The effect of weathering on residual stresses and mechanical properties in injection-moulded semi-crystalline polymers

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Injection-moulded bars made from polypropylene (PP), polyacetal (POM) and nylon 6,6 (N6,6), have been weathered outdoors in Jeddah, Saudi Arabia, for varying periods. In POM and N6,6 the residual stresses became tensile near the surface, though this happened even with unexposed bars. Prolonged ageing or weathering of PP caused the residual stresses to fall to very low values. With POM and N6,6 significant surface damage developed on weathering, and multiple surface cracks opened up during uniaxial tensile testing. With N6,6 these developed into the form of diamond-shaped ductile fracture cavities, and the failure mechanism appeared quite different to that obtained with unexposed mouldings. With weathered PP no significant surface damage was visible even in the scanning electron microscope, but prolonged weathering caused a change in the failure mechanism, with fracture usually occurring without necking and drawing with specimens weathered for two years or more.

1. Introduction

The properties of many polymers are significantly influenced by exposure to outdoor weathering [1]. Serious deterioration often shows within a few weeks, especially in extreme climates, and articles may be rendered unserviceable because of a loss of strength, distortion or discoloration. It is important to identify the fundamental changes that occur on weathering and which lead to the reduced properties, in order that ways may be devised to counteract or control the problem. In an earlier paper [2] we reported on a study in which residual stresses were measured in injection-moulded bars made from four glassy polymers, after weathering for periods of between 8 weeks and 2 years in Jeddah, Saudi Arabia. It was found that for polystyrene (PS) and poly(vinyl chloride) (PVC) the sense of the residual stresses in the mouldings reversed after an extended period of weathering ($\leqslant 1$ year). Thus, the residual stresses near the surface of the bars became tensile.

Gel permeation chromatographic analysis of material cut from near to the surface exposed to sunlight confirmed that significant molecular weight reduction had taken place. Furthermore, studies in the scanning electron microscope showed that significant surface degradation occurred with these materials. Thus, near to the surface, material weakened by molecular weight degradation contained flaws, and tensile stresses became located there, providing conditions most favourable for failure by fracture. Tensile tests, three-point bend tests and impact tests all showed marked reduction in properties with weathering with these materials. Poly(methylmethacrylate) and polycarbonate showed a reduction in the levels of moulding stresses, but reversal had still not occurred after 1 year. Surface deterioration and molecular degradation were less pronounced with these materials, and their mechanical properties were less sensitive to weathering.

Many semi-crystalline polymers are used in outdoor applications and we have attempted to find out whether weathering causes similar changes to those promoted in non-crystalline polymers. In the previous study of glassy polymers [2] the materials chosen were European grades and were not specifically designed for the extreme climate to which they were exposed for the purpose of our studies. In the investigation reported here three semi-crystalline polymers have been studied: polypropylene (PP), polyacetal (POM) and nylon 6,6 (N6,6). The grades chosen were all recommended for outdoor use, but not specifically for an extreme climate.

2. Experimental procedure

The experimental strategy followed closely that employed in the previous study of glassy polymers [2]. The residual stresses and mechanical properties were measured for injection-moulded bars after varying periods of natural (outdoor) weathering in Jeddah, Saudi Arabia. Scanning electron microscopy (SEM) was used to examine weathered moulded surfaces, and the deformation and fracture morphology of samples tested to failure.

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TABLE I Moulding conditions

Code	Polymer	Manufacturer and grade	Temperatures (° C)			Injection pressure (MPa)
			Barrel (3 zones)	Nozzle	Mould (fixed/moving)	
PP	Polypropylene	ICI Propathene GWM22	225/230/230	230	50/47	76
POM	Poly(oxymethylene)	Du Pont Delrin 507	215/205/200	180	80/85	152
N6,6	Nylon 6,6	ICI Maranyl A101 black 936	260/265/275	300	60/55	106

2.1. Materials and specimen production
The materials used are listed in Table I. Samples were injection-moulded into ASTM D638 tensile test bars 190 mm long with gauge length cross section ~ 12.7 mm × ~ 3.2 mm using a single end-gated cavity. The bars were made at the Rubber and Plastics Research Association (Shawbury, Shrewsbury) on a Stubbe SKM76 reciprocating screw machine using the moulding conditions listed in Table I. In the case of N6,6 the material was dried for 12 h at 95° C prior to moulding.

2.2. Ageing and weathering
Specimens were aged indoors at room temperature for several weeks prior to testing or outdoor exposure. Semi-crystalline polymers are known to age significantly at room temperature [3, 4], and a number of specimens were stored at room temperature and retained for occasional testing to check to what extent the changes measured in the weathered bars could be attributed to physical ageing.

Samples were weathered outdoors in Jeddah, Saudi Arabia, for periods of up to 3 years before testing. Details of the Jeddah climate have been reported before [2, 5], and the most relevant data are repeated in Fig. 1. All exposure periods commenced in April. Most samples were placed in open frames inclined at 20° to the horizontal, facing south. We will refer to such samples as having received *direct* exposure. In subsequent analyses care was taken to distinguish between the upper surface (facing the sun) and the lower surface, which received reflected radiation only. Further samples were weathered outdoors in the shade provided by a shelter which prevented direct sunlight from impinging on the specimens.

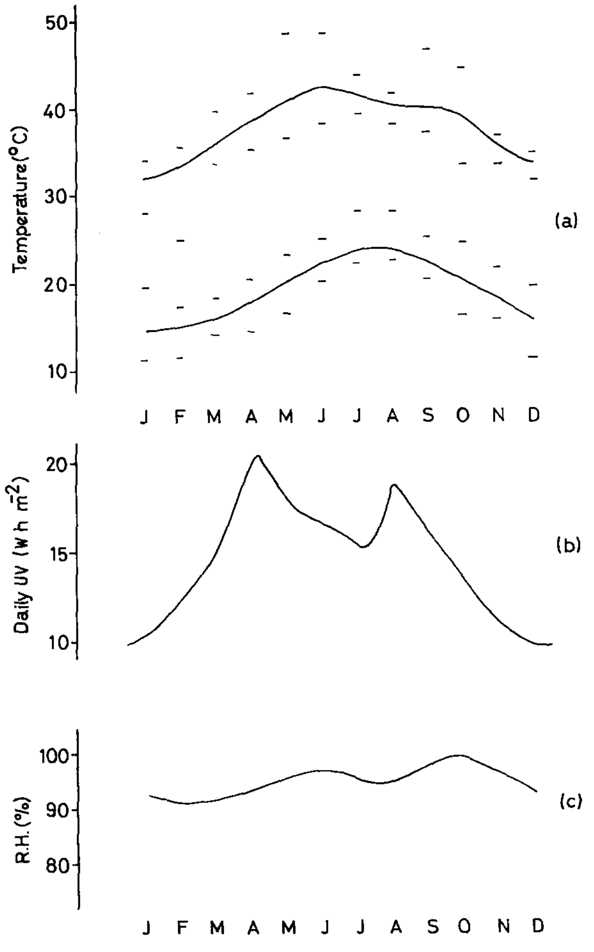


Figure 1 (a) Temperature variations in Jeddah month by month showing highest and lowest daily temperatures (average of 14 years). The highest and lowest values recorded during the 14-year period are also shown. (b) Daily dose of ultraviolet radiation received in Jeddah by monitors at 20° to the horizontal plotted against the time of the year. (c) Relative humidity in Jeddah plotted against the time of the year.

2.3. Mechanical testing
Uniaxial tensile tests were conducted on an Instron 1193 machine using a crosshead speed of 20 mm min^{-1}.

