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Weathering of injection-moulded glassy polymers: changes in residual stress and fracture behaviour

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Injection-moulded bars made from poly(methyl methacrylate) (PMMA) polystyrene (PS), polycarbonate (PC) and poly(vinyl chloride) (PVC), have been weathered outdoors in Jeddah, Saudi Arabia, for varying periods. The residual stresses in the bars have been found to vary considerably with exposure and in some cases the surface stress has reversed, becoming tensile. With PS and PVC, significant surface damage developed on exposure and the presence of surface flaws together with tensile residual stresses at the surface can be expected to reduce the resistance to fracture, especially in the case of PS which suffers considerable molecular weight reduction near the surface. The changes in residual stress in PMMA and PC were smaller, and the surface deterioration, examined by scanning electron microscopy, was much less than with PS and PVC. The performance of PMMA and PC in fracture tests generally declined less with weathering than did that of PS and PVC but the materials used were all commercial grades designed for use in Europe and the results obtained here should not be taken to indicate the relative weatherability of the different polymers. The significance of the results relate to the mechanism of failure involving the interaction of reversed residual stresses and surface flaws.

1. Introduction

The performance of many polymers is drastically reduced by exposure to the weather. Ultra violet light can cause molecular weight degradation which alone can weaken a component. Other factors may contribute to a deterioration in the properties of polymeric articles which are used outdoors, including extremes of temperature, temperature cycling, development of a temperature gradient (e.g. if one side of the component is in direct sunlight and the other side is in contact with a heat sink), and erosion by rain or by wind-borne particles. The process of weathering is consequently a most complicated process and mechanisms which dictate the deterioration in properties are not easily decided.

Resistance to fracture is markedly changed on weathering with many polymers. This is a key property and much attention has been paid to the weathering sensitivity and to possible remedies. Many polymers become very brittle after exposure to natural outdoor weathering, showing a marked reduction in strength and an even greater reduction in toughness. These properties are easily measured using standard laboratory mechanical testing procedures. The appearance of mouldings often changes on weathering. Transparent articles often show yellowing (e.g. when made from clear polystyrene) and discolouration of pigmented grades is another common problem. When inspected under a microscope, or preferably by scanning electron microscopy (SEM), some polymers are

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found to have developed surface cracking on weathering. The presence of such flaws could, of course, account at least partially for the reduction in the resistance to fracture.

Changes in the chemical structure promoted by weathering are often followed using infrared spectroscopy [1]. For example, an increase in the concentration of carbonyl groups resulting from photo-oxidation can be measured for polystyrene, poly(vinyl chloride) and other polymers. Another popular technique is gel permeation chromatography (GPC) which can be used to indicate the extent of scission and/or cross-linking [1]. Breaking of molecular chains will necessarily lead to a reduction in strength and toughness, and cross-linking will often lead to embrittlement, hence the popularity of the GPC method of characterization in weathering studies.

In the studies reported here much of the work replicates a quite standard approach, as outlined below.

1. Injection-moulded specimens of several polymers were exposed for various periods of time to the weather (in the very extreme climate experienced in Jeddah, Saudi Arabia).

2. Samples with different exposures were tested to failure using monotonic uniaxial tension and three-point bend tests. Some Charpy impact tests were also conducted.

3. The fracture surfaces obtained in these tests were inspected in the SEM. In addition, the moulded surfaces were examined in the SEM to see whether surface markings developed on weathering.

4. Material cut from exposed samples was subjected to GPC molecular weight distribution analysis and to thermal analysis.

In addition, the residual stress distribution was measured for samples with different exposures. Previous studies of the modification of residual stress distributions in injection-moulded thermoplastics on ageing or annealing at a uniform temperature or in a temperature gradient led us to expect a significant effect of weathering. This has been confirmed and, for some of the materials investigated, the effect is quite large and may have an important influence on the performance of the moulding. This aspect of weathering has not been reported before to our knowledge, and for this reason these results will be dealt with in detail. It is not the purpose of this paper to deny the importance of molecular weight reduction as a prime cause of deterioration in the resistance to fracture of mouldings exposed outdoors, but it will be shown that changes in the residual stress distribution may also have a strong influence and that remedies based solely on the provision of protection from ultra violet degradation may not be sufficient.

