as a result of the irradiation and deformation (Fig. 10).

Fig. 11 shows the surface of a bar that had 0.6 mm removed from both faces, was exposed to u.v. for three weeks, then tested in uniaxial tension. The same basic features found with the sample exposed for three

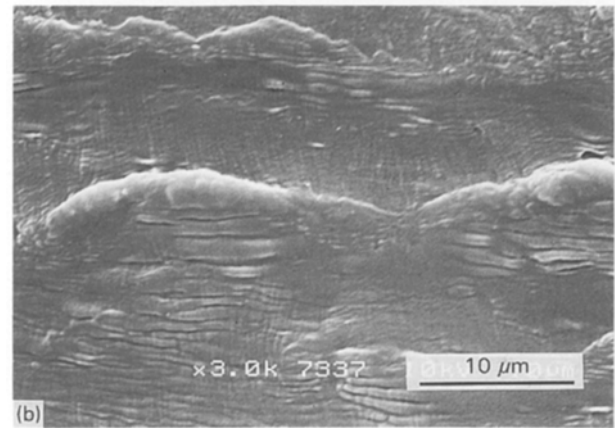
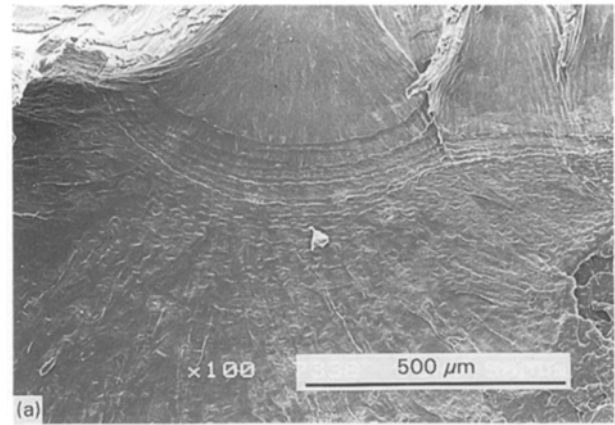


Figure 9 Exposed surface of bar from which 0.2 mm had been removed, then the machine marks polished away: images recorded after uniaxial tensile test. (a) Low magnification, and (b) high magnification (three weeks exposure).

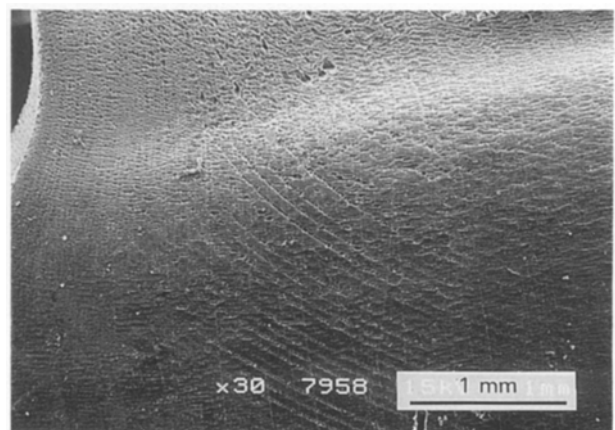


Figure 10 The other surface of the bar shown in Fig. 9.

weeks are in evidence again, though if anything the surface has fragmented to a lesser degree. The same remarks apply to the unexposed surface. The end surfaces, which were not machined and remain as-moulded, contained a dense pattern of fine brittle cracks (Fig. 12).

3.3.3. Longer exposures

After 12 weeks exposure the milling marks appeared to have much less importance. At a depth of 0.2 mm the exposed surface appeared to be very brittle such that, after conducting the tensile test, cracks formed in

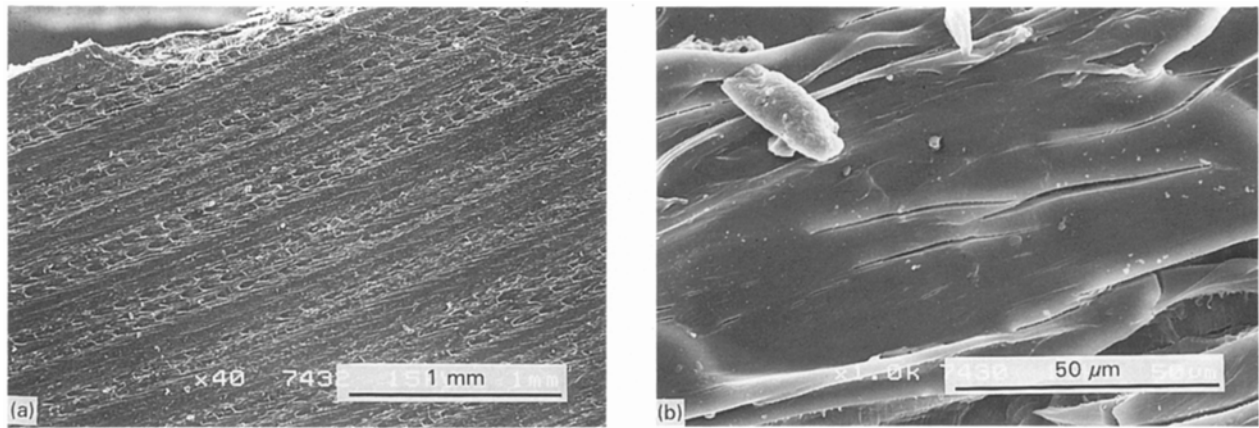


Figure 11 Exposed surface of bar from which 0.6 mm had been removed: images recorded after uniaxial tensile test. (a) Low magnification, and (b) high magnification (three weeks exposure).