No impact test pieces of standard dimensions were made from the materials under investigation here, but a limited programme of tests was conducted on specimens cut from the tensile bars to investigate whether weathering caused any deterioration in impact properties. The ends of the bar were sawn off, leaving the central 63.5 mm of the gauge length. A notch of standard dimensions (2 mm deep and with 45° entrance angle and 0.25 mm tip radius) was cut across the bar thickness using a Daventest notching apparatus which uses a broach to form reproducible notches. Notches were made just before testing, that is after ageing and/or weathering. The specimen was then mounted in a Daventest Izod impact machine with the notch facing the pendulum in the usual way, and the energy to break the specimen was recorded.

2.4. Scanning electron microscopy
Fracture surfaces obtained in the mechanical testing programme were gold-coated and inspected in the SEM. The moulded surfaces from these specimens and from untested samples were also examined. Both upper and lower surfaces were inspected.

Specimens were viewed using the secondary electron image with an accelerating potential of 7.5 kV for PP and N6,6, and at the magnifications used here both materials showed reasonable stability in the electron beam. POM is very sensitive to electron irradiation [6, 7] and at 7.5 kV showed serious charging effects and the development of surface cracking which was not easy to distinguish from the pre-existing damage caused by weathering in some cases. Thus, most

TABLE II Young's modulus and Poisson's ratio

Code	E (GN m^{-2})	ν
POM	2.1	0.35
N6,6	2.9	0.38

studies on POM were conducted at 1.5 kV at which the specimens were much more stable. Even at 1.5 kV, high-magnification observation prompted damage and charging effects and care was necessary to avoid image artefacts.

2.5. Residual stress assessement

The residual stress distribution in samples exposed for various times was determined using the layer removal procedure [8–11]. Thin uniform layers were removed from one surface of the bar by high-speed milling using a single point cutter with fly-cutting action. After each layer removal the radius of curvature of the bar parallel to the bar axis was measured using a technique based on the optical lever principle [3, 10], and a plot developed of curvature (the reciprocal of the radius of curvature) against the depth of removal. From this the residual stress distribution was determined using the formula presented by Treuting and Read [8–11]. The form of the Treuting and Read formula used here is given below as Equation 1, and is modified for the case where the curvature perpendicular to the bar axis is negligible. The curvature is difficult to measure in this direction but visual inspection confirmed that it was small. Thus, the error resulting from the use of Equation 1 instead of the more accurate biaxial form will be small, and the

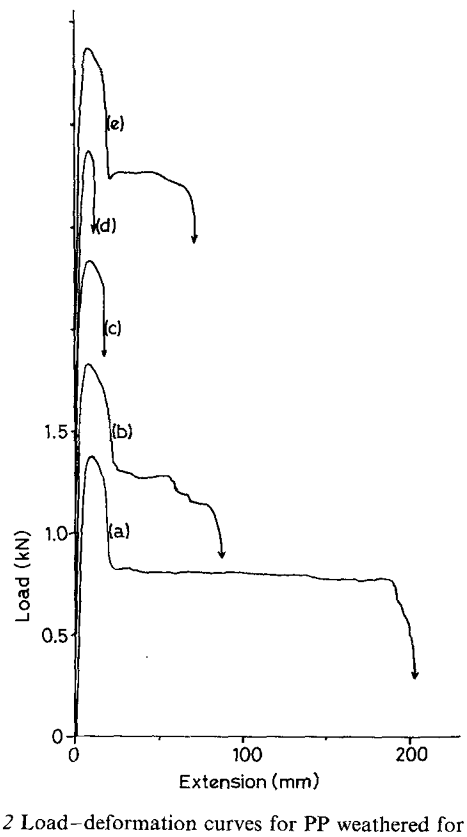


Figure 2 Load–deformation curves for PP weathered for (a) zero, (b) 80, (c) 104, (d) 156 weeks direct exposure and (e) 156 weeks in the shade. Successive curves are shifted 0.5 kN parallel to the load axis.

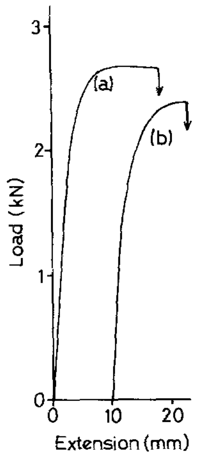


Figure 3 Load–deformation curves for POM (a) unexposed and (b) weathered for 156 weeks (displaced 10 mm parallel to the extension axis).

analyses presented here are perfectly adequate to make the kinds of comparison and deduction made here. Further discussion of the alternative forms of the Treuting and Read formula and examples of the kind of error that can be made by using the wrong form are found elsewhere [11, 12].

If after removing material until the machined surface is located at a height z_1 from the central plane of the bar prior to layer removals, the curvature parallel to the bar axis is $\varrho(z_1)$ and that perpendicular to the bar axis is zero, then the residual stress at the position z_1 (prior to layer removals) measured in the bar axis (x) direction is given by

$$\sigma_{i,x}(z_1) = \frac{E}{6(1-\nu^2)}\left((z_0+z_1)^2\frac{d\varrho(z_1)}{dz_1} + 4(z_0+z_1)\varrho(z_1) - 2\int_{z_1}^{z_0}\varrho(z)\,dz\right) \quad (1)$$

where the bar surfaces, prior to removals, are located at $z = \pm z_0$. In this formula E, Young's modulus, and ν, Poisson's ratio, are both assumed to be uniform. The consequences of Young's modulus varying through the depth of the bar have been examined in a recent publication [13]. The values for E and ν used in the analyses presented here are shown in Table II.

3. Results

3.1. Mechanical testing

A selection of load–extension curves for uniaxial tests are shown in Figs 2 to 4. As with glassy polymers [2], the most significant effect of weathering is to reduce the elongation to break for all of the materials included in this programme.

With PP the mode of failure changed during the period of 1 to 2 years exposure. Specimens weathered for less than one year suffered necking and cold drawing but those weathered for 2 years and more fractured without the formation of a stable neck, usually breaking without a neck appearing at all. The results are summarized in Fig. 5, which shows that the upper yield point remained almost unchanged whereas the extension to break reduced catastrophically on extended weathering. Results are also plotted for specimens weathered in the shade and show that the

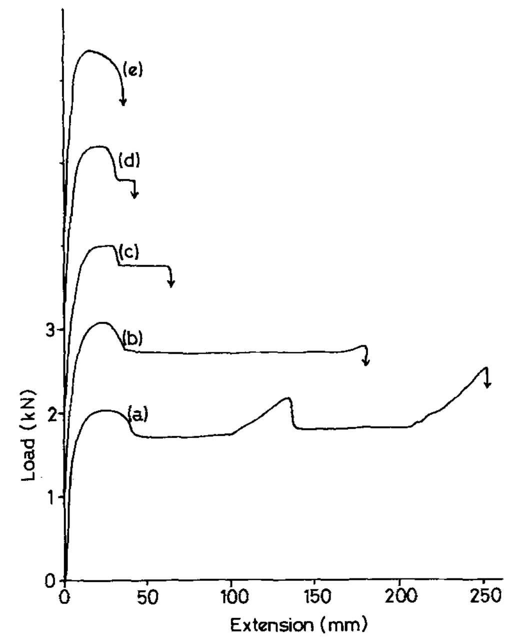


Figure 4 Load–deformation curves for N6,6 weathered for (a) zero, (b) 52, (c) 80, (d) 104 and (e) 156 weeks. Successive curves are displaced 1 kN parallel to the load axis.

fall-off in elongation was much less pronounced; even specimens exposed for 2.5 and 3 years formed stable necks. For specimens which broke without necking a flaw was seen to develop prior to fracture. This was usually located in the interior but sometimes began at a corner site. The flaw had the appearance of a crack or craze and grew progressively in the plane perpendicular to the bar axis. Up to the time of fracture this crack/craze stopped some distance short of the surface (possibly at the skin/core boundary), as has been observed in the case of crazes formed in uniaxial tension in polystyrene injection-moulded bars [14–16]. Some specimens developed several of these flaws in addition to the one from which failure ultimately occurred, and they remained clearly visible after the bar had broken. In one case a flaw of this kind was found in the undrawn part of a bar which had failed in the drawn region after the formation of a stable neck; this specimen had been weathered for 80 weeks, which is within the period during which the failure mechanism changed.