2. Experimental details

2.1. Materials and specimen production

All specimens were injection moulded on a Stubbe SKM 76-110 reciprocating screw machine at RAPRA (Shawbury, Shrewsbury) using (i) a single end-gated tensile test bar cavity with a gauge length section ~ 12.7 mm wide × ~ 3.2 mm thick, or (ii) a single end-gated Charpy test bar cavity measuring 127 mm × 12.7 mm × 12.7 mm. The materials used are listed in Table I together with the principal moulding conditions. In the cases of PMMA and PC the material was pre-dried prior to moulding.

TABLE I Moulding grades and conditions

Polymer	Grade	Mould temperatures (° C) Moving plate/ fixed plate	Injection temperatures* (° C) Nozzle/Zone 3/Zone 2/Zone 1	Injection pressure (MPa)
Poly(methylmethacrylate) PMMA	ICI Diakon	60/60	T: 245/230/220/210 C: 230/240/250/260	T: 114 C: 133
Polystyrene PS	Hoechst Hostyren N4001	33/30	T, C: 215/200/200/190	T: 114 T: 129
Polycarbonate PC	Bayer Makrolon 2603	89/85	T, C: 325/335/335/335	T, C: 95
Poly(vinyl chloride) PVC	ICI: Welvic ZR18/1734/854	40/40	T, C: 185/185/180/170	T, C: 133

*T = tensile test bars, C = Charpy test bars.

2.2. Ageing and weathering

Specimens were permitted to age indoors at room temperature for several weeks prior to testing or outdoor exposure. Unexposed specimens were tested after various ageing periods to check the extent to which any changes observed in outdoor exposed samples could be attributed to normal physical ageing as opposed to weathering. Samples were exposed for 8, 16 and 52 weeks outdoors in Jeddah, inclined at 20° to the horizontal facing South. Some Charpy specimens were exposed for 104 weeks. On completion of the period of outdoor exposure the mouldings were wiped clean with soft tissue. Details of the Jeddah climate have been reported before [2], and some of the most relevant information is shown in Fig. 1. All exposures of specimens for which results are reported here were begun at the end of April.

2.3. Molecular weight

Samples were cut from unexposed and 8 week and 52 week exposed bars and analysed by gel permeation chromatography using a Waters Associates ALC 200 operating at room temperature with a flow rate of 1 ml min^{-1} using tetrahydrofuran as solvent. Specimens were machined from near the centre of the gauge length of the dumb-bell by milling away material from the back (unexposed) face to leave a sample of material from the exposed face.

2.4. Thermal analysis

A Perkin-Elmer DSC I differential scanning calorimeter was used to monitor changes in the glass transition temperature (T_g) of polymers at different states of exposure. 8 to 12 mg of material in the from of chips was used for each run and tests were conducted in flowing nitrogen with a heating rate of 4° C min^{-1}.

2.5. Mechanical testing

Uniaxial tensile tests were conducted on a Instron 1115 machine using a crosshead speed of 10 mm min^{-1} (PMMA, PS) or 20 mm min^{-1} (PC, PVC). Three-point bend tests were conducted on a JJ Lloyd T5003 machine using the attachment supplied by the manufacturer which applies the load through cylinders 62.5 mm apart. The crosshead speed was set at 20 mm min^{-1}. For the Charpy impact tests notches were cut before exposure to a depth of 2.5 mm, having a notch tip radius of 0.25 mm and a 45° entrance angle.