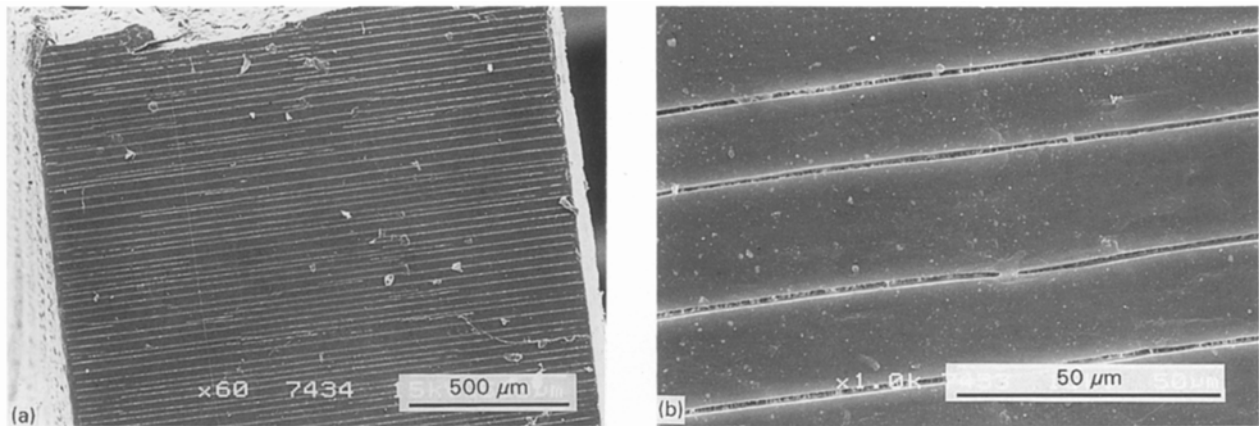


Figure 12 End surface of the bar shown in Fig. 11: (a) low magnification, and (b) high magnification.

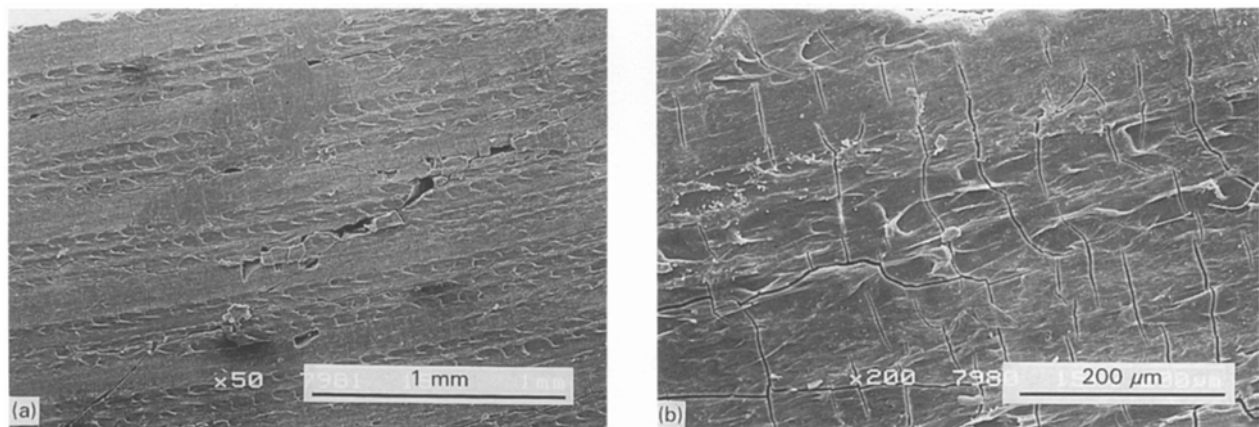


Figure 13 Exposed surface of bar from which 0.2 mm had been removed: images recorded after uniaxial tensile test. (a) Low magnification, and (b) intermediate magnification (12 weeks exposure).

all directions and some fragments actually broke away leaving behind irregular shaped cavities (Fig. 13). The unexposed face was rather similar, except that the damage appeared to be less deep and there were no cavities. Similar observations were made with a bar that was milled to a depth of 0.6 mm (Fig. 14). Fracture appeared to have nucleated at or near the unexposed surface (Fig. 15). During tensile testing sharp narrow cracks formed within the as-moulded face of

bars that were exposed for 12 weeks in the as-moulded state (Fig. 16). The cracks in the exposed surface are longer and more widely spaced than those in the side that faced away from the u.v. source (Fig. 16).