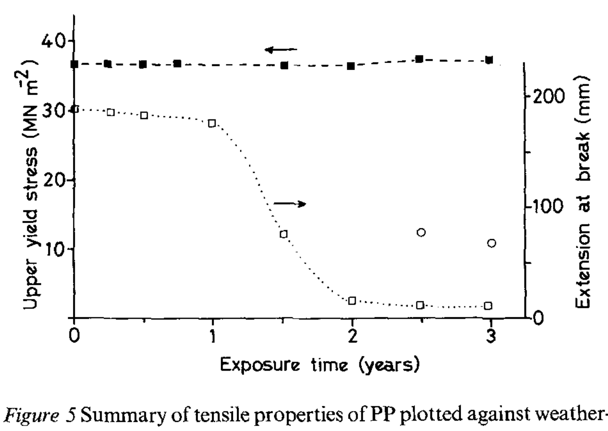


Figure 5 Summary of tensile properties of PP plotted against weathering time: (■) upper yield stress for directly exposed specimens (specimens weathered in the shade for 2.5 years and 3 years gave the same values as directly exposed samples weathered for the same time); (□) extension at break for directly exposed specimens; (○) extension at break for specimens weathered in the shade.

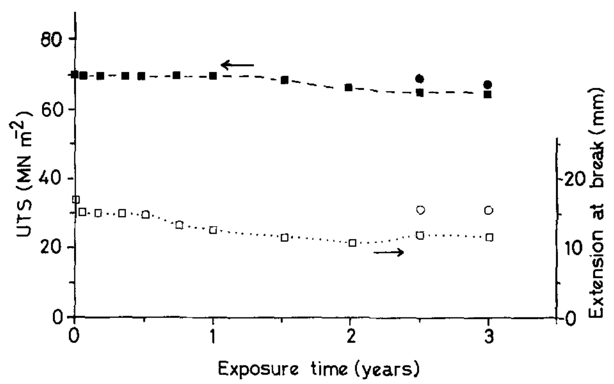


Figure 6 Summary of tensile properties of POM plotted against weathering time: (■) UTS for direct exposed specimens; (●) UTS for specimens weathered in the shade; (□) extension at break for directly exposed specimens; (○) extension at break for specimens weathered in the shade.

POM specimens did not neck and the strength is represented in Fig. 6 as the ultimate tensile stress (UTS). A small but significant reduction in strength occurred on weathering. Specimens weathered in the shade for 2.5 and 3 years showed a smaller reduction in strength. The extension at break fell steadily in the first year but did not change markedly thereafter. The extension at break showed a much smaller reduction for specimens weathered in the shade.

Unexposed N6,6 showed necking and cold drawing. A curious feature of the tests conducted on the material in this state was that after formation of a neck and considerable drawing, the drawing ceased or slowed down until it was much less than the deformation rate applied by the moving crosshead. This resulted in an increase in the load and ultimately produced a second neck somewhere else in the undrawn part of the gauge length. Formation of the new neck was

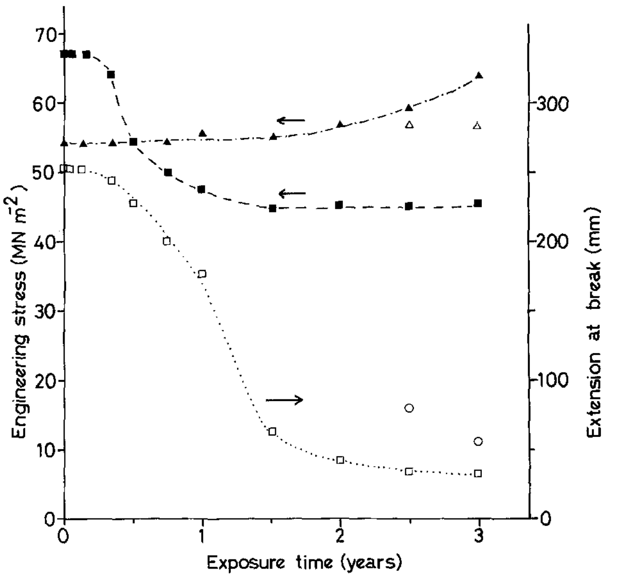


Figure 7 Summary of tensile properties of N6,6 plotted against weathering time: (■) upper yield stress for directly exposed specimens (specimens weathered in the shade for 2.5 years and 3 years gave the same values as directly exposed specimens weathered for the same time); (▲) fracture stress, expressed as engineering stress, for directly exposed specimens; (△) fracture stress for specimens weathered in the shade; (□) extension at break for directly exposed specimens; (○) extension at break for specimens weathered in the shade.

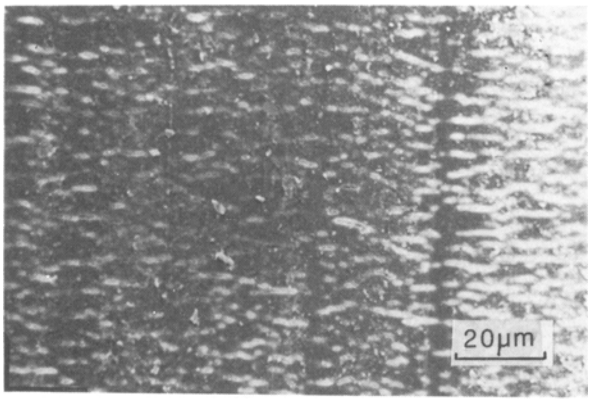


Figure 8 Moulded surface of PP specimen weathered for 2 years and then broken in uniaxial tension.

accompanied by another yield drop and was followed by a further period of cold drawing, apparently exclusively from the new neck. An example is shown in Fig. 4a. Multiple necking was never observed with weathered samples. The total extension to break reduced with increasing exposure time, and after 80 weeks the extension fell to less than one-third of the value for the unexposed condition (Fig. 7). For exposures of two years in direct sunlight, failure occurred soon after the formation of the neck and for three years exposure failure occurred without a stable neck forming. Specimens weathered in the shade did not deteriorate as much (Fig. 7). The tensile yield strength is seen to change only slightly for exposures up to 80 weeks but then begins to increase significantly with exposure time (Fig. 7).

Results of the impact tests are given in Table III. Significant reductions in the impact energy were observed with all materials after three years weathering. N6,6 showed the greatest deterioration, giving a value approximately one-quarter of that obtained in the unexposed state. The value obtained with N6,6 after 1 year exposure was approximately one-third of that for the unexposed state.