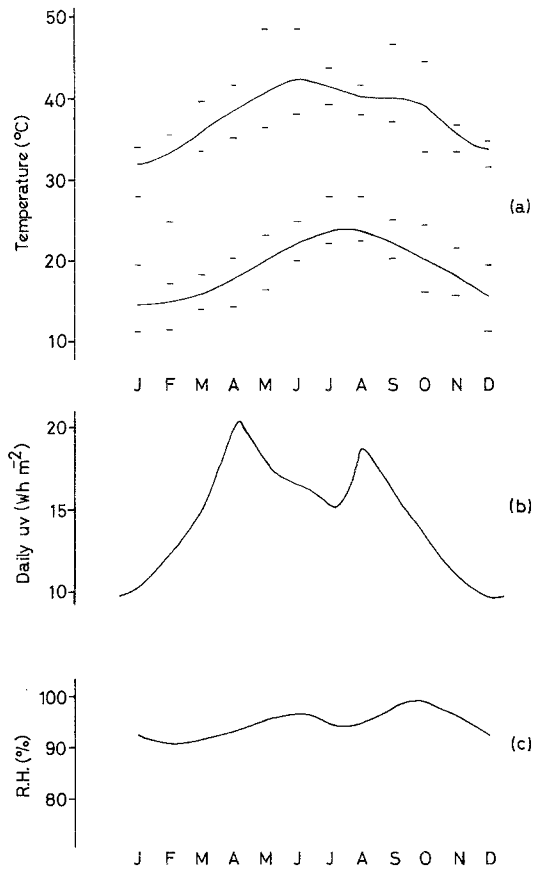


Figure 1 (a) Temperature variations in Jeddah month by month showing highest and lowest daily temperatures (average of 14 years). The highest and lowest values recorded during the 14 year period are also shown (b) Daily dose of ultra violet radiation received in Jeddah by monitors at 20° to the horizontal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

The notched surface was exposed. Tests were conducted on an Avery–Denison 6709U machine using a striking velocity of 3.46 m sec^{-1}.

A limited number of stress relaxation tests were conducted according to procedures described in detail elsewhere [3–5]. During some of these tests birefringence was measured as a function of time; birefringence measurements were continued for a significant time after unloading at the end of the stress relaxation test. Similar tests have been described previously [6–8].

2.6. Scanning electron microscopy

Fracture surfaces were gold-coated and inspected in the SEM. The moulded surfaces from these specimens were also examined, but to be certain that surface features were not a consequence of

TABLE II

Polymer	Weeks exposed	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n	T_g(°C) (by DSC)
PMMA	0	87	44	2.0	101
	8	82	40	2.0	
	52	62	32	1.9	97.5
PS	0	365	163	2.2	100
	8	345	134	2.6	
	52	185	58	3.2	80
PC	0	43.4	24.0	1.8	143.5
	8	42.8	23.1	1.8	
	52	40.2	22.2	1.8	142
PVC	0	126	53	2.4	87
	8	118	54	2.2	
	52	74	37	2.0	70

the applied deformation, untested mouldings were observed also. This is especially important in the case of ductile samples which showed considerable deformation before fracture.

Specimens were viewed using the secondary electron image using an accelerating potential of 7.5 kV. No beam damage was detected with PS or PVC, but limited radiation damage was noted with PMMA and PC.

2.7. Residual stress assessment

The residual stress distribution in samples exposed for various times was determined using the layer removal procedure [9–12]. 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 was measured using the technique described before [5, 11], and a plot developed of curvature against depth of removal. From this the residual stress distribution was determined using the formula presented by [9–12].

3. Results

3.1. Molecular weight

The results of the measurements of molecular weight by GPC are shown in Table II. Molecular weight degradation occurs with each of the polymers, but the effect is not large with PC. PS and PVC both show marked reductions. It is interesting to note that M_w/M_n increases with exposure for PS but decreases with PVC.

3.2. Thermal analysis

The measurements of T_g obtained from the DSC analysis are also shown in Table II. In each case a reduction in T_g is observed after 52 weeks exposure and once again the effect is small for PC and modest for PMMA, but large with both PS and PVC.

3.3. Mechanical testing

Load–extension curves for uniaxial tensile tests are shown in Figs. 2 to 4. For all polymers the principal effect of weathering is to reduce the elongation to break. In the case of PVC the strength is not changed very much, but with polymers which fracture before yielding (PMMA, PS) the strength is considerably reduced. The strength of PC also drops sharply for low exposures, but then much more slowly. The dependence of tensile strength and of the extension at break on exposure time are shown in Figs. 5a to d. The tensile strength presented is the maximum engineering stress recorded during the test and the extension at break is taken to be the crosshead displacement, uncorrected for machine complicance.