3.3.4. Samples exposed under tension

The bars which broke during exposure while held in uniaxial tension showed some features that were not

observed in the bars that were broken in a separate test conducted after the u.v. exposure. Fig. 17 shows part of the fracture surface from a bar that had 0.2 mm removed from both faces prior to u.v. exposure. The central region shows extensive ductile failure. The exposed face showed cracking similar to that which develops during uniaxial testing of bars exposed un-stressed for extended periods (Fig. 18).

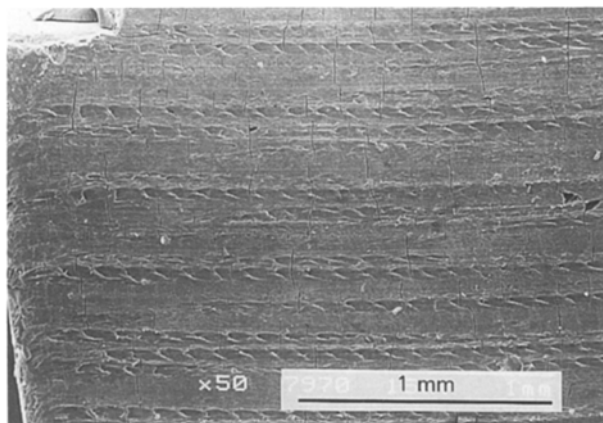


Figure 14 Exposed surface of bar from which 0.6 mm had been removed: image recorded after uniaxial tensile test (12 weeks exposure).

3.4. Differential scanning calorimetry

Typical thermograms are shown in Fig. 19. They are for a sample from a bar that was in the unexposed state, and a sample from a bar that was exposed to u.v. for 18 weeks. Thermograms are shown for (a) the first heating, and (b) cooling. The temperature axis corresponds to the programme temperature. The sample temperature lags behind the programme temperature, and the values at the peaks that are reported here are

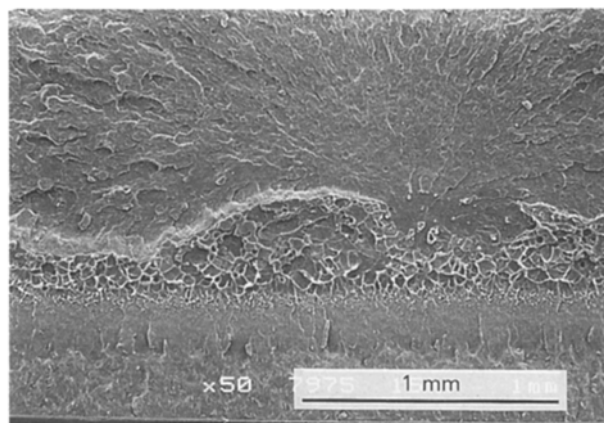


Figure 15 Part of the fracture surface of the bar shown in Fig. 14. The unexposed surface is at the bottom.

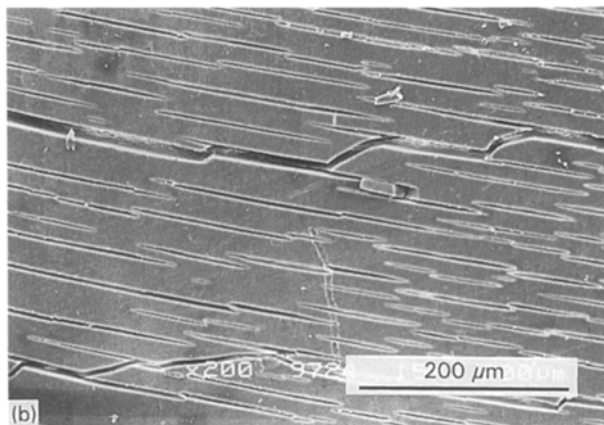
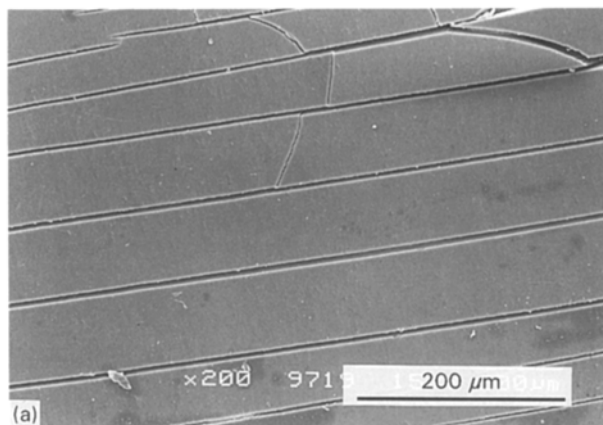


Figure 16 Exposed surface of a bar irradiated for 12 weeks in the as-moulded state then broken in uniaxial tension: (a) exposed surface, and (b) surface facing away from the u.v. source.