3.2. Scanning electron microscopy

3.2.1. PP

3.2.1.1. Moulded surface. The moulded surfaces of untested PP specimens did not show any significant visible change on weathering. The moulded surfaces

TABLE III Impact energies using the non-standard method described in Section 2.3. Impact energies in joules

Code	Exposure time (weeks)				Ratio of 156 weeks value to unexposed value
	0	52	104	156	
PP	0.49	–	–	0.43	0.88
POM	0.75	–	–	0.57	0.76
N6,6	2.71	0.85	0.69	0.62	0.32

of PP specimens which failed without forming a stable neck when tested in uniaxial tension often did not show any prominent flaws, but sometimes contained tiny fissures perpendicular to the tensile axis (Fig. 8). The appearance of the drawn material in specimens which formed a stable neck will be dealt with below in the discussion of the fracture surface.

3.2.1.2. Fracture surface. Unexposed specimens suffered the typical fibrillar fracture found with drawn PP, with adjacent fibrils breaking at very different positions along the bar axis to give a tufted appearance. With specimens weathered for short periods or weathered in the shade, fracture again took place in the drawn region but had a cleaner appearance, with the fibrils breaking approximately in the same plane (Fig. 9a). That extensive fibrillation had developed on drawing was evident on high-magnification inspection (Fig. 9b). Specimens which broke without necking usually did so from an internal flaw, as explained in Section 3.1, and clear evidence of this is found on the fracture surfaces. Fig. 10 is a typical example and shows a region of flat fracture which developed prior to the final fast fracture. At the centre of the slow fracture zone can be seen the original flaw, around which cavitation took place during the early part of the fracture process. The exact form of the original flaw could not be deduced.

3.2.2. POM

3.2.2.1. Moulded surface. The moulded surfaces on POM specimens showed marked deterioration on weathering (Fig. 11). Moulded surfaces of specimens tested in uniaxial tension were also inspected. These sometimes displayed directional damage as illustrated by Fig. 12, which shows fissures running perpendicular to the bar axis (the tensile axis). These fissures

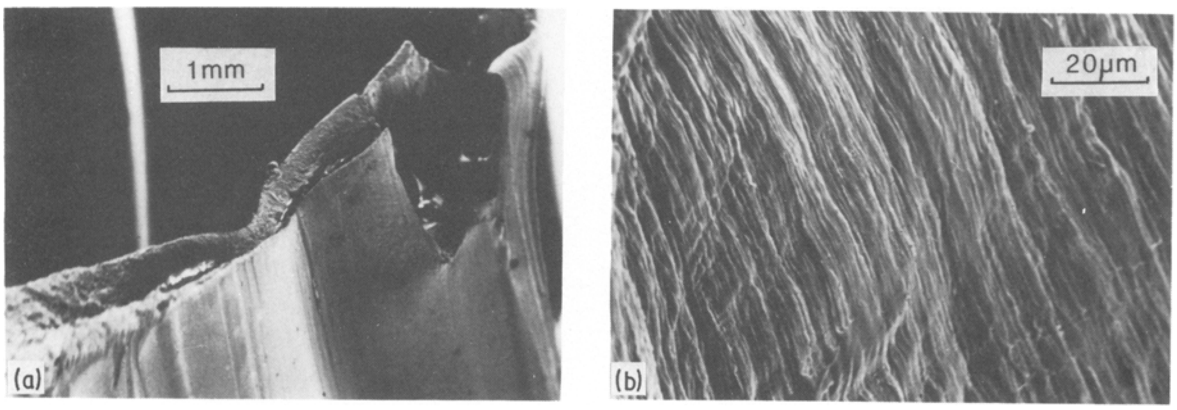


Figure 9 PP weathered in the shade for 3 years and then broken in uniaxial tension: (a) general view of fracture surface; (b) high magnification of part of (a) showing the internal surface exposed by the fracture.

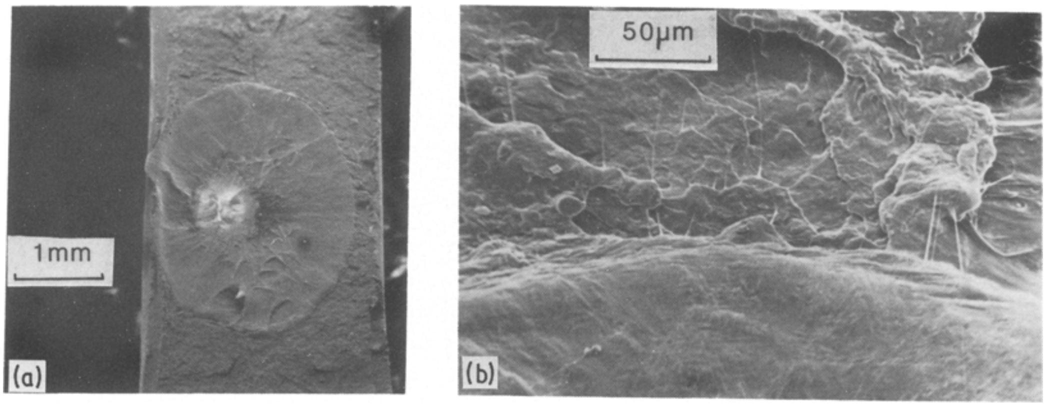


Figure 10 Fracture surface of PP weathered for 2 years then broken in uniaxial tension: (a) general view, showing flaw and original slow crack-growth region; (b) high-magnification image of the boundary between the slow crack-growth and fast-fracture regions.

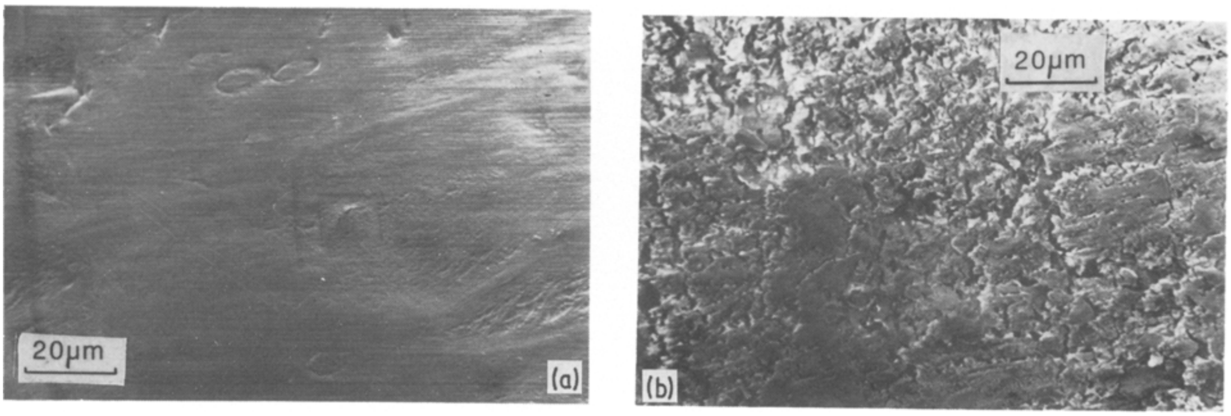


Figure 11 Moulded surfaces of POM specimens: (a) unexposed; (b) weathered for 2 years.