Some tests were conducted on specimens on which the exposed surface was milled away. The reason for this was that it is expected that ultra violet-promoted degradation will be greatest near to the surface and there may, therefore, be less difference in the properties of the cores of unexposed and weathered samples than in the properties of whole bars. In case there were skin-core effects and because of possible influences of surface finish and differences in cross section, unexposed specimens were prepared in a similar manner, with one surface removed, and tested for comparison. With PMMA the weathered

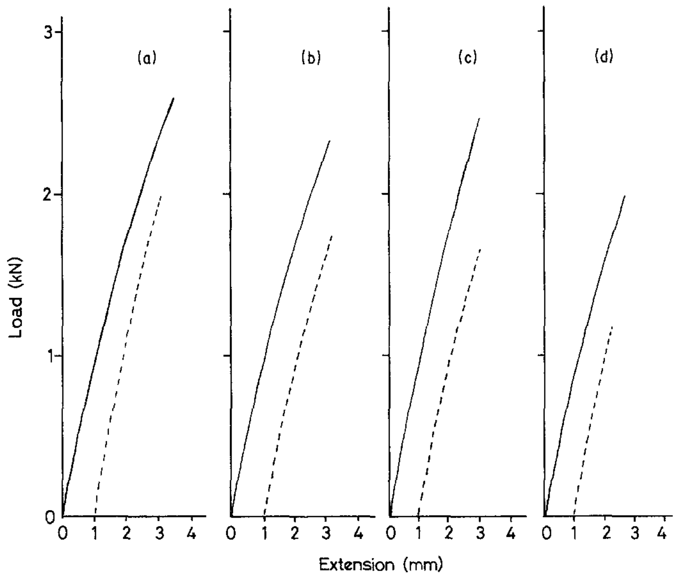


Figure 2 Load–extension curves for PMMA (solid lines) and PS (broken lines – displaced 1 mm parallel to extension axis) for samples weathered for (a) 0 weeks (b) 8 weeks (c) 16 weeks (d) 52 weeks.

specimens with the exposed surface removed, had a tensile strength approximately 12% higher than the specimens weathered for the same period but tested intact, but the unexposed samples showed almost 20% increase in tensile strength when one surface was removed. This seems to indicate that degradation was not confined to the exposed surface. A similar conclusion could be drawn from results with PS for which the removal of the surface produced very little difference in tensile strength either with the unexposed or with the weathered specimens. Removal of the surface did not produce any significant change in tensile strength with PC.

Broadly similar results were obtained from three-point bend tests which were arranged so that the exposed surface of the specimen became tensile on applying the bending deformation. With PMMA the flexural strength fell fairly slowly with exposure, reminiscent of the behaviour in uniaxial tension, but with PS the deterioration in flexural strength was greater and developed more rapidly than the deterioration in uniaxial tension (Fig. 6). PC and PVC specimens pulled through the straining rig without fracture at all weathering states.

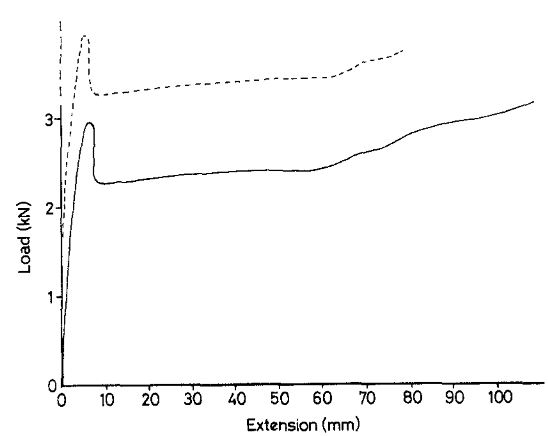


Figure 3 Load–extension curves for PC. Solid line; unexposed; broken line, displaced 1 kN parallel to load axis: weathered for 52 weeks.