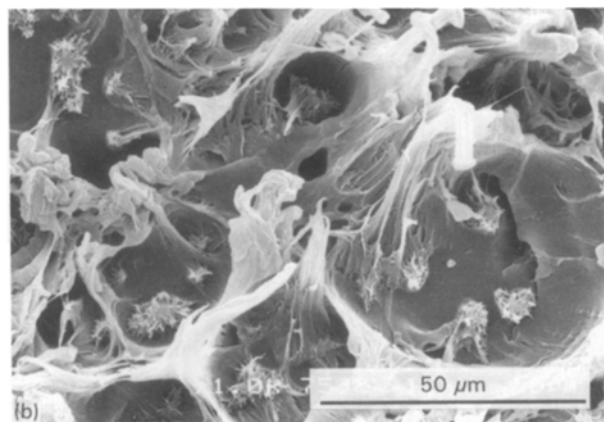
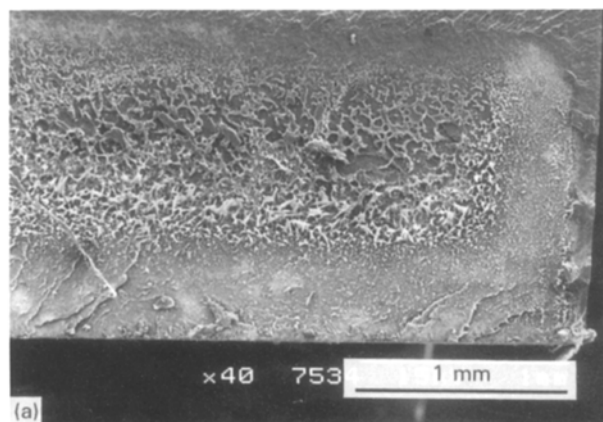


Figure 17 Part of the fracture surface from a bar that had 0.2 mm removed from both faces and broke during u.v. exposure under a tensile stress of 10 MN m^{-2} : (a) near one end, and (b) detail of the drawn region.

the corrected values, which therefore appear to be in disagreement with the uncorrected plot. The parameters derived from the thermograms in this study are:

1. $T_{m,1}$, the temperature at the crystal melting peak on the first heating run;
2. ΔH_1 , the enthalpy of melting in the first heating run (proportional to the area under the melting peak),
3. T_c , the temperature at the crystallization peak during the cooling run;
4. $T_{m,2}$, the temperature at the crystal melting peak on the second heating run; and
5. ΔH_2 , the enthalpy of melting in the second heating run.

The temperatures $T_{m,1}$, $T_{m,2}$, and T_c for samples removed from bars exposed in the as-moulded state

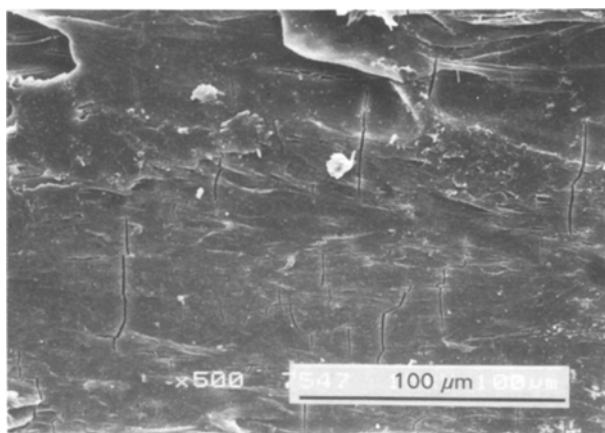


Figure 18 Exposed surface of the bar shown in Fig. 17.

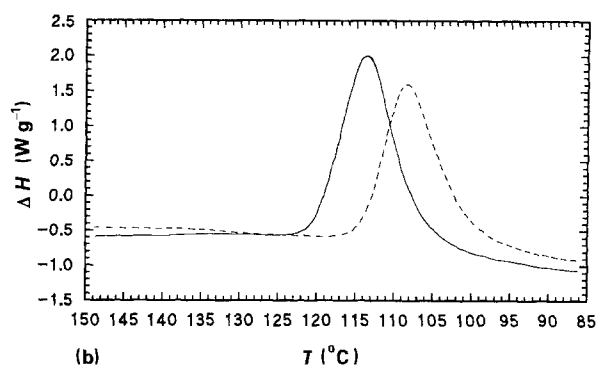
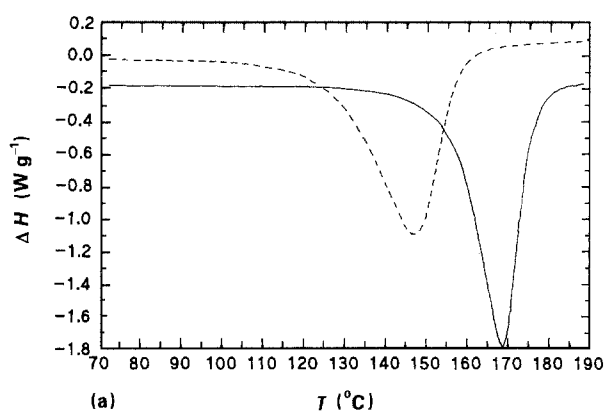