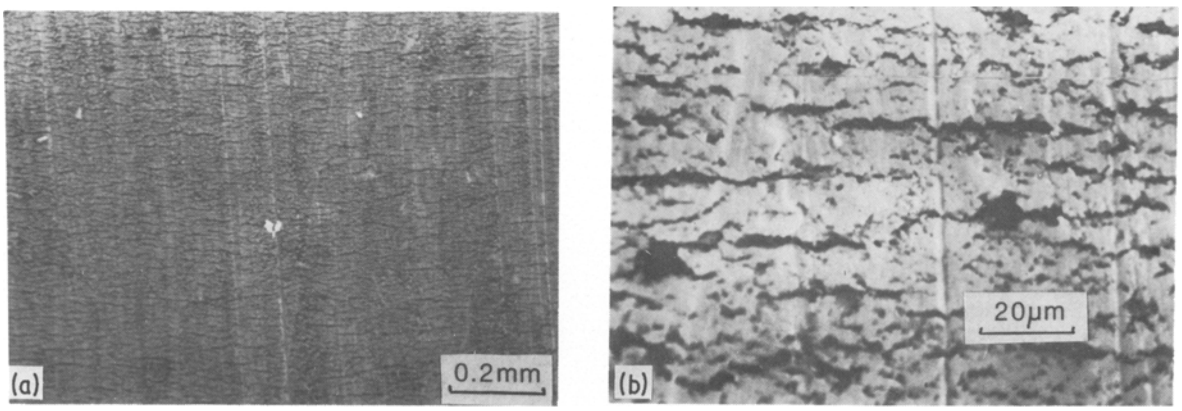


Figure 12 Moulded surface of POM specimen weathered for 3 years in the shade then broken in uniaxial tension: (a) general view; (b) high-magnification image of part of the area shown in (a).

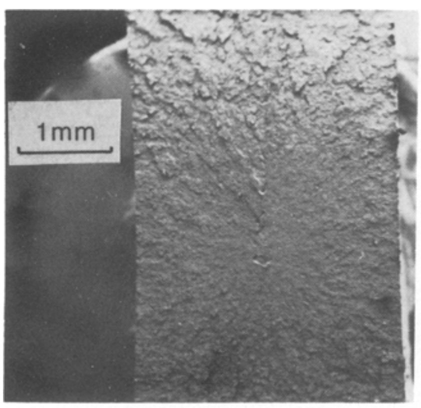


Figure 13 Fracture surface from unexposed POM specimen broken in uniaxial tension.

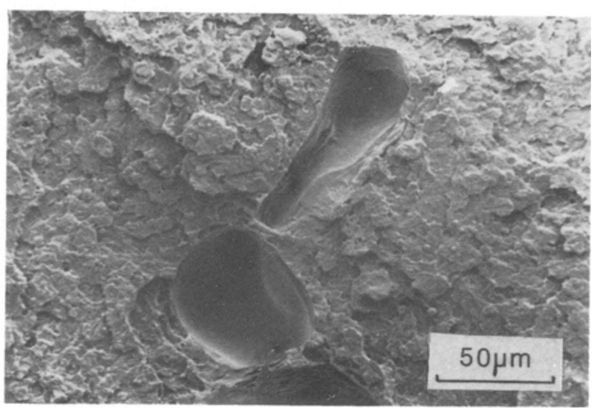


Figure 14 Voids located on the central plane of the POM bar shown in Fig. 13.

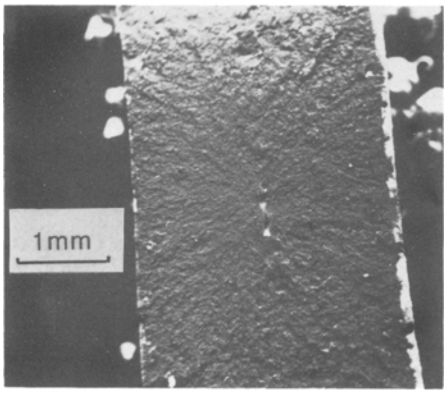


Figure 15 Fracture surface of POM specimen weathered for 2 years and then broken in uniaxial tension.

presumably opened up in the degraded surface layer during testing. It is of interest to note that the opposite face of this specimen did not show this kind of directional feature. This particular specimen was weathered in the shade and the "front/back" effect cannot be attributed to a difference caused by direct sunlight falling on one side but not on the other. It is possible that the reflected light received may not have been uniform, but we do not have any firm evidence or observations to offer which help to explain this result.

3.2.2.2. Fracture surface. One end of the fracture surface of an unexposed bar broken in uniaxial tension is shown in Fig. 13. Fracture appears to have been nucleated by a flaw (or flaws) located along the line that bisects the bar cross-section from top to bottom in Fig. 13. High-magnification inspection of the flaws reveals that they are voids (Fig. 14), which are not uncommon in POM mouldings. A similar mode of failure was in evidence with the specimens tested after weathering; the fracture surface shown in Fig. 15 was obtained with a specimen weathered for 104 weeks.

One further observation made with POM was the occasional presence on fracture surfaces of patches of material with a curious fused appearance reminiscent of structures sometimes seen in inorganic glasses or ceramics. An example is presented in Fig. 16a, and shows in addition very fine fibrils associated with the patch, a feature displayed also by the other examples found. The area shown in Fig. 16a was not very extensive nor very typical, as can be confirmed by inspection of the lower-magnification image containing the area (Fig. 16b).

3.2.3. N6,6

3.2.3.1. Moulded surface. The moulded surface of N6,6 showed a marked change on exposure (compare Figs 17a, b and c). Even greater differences were apparent on the moulded surfaces of specimens which had been tested in uniaxial tension. Fig. 18 shows a typical region from the moulded surface near to the fracture surface of an unexposed sample. The moulding marks in evidence on the surface of unexposed and untested samples (e.g. Fig. 17a) are apparent once again here. With a specimen weathered outdoors for 8 weeks a new feature appeared in the form of small diamond-shaped surface fractures (Fig. 19). These diamond fractures have an appearance generally similar to those observed and described by Haward, Hay and co-workers in their studies of ductile failures in poly(vinylchloride) and other polymers [17–22]. The small diamond fractures in Fig. 19 are formed into lines parallel to the bar axis, possibly located along the moulding marks. The largest of the diamonds shown in Fig. 19 is less than 10 μm across.

With specimens weathered for longer periods the diamonds produced during uniaxial extension were much larger and covered the moulded face much more extensively both on the direct exposed side (Fig. 20) and on the side away from the sun (Fig. 21). The diamond cavities expanded in all directions, but there was a noticeable tendency for them to coalesce in a direction perpendicular to the bar axis (and hence to the tensile direction) rather than parallel to the bar axis (Fig. 21). This often led to a ragged stratified appearance (Fig. 22). Very large diamonds often developed at corner sites (Fig. 23) and it often appeared that a corner-site diamond had become the dominant flaw from which final fracture developed.

3.2.3.2. Fracture surface. The unexposed bars formed a stable neck in the uniaxial tension test, and fracture occurred after some drawing had taken place (Fig. 24a). Part of the fracture ran along the neck itself, revealing a granular appearance (Fig. 24b). Near the centre of the specimen, in the drawn region, fibrillation occurred