The results of the Charpy impact tests are shown in Fig. 7. All four polymers show a significant reduction in impact performance on weathering with PC showing the smallest fractional change after 2 years exposure (~ 14%) and PVC the greatest (~ 40%).

In a limited series of stress relaxation tests on PMMA and PS at 40° C no significant difference was noted between unexposed specimens and those which had weathered for 52 weeks. When testing at 60° C a marked difference was noted for PS mouldings in the unexposed and 52 weeks weathered states respectively (Fig. 8a). The effect of weathering was apparently to reduce the relaxation rate in uniaxial tension. On removing the samples from the straining rig after stress relaxation at 60° C it was found that the weathered sample was shorter than the unexposed sample and that it had developed a considerable curvature at one end, with the exposed face becoming concave. It should be recalled that the glass transition temperature of weathered PS is only 20° C higher than the test temperature,

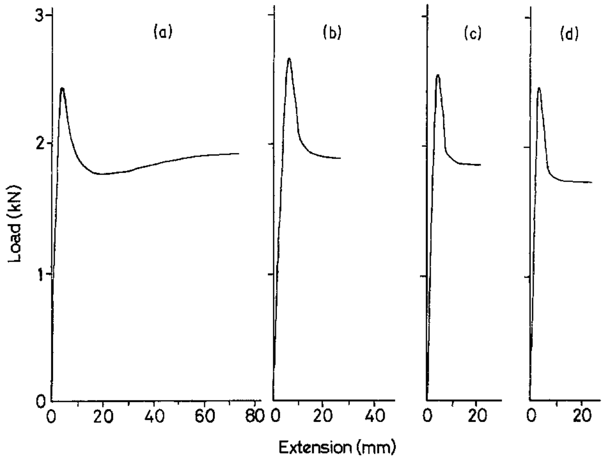


Figure 4 Load–extension curves for PVC for samples weathered for (a) 0 weeks (b) 8 weeks (c) 16 weeks (d) 52 weeks.

whereas T_g for the unexposed material is 40° C higher than the test temperature. Thus we speculate that the entropy elastic effect associated with molecular orientation may be active at the 60° C test temperature in the case of weathered material but not with unexposed material, and that molecular recoil is responsible for some axial shrinkage which opposes the viscous processes. The net effect is that the viscous processes dominate but that the measured stress relaxation proceeds more slowly than in the unexposed material in which recoil will be negligible.

The change in birefringence occurring during stress relaxation at 60° C showed a different time dependence for weathered and unexposed PS respectively (Fig. 8b). The negative birefringence observed in injection mouldings is caused by molecular orientation, but PS has a positive stress optical coefficient. Hence relaxation of tensile