Figure 19 Thermograms for samples from the surfaces of an unexposed bar (—) and one exposed (---) to u.v. for 18 weeks: (a) initial melting, and (b) cooling.

for various periods are presented in Fig. 20. $T_{m,1}$ falls progressively with exposure time. If, as is generally believed, molecular degradation takes place almost exclusively in the non-crystalline regions, then the effect observed is probably the result of scission of tie molecules and chain folds at the crystal surfaces. Both tie molecules and chain folds are likely to contain heavily strained bonds, increasing their vulnerability to photo-oxidation. The loss of either kind of bond will make crystal melting easier and lower the melting temperature. $T_{m,1}$ is greater than $T_{m,2}$ at all exposures. It is speculated that this is because the crystals that form after the first melting will include molecular defects, such as carbonyl groups that are produced in the non-crystalline phase during u.v. exposure and/or because of the reduction in molecular weight. The crystallization temperature, T_c , reduces progressively with exposure time, as expected if the molecules contain defects.

Fig. 21 shows the temperatures $T_{m,1}$, $T_{m,2}$ and T_c for samples removed from bars exposed after removing 0.2 mm from the surface. The lines are copied from Fig. 20 and are not drawn specifically for the data points in Fig. 21. This shows that the melting temperatures are indistinguishable from those obtained with

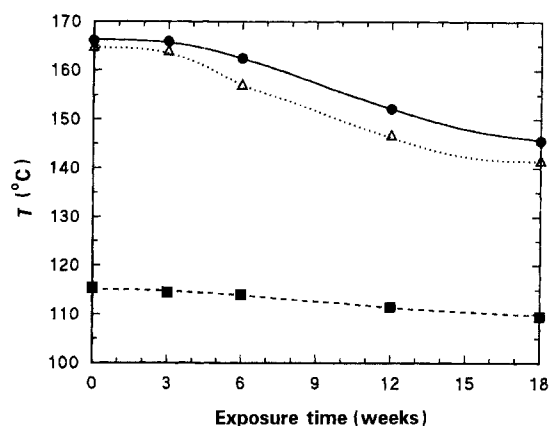


Figure 20 Temperature, $T_{m,1}$ (●), $T_{m,2}$ (△), and T_c (■) for samples extracted at 0–0.2 mm from the surfaces of bars exposed in the as-moulded state for different times.

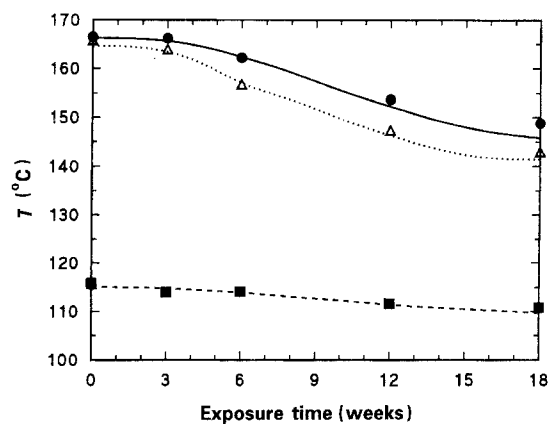


Figure 21 Temperatures, $T_{m,1}$ (●), $T_{m,2}$ (△), and T_c (■), for samples extracted from the surfaces of bars exposed for different times after 0.2 mm had been milled away from both surfaces. The depth is in the range 0.2–0.4 mm from the original moulded surface.

the samples taken from the bars exposed in the as-moulded state, except at longer exposure times (12 weeks and 18 weeks) when the values for $T_{m,1}$ for the bars that had the top 0.2 mm removed before exposure lie above those obtained from the bars that were exposed as-moulded; the reported values of $T_{m,2}$ are also higher but by an insignificant amount. The results from bars from which 0.6 mm was removed before u.v. exposure showed essentially the same features as those from bars from which 0.2 mm was removed before exposure (Fig. 22).

Fig. 23 shows the values of $T_{m,1}$, $T_{m,2}$ and T_c for samples removed at a depth 0.2–0.4 mm from bars exposed in the as-moulded state. Thus, the material was from the same position as that corresponding to Fig. 21. It is evident that the melting and crystallization temperatures fell less with progressive photo-oxidation than those given in Figs 20–22. This is attributed to the fact that the samples used to obtain the data given in Fig. 23 were extracted from a region that was separated from the surface by 0.2 mm of polymer, restricting the oxygen concentration and reducing the rate of photo-degradation. The changes observed in samples extracted at a depth of 0.6–0.8 mm were much smaller still (Fig. 24). Earlier

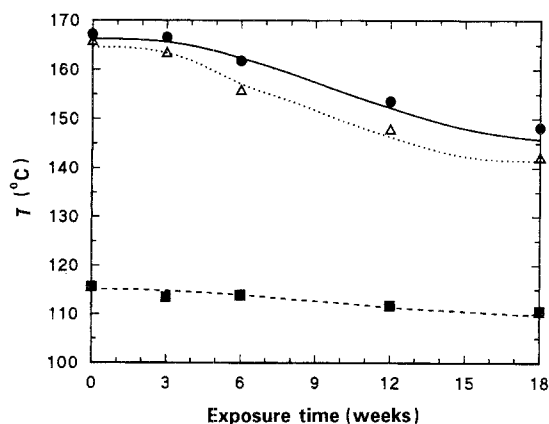


Figure 22 Temperatures, $T_{m,1}$ (●), $T_{m,2}$ (△), and T_c (■), for samples extracted from the surfaces of bars exposed for different times after 0.6 mm had been milled away from both surfaces. The depth is in the range 0.6–0.8 mm from the original moulded surface.