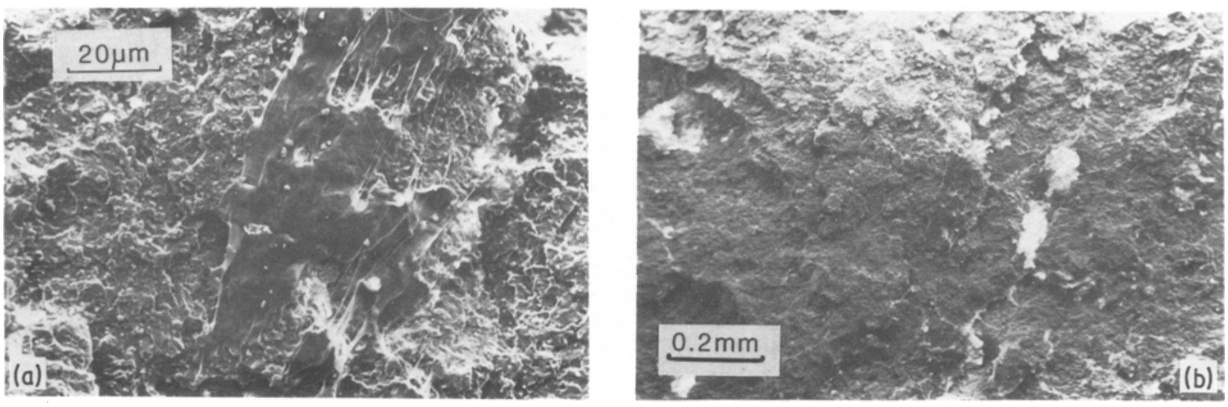
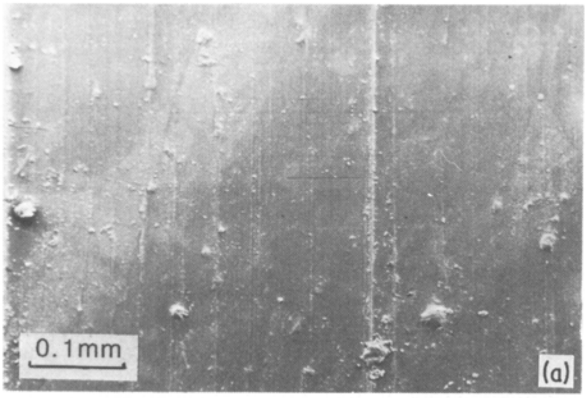
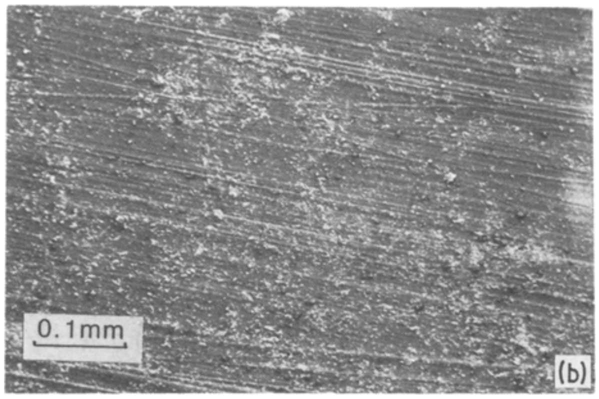


Figure 16 Part of the fracture surface shown in Fig. 15: (a) high magnification; (b) intermediate magnification, containing the area shown in (a) at the centre.





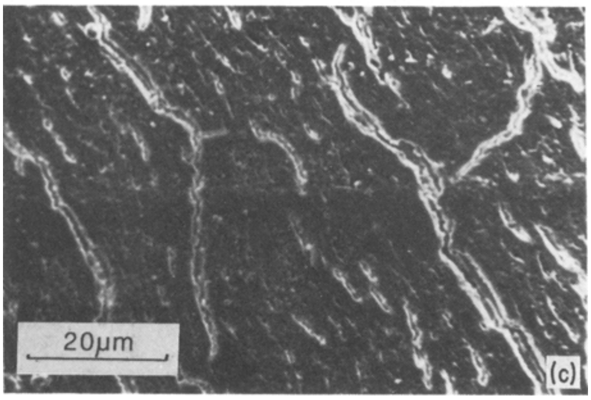


Figure 17 Moulded surface of N6,6: (a) unexposed; (b) weathered for 1 year; (c) weathered for 2 years (shown at high magnification).

and the final fracture was by fibre drawing and thinning, a feature displayed also by specimens weathered for 52 weeks (Fig. 25) and 156 weeks (not shown). Specimens weathered for up to 156 weeks showed the same general features, even though long exposures resulted in specimens which did not extend as much before failure. Fracture was wholly through the drawn region with exposed samples, without an excursion to the neck as found in the unexposed specimen shown in Fig. 24. Fracture was found to be nucleated by an internal flaw (Fig. 26), though the locus of fracture near to the surface seemed to be governed by prominent diamond fractures growing in from the surface and joining up with the crack growing outwards from the internal flaw.

3.3. Residual stress analyses

3.3.1. PP

In PP both aged indoors and weathered outdoors the residual stress levels were so small that accurate measurement by the layer-removal procedure was not possible. The change in curvature over the whole of the measurement interval (with removals down to half of the original bar thickness) was less than $0.2\,m^{-1}$. Therefore, with the possible exception of the region very close to the surface of the bar (say within 0.1 to 0.2 mm) for which the layer-removal procedure is incapable of reliable measurement in any case, the residual stress magnitude must be less than $0.5\,MN\,m^{-2}$. This is consistent with the results of earlier studies of the ageing of PP indoors [3, 12].

3.3.2. POM

In the unexposed state polyacetal bars were found to have very small residual stress levels (Fig. 27). The agreement between the two examples shown in Fig. 27 is not particularly good, perhaps because the stresses are so small, but it is interesting to observe that the stress near the surface is tensile. These bars had been aged at room temperature for at least two years before measuring the residual stress levels, and it is possible that this stress distribution is not the same as that present in the as-moulded state. We are not aware of any reported measurements of surface tensile residual stresses in as-moulded injection mouldings, but there have been several reports of tensile stresses developing as the result of post-moulding conditioning [2, 23–26]. After prolonged outdoor exposure the stress levels were found to have increased, retaining the same sense

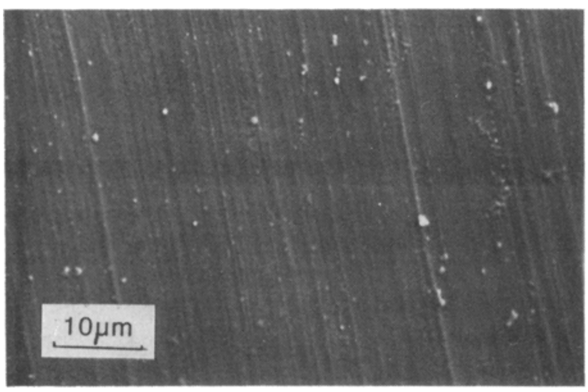


Figure 18 Moulded surface of an unexposed N6,6 bar broken in uniaxial tension.

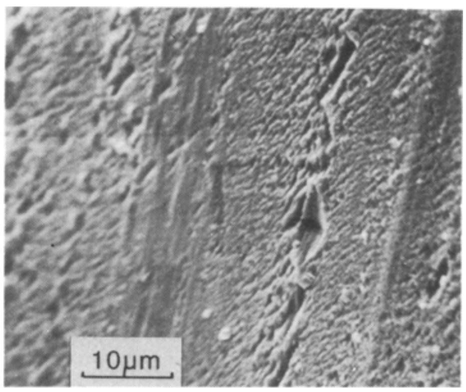


Figure 19 Part of the moulded surface of an N6,6 bar weathered for 8 weeks then broken in uniaxial tension. Note the diamond-shaped cavities.

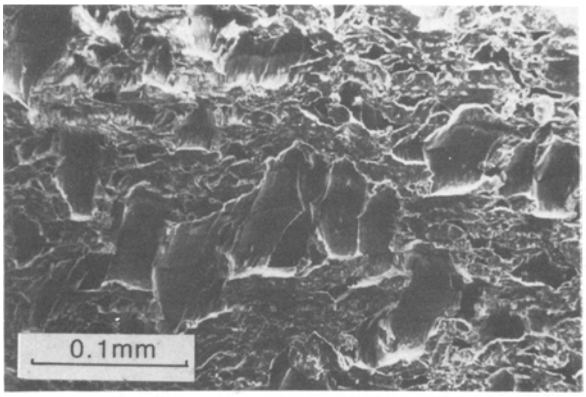


Figure 20 Diamond-shaped cavities on the directly exposed moulded surface of an N6,6 bar weathered for 2 years and then broken in uniaxial tension.

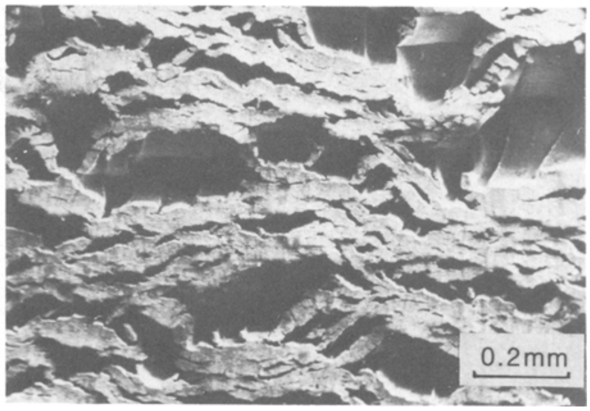


Figure 22 Moulded surface of N6,6 bar weathered for 3 years and then broken in uniaxial tension.

(tensile near the surface and compressive in the interior). Fig. 28 shows analyses for bars exposed for two years and for three years; in the case of bars weathered for three years results are shown for both the side facing the sun and for the side away from the sun. The method of presentation of these results follows that introduced before [25].

3.3.3. N6,6

N6,6 which was stored indoors at room temperature for more than two years also possessed tensile residual stresses near to the surface (Fig. 29). Again this result is unexpected, though Russell and Beaumont [24] have reported the development of tensile stresses near to the surface of nylon 6 mouldings treated in water. Outdoor weathering produced a modest increase in the level of tensile stresses near the surface of N6,6 (Fig. 29).

4. Discussion

The materials used in this study were commercial grades designed, presumably, for European conditions and not for the severe climatic conditions to which they were subjected here. It is therefore important to note that the results presented relate to the particular grades used and that the kind and quantity of protective additives that they contain are unknown. As with the earlier study of the weathering of several commercial grades of glassy polymers [2], the vulnerability to weathering of the particular materials used here reflects general field experience with the polymers studied. Therefore the results are of interest primarily in so far as they indicate the influence of weathering on the mechanisms of failure. We have begun to investigate the degree of control over the properties which we measure that can be exercised by the use of additives, and we intend to report on this aspect of weathering at a later date.

In the present work it has been shown that injection mouldings made from semi-crystalline polymers develop tensile residual stresses near the surface during weathering, just as was found with glassy polymers [2]. With POM and N6,6 this appears to be possible on extensive ageing indoors, but outdoor exposure accelerates the process. As was noted before [2], the presence of tensile residual stresses near to the surface renders a component vulnerable to fracture.

PP did not show much visible surface deterioration on weathering, but surface flaws developed with both POM and N6,6. With both of these materials surface cracks appeared during tensile testing. In the case of POM, failure still occurred from an internal flaw (as with unexposed bars) though the mechanical test results show that weathering weakened the material even if the failure mechanism remained unaltered. With N6,6 the surface cracks developed into the diamond-like plastic fracture features discussed by

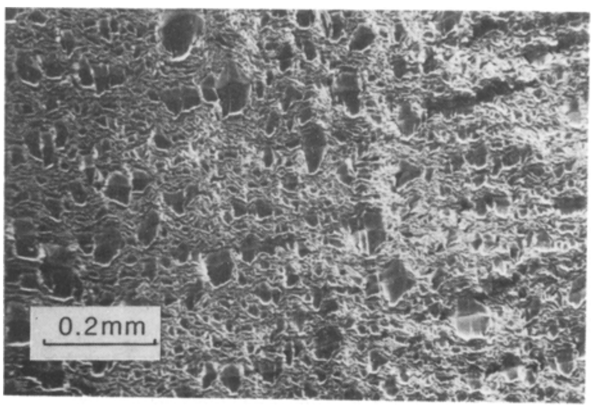


Figure 21 Diamond-shaped cavities on the side away from the sun of the bar shown in Fig. 20.

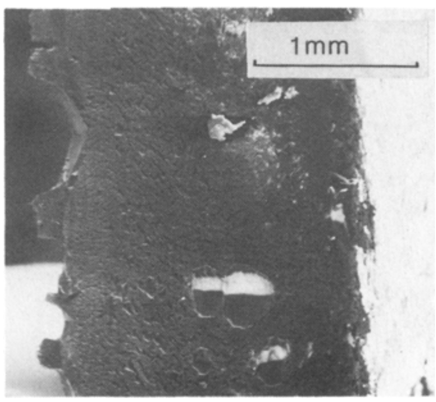


Figure 23 N6,6 bar weathered for 2 years and then broken in uniaxial tension, showing diamond cavities growing both on the moulded faces and at corner sites along the line of intersection between two moulded faces.

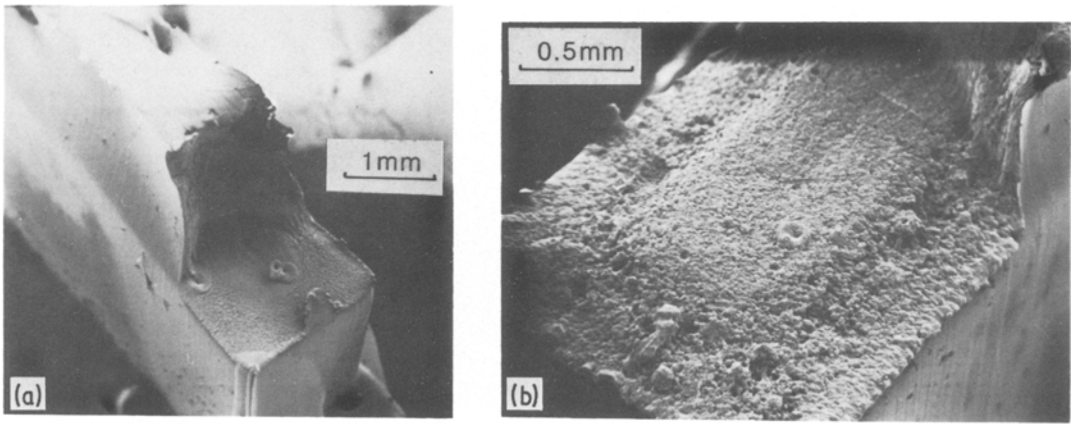


Figure 24 **Unexposed N6,6 bar, broken in uniaxial tension: (a) part of the fracture surface, showing necking; (b) higher-magnification image of another part of the fracture surface.**

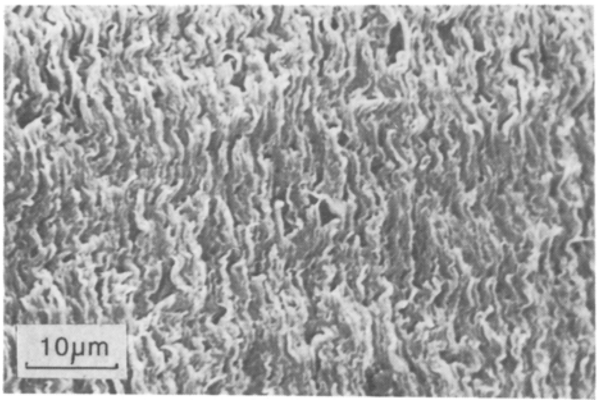


Figure 25 **Fibrillation on the fracture surface of an N6,6 bar** weathered for 1 year and then broken in uniaxial tension.