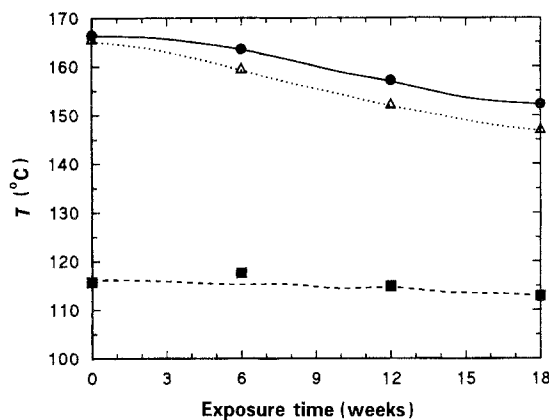


Figure 23 Temperatures, $T_{m,1}$ (●), $T_{m,2}$ (△), and T_c (■), for samples extracted at a depth of 0.2–0.4 mm from bars exposed in the as-moulded state for different times.

studies indicated that degradation was severely limited at this level in polypropylene [27].

The enthalpy changes during melting, ΔH_1 and ΔH_2 , are given in Fig. 25 for material that was taken from the surfaces of bars that were exposed as-moulded. ΔH_1 increases progressively with exposure; this is probably the result of chemi-crystallization, whereby molecule segments become freed from entanglements by scission events and give rise to secondary crystallization, probably through growth of the preexisting crystals. ΔH_2 rises slightly initially, possibly because the reduction in molecular weight results in higher crystallinity in the early stages of degradation, before the number of molecular defects (carbonyls) becomes excessive. ΔH_2 then falls significantly on extended exposure. The fall is probably because the crystallinity of the remelted polymer reduces as the fraction of defective molecules increases.

Essentially the same features were observed with samples that were taken from the surfaces of bars that were exposed to u.v. after milling away 0.2 (Fig. 26) or 0.6 mm (Fig. 27), respectively. The values of ΔH_1 at these depths for the unexposed samples were larger than those for the skin, indicative, probably, of higher crystallinity. The values of ΔH_1 for the two

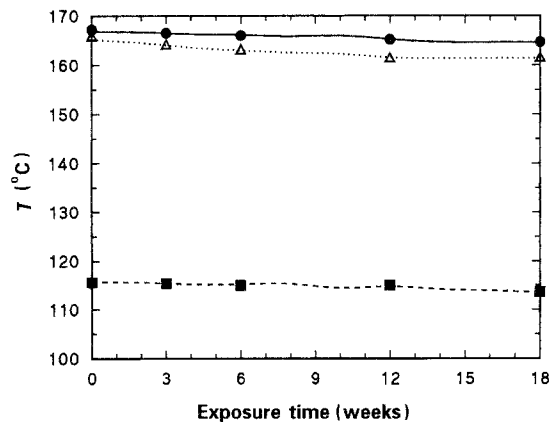


Figure 24 Temperatures, $T_{m,1}$ (●), $T_{m,2}$ (△), and T_c (■), for samples extracted at a depth of 0.6–0.8 mm from bars exposed in the as-moulded state for different times.

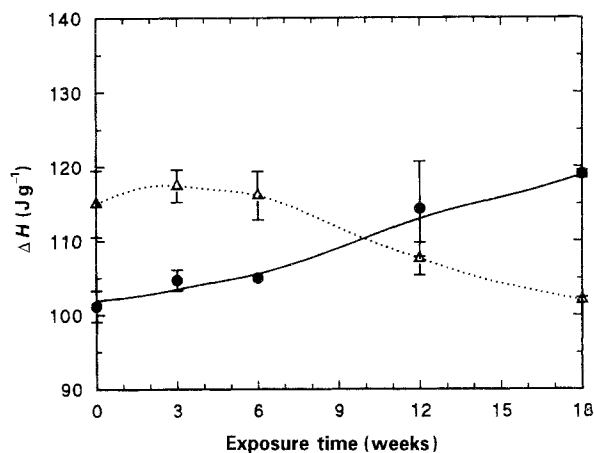


Figure 25 Enthalpy changes, (●) ΔH_1 and (△) ΔH_2 , for samples extracted at 0–0.2 mm from the surfaces of bars exposed in the as-moulded state for different times.

interior sites (0.2–0.4 and 0.6–0.8 mm from the surface, respectively) were almost indistinguishable. The corresponding densities were also very close [26]. That the crystallinities calculated from the X-ray diffraction measurements did not show such close agreement may be because of the polymorphic nature of polypropylene or of the oriented state in the intermediate layer.