Haward, Hay and co-workers [17–22]. The diamonds multiplied and grew in all directions on continued tensile deformation. Neighbours coalesced in directions perpendicular to the tensile axis and eventually a dominant flaw developed from which final fracture occurred. No diamonds were observed on the surface of tensile-tested unexposed specimens, and the nucleation density and the size of the diamonds were dependent on the extent of weathering prior to tensile testing. Therefore weathering is seen to have a marked influence on the fracture mechanism with N6,6. This may arise as a consequence of weathering-related changes which might control both nucleation and growth of these features. Similar behaviour has been found with weathered polycarbonate and poly(vinyl chloride), and the mechanism will be discussed in a future publication [27].

Although PP showed less evidence of surface damage than POM or N6,6, the effect of weathering was in some ways more severe, causing a change in the failure mechanism. Specimens weathered for two years or more failed without drawing. It is interesting that with these specimens fracture usually occurred from an internal flaw, contrary to the expectation that weathering damage would be most severe near to the surface. It is possible that weathering caused a reduction in the ductility of the skin so that necking was inhibited. A slight increase in yield stress was observed, which is consistent with this idea. The stress measurements are overall values and it is not known how the corresponding stress values differ in the skin and core regions, in either the unexposed or the weathered samples. Skin and core stiffnesses are known to be different in PP [28–30], but it is not known whether they change on weathering. Therefore, the core region may be under quite different stress conditions in the unexposed and weathered bars, and the change in fracture mechanism need not necessarily mean that a change has developed in the interior of the weathered bars. That catastrophic weakening of the material had not occurred throughout the bar seems indicated by

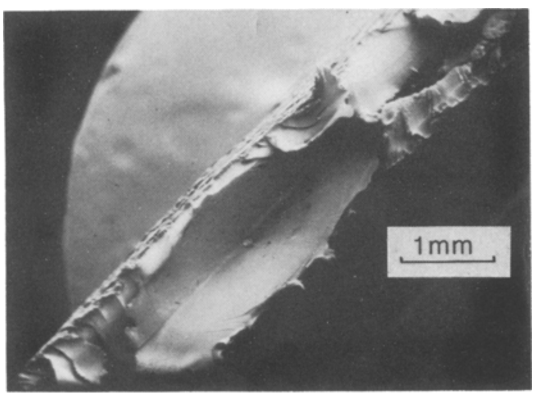


Figure 26 **Fracture surface of N6,6 specimen weathered for 3 years** and then broken in uniaxial tension.

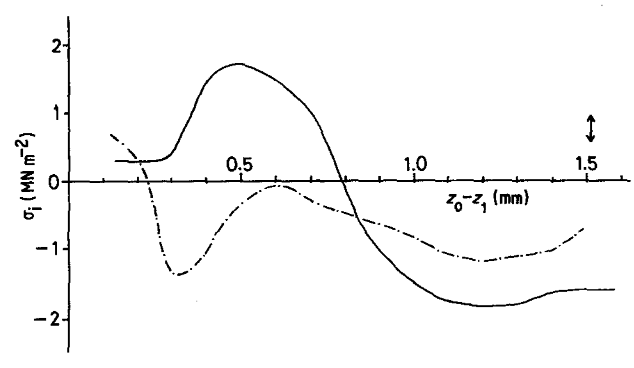


Figure 27 Residual stress distribution in unexposed POM bars (two examples). The moulded surface is located at $(z_0 - z_1) = 0$ and the centre of the bar is marked by the vertical arrow.

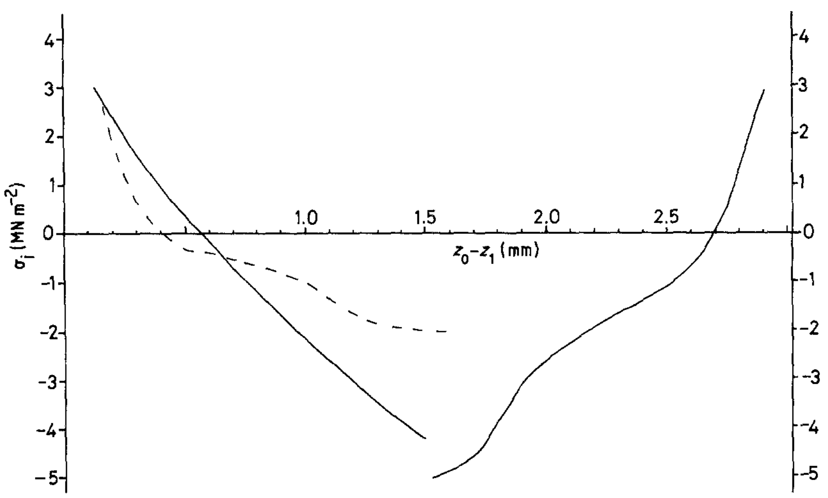


Figure 28 Residual stress distributions in POM bars weathered for 2 years (broken line) and 3 years (solid lines). Results are shown for two specimens exposed for 3 years: one was machined away from the directly exposed side and the results are presented on the left-hand side; the other was machined away from the side away from the sun and the results are presented on the right-hand side, with the right-hand axis coincident with the (back) face of the moulded bar. The analyses shown in solid lines should therefore meet at the bar centre; the discrepancy is not large.

the impact test results, which show that PP retained a higher fraction of its unexposed toughness than either POM or N6,6.

5. Conclusions

The change in residual stresses promoted by weathering in PP, POM and N6,6 is not as severe as with PS and PVC [2]. With POM and N6,6 tensile residual stresses develop near to the surface of the moulding but outdoor exposure is not necessary to make this happen. Their presence is, nevertheless, probably important, for the detrimental effect of weathering with these materials seems to be caused by the development of surface flaws and this process will be assisted by the tensile residual stresses. With PP, weathering causes a change in the failure mechanism without significant visual changes occurring at the surface. In order to develop a detailed understanding of the observed behaviour a knowledge is required of the properties of skin and core material in injection mouldings and the changes in these properties as a consequence of weathering, and some preliminary work is in progress in which this information is being sought.

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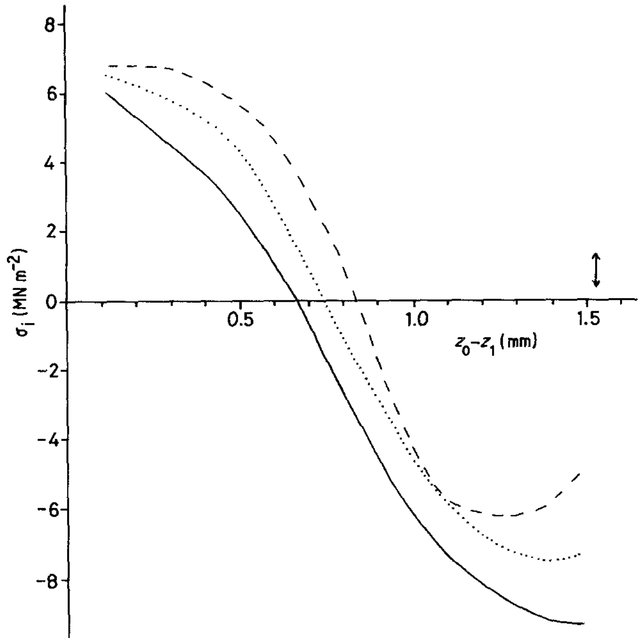

Figure 29 Residual stress distributions in N6,6 bars weathered outdoors for zero weeks (solid line); 52 weeks (dotted line); and 104 weeks (dashed line). The unexposed bar was aged indoors for an extended period before measuring the residual stresses.

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