The increase in ΔH_1 with exposure time was less steady than that shown in Fig. 25, with a much steeper climb between six and 12 weeks exposure, giving rise to a much higher value for ΔH_1 after 12 and 18 weeks. The values of ΔH_2 obtained from samples extracted from surfaces that were exposed after milling were higher than those obtained from the surface of the bars exposed as-moulded. The changes in ΔH_1 and ΔH_2 with exposure were much smaller in samples extracted from depths below the surface of bars exposed as-moulded (Figs 28 and 29) confirming that degradation has been restricted, as noted above.

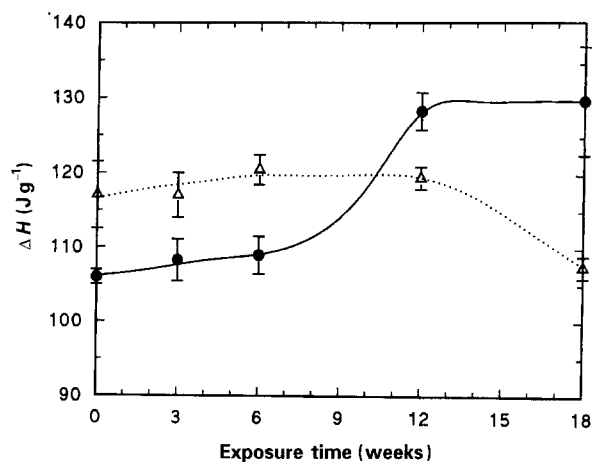


Figure 26 Enthalpy changes, (●) ΔH_1 and (Δ) ΔH_2 , for samples extracted from the surfaces of bars exposed for different times after 0.2 mm had been milled away from both surfaces. The depth is in the range 0.2–0.4 mm from the original moulded surface.

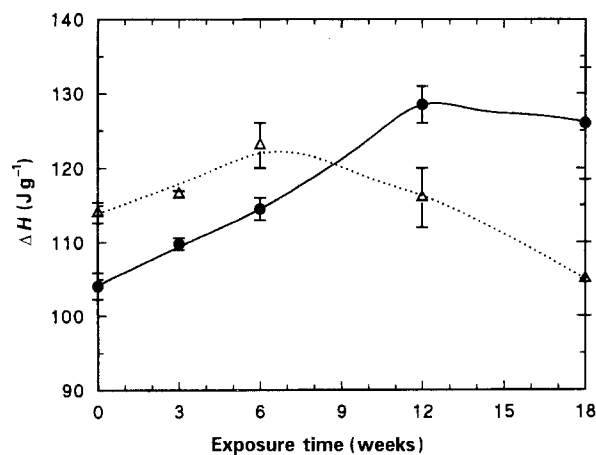


Figure 27 Enthalpy changes, (●) ΔH_1 and (Δ) ΔH_2 , for samples extracted from the surfaces of bars exposed for different times after 0.6 mm had been milled away from both surfaces. The depth is in the range 0.6–0.8 mm from the original moulded surface.

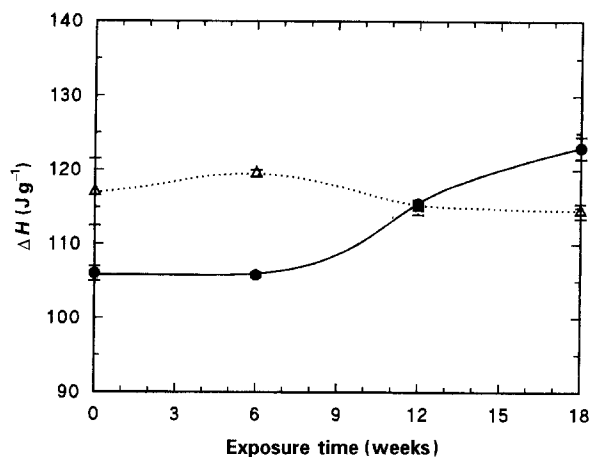


Figure 28 Enthalpy changes, (●) ΔH_1 and (Δ) ΔH_2 , for samples extracted at a depth of 0.2–0.4 mm from bars exposed in the as-moulded state for different times.

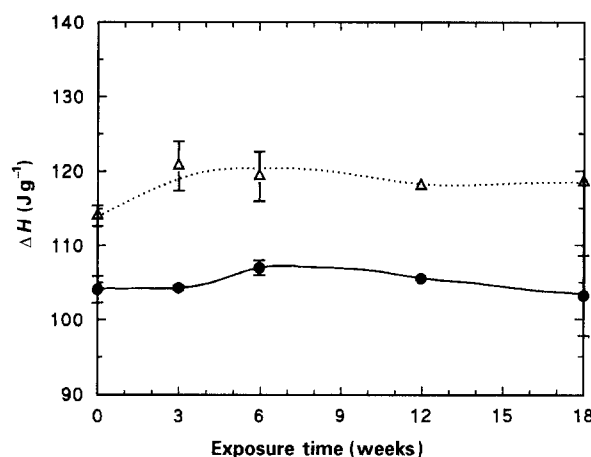


Figure 29 Enthalpy changes, (●) ΔH_1 and (Δ) ΔH_2 , for samples extracted at a depth of 0.6–0.8 mm from bars exposed in the as-moulded state for different times.

4. Discussion

It has been observed in earlier studies that polypropylene rapidly forms a brittle surface layer during natural weathering [40] and during artificial weathering, as applied here [27]. The fractographic studies of bars that were milled prior to exposure have shown that the machine marks have a significant influence over the form of the cracking pattern that forms in the brittle layer when the exposed bar is tested in tension. The drawing and fracture behaviour of the unexposed bars is not much altered by machining away layers and it is deduced that the flaws introduced by machining are not critical prior to u.v. exposure. That the machined bars which were exposed for three weeks failed without drawing, whereas the bars which were exposed in the as-moulded state drew considerably, seems to indicate that some kind of preferential degradation may have occurred in the machined samples. The bars which were polished to remove the machine marks displayed drawing after three weeks exposure, confirming the importance of the machining marks. After longer periods of u.v. exposure the effects of the machining seem to become reduced and possibly negligible. This would be expected if the depth of degradation exceeded the depth of the machine marks, as is

likely when a reasonably good machined finish is achieved, and if the degraded layer becomes very fragile. In this case, when the bar is put under tension the degraded surface layer tends to break in many places, rather than form large cracks that act as stress concentrations which can drive the crack into the (relatively) undamaged material beneath. Further confirmation of this is found in the observation that cracking often nucleates in the unexposed face. The u.v. intensity at the unexposed face is about 50% of that at the exposed face, so photo-degradation will proceed here at a reduced rate [31]. The lower rate may even permit a greater depth of degradation to occur, because under strong continuous u.v. intensities, as used here, the reaction is so rapid that oxygen is used up before it can diffuse very far into the sample. Thus a slower rate may permit reactions to occur at a greater depth from the unexposed face and eventually result in the formation of a thicker brittle layer than that which forms at the exposed face.

The deterioration of the mechanical properties in bars exposed to u.v. for six weeks or longer was greater in those samples in which the core material had been exposed (by the removal of layers at 0.6 or 1.2 mm). Samples in which only part of the skin-intermediate layer was removed (0.2 mm) performed better than the bars in which the core was exposed, but not as well as the bars which were irradiated in the as-moulded state. There are two possible explanations for this. The first is that there is a real influence of the morphology; this is discussed further below. The second possibility is that there is a thickness dependence. This was the reason for carrying out some tests on bars from which material was removed from one side only. Although these results seem to indicate that there is no serious thickness dependence, there are not enough data to prove this conclusively.

One is inclined to favour the morphological explanation. If this is true, then it is noted that the greatest deterioration in mechanical properties is observed when the layer with the greatest crystallinity is exposed. At first sight this seems to contradict the expectation that molecular damage is confined to the non-crystalline regions. There are several factors that may explain the observations. First, it is expected that strained bonds will break preferentially [27,31]. Tie molecules will generally contain a high proportion of strained bonds and will generally support a disproportionate share of the load in the non-crystalline regions. Thus they are more likely to break and their loss will have a disproportionate effect on the deterioration of properties. It is expected that there will be more taut tie molecules in regions of high crystallinity. Furthermore, the spherulite size is greatest in the core and scission of tie molecules at interspherulitic boundaries (as opposed to interlamellar boundaries) will be particularly detrimental. The DSC results also indicate that there was greater molecular damage in samples that were machined to depths of 0.2 and 0.6 mm, respectively, prior to exposure, than in those that were exposed to u.v. in the as-moulded state.

The second effect of morphology is on the rate of diffusion. Oxygen (and other reagents) diffuse almost

exclusively through the non-crystal phase, and the overall rate of diffusion will be determined largely by the crystallinity. There will be, in addition, some influence of the orientation and density of the non-crystal phase on diffusion rates. The diffusion rate will influence the depth to which oxygen penetrates and the depth within which significant degradation occurs. A third effect is also related to the depth of degradation. The reaction rate can be expected to be higher in regions of low crystallinity because of the higher concentration of non-crystalline material. Thus although the rate of diffusion of oxygen will be higher it does not necessarily follow that oxygen will penetrate further and promote damage at deeper levels.

5. Conclusions

1. Machine marks appear to provide sites for preferential photo-oxidation in polypropylene. At moderately low exposures this leads to the formation of flaws that weaken the material. After prolonged exposure the damage may extend sufficiently deeply to obliterate the effect of the machine marks.

2. The damage caused by photo-oxidation is more severe when material of higher crystallinity is exposed. This is probably because scission is expected to occur preferentially in tie molecules and other molecules that are carrying a disproportionate fraction of the load, and this effect will be progressively more influential as the crystallinity increases.

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