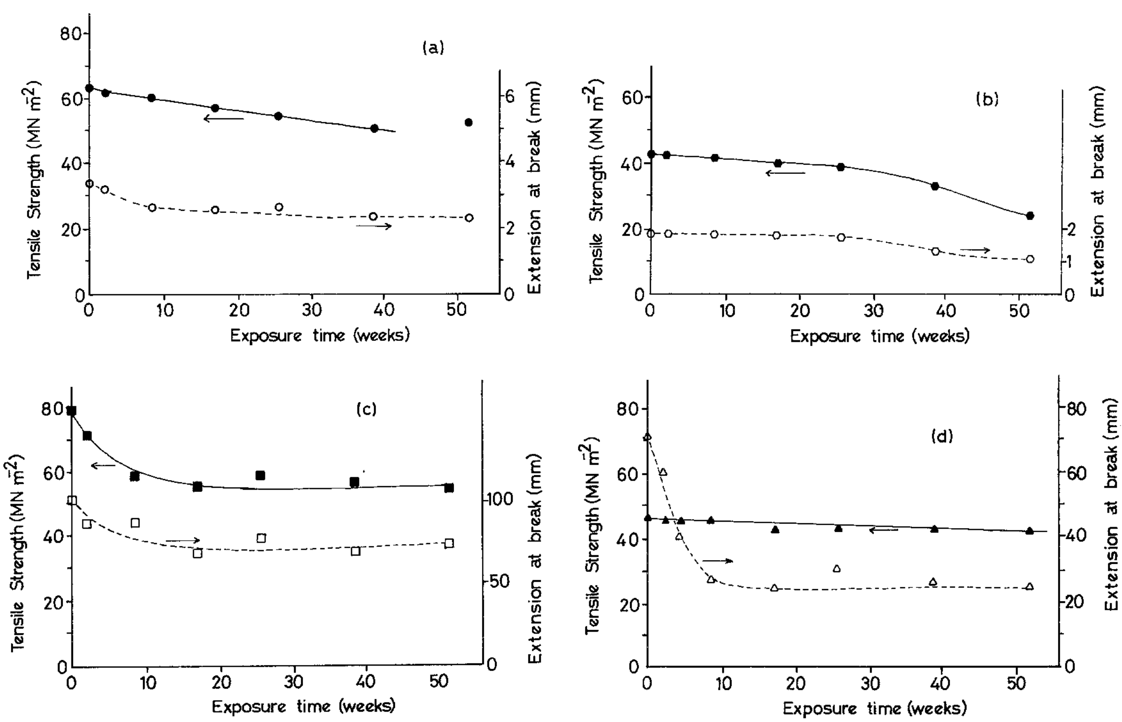


Figure 5 Tensile strength (solid symbols and lines) and extension to break (open symbols, broken lines) as a function of exposure time (a) PMMA; (b) PS; (c) PC; (d) PVC.

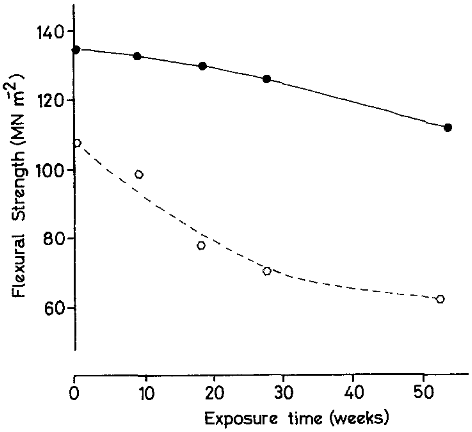


Figure 6 Flexural strength as a function of exposure time (a) PMMA: solid symbols and line; (b) PS: open symbols, broken line.

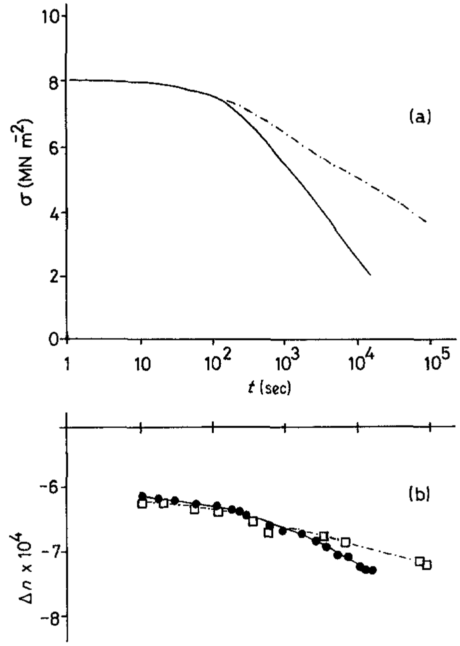


Figure 8 (a) Stress relaxation of PS at 60° C. (b) Birefringence as a function of time during the stress relaxation tests in (a). Unexposed: solid symbols, solid lines; weathered 52 weeks: open symbols, broken lines.

stress will produce a negative increment of birefringence, and if the mechanism of relaxation involves molecular orientation then this would provide a further negative increment. Conversely, any recoil of molecules will provide a positive increment in birefringence. The results shown in Fig. 8b are thus consistent with the hypothesis advanced above to explain the relaxation behaviour shown in Fig. 8a.

No marked effect of weathering on stress relaxation was found with PC, but an effect attributed to ageing was noted in the birefringence behaviour, Fig. 9. In previous studies on samples from the same batch of mouldings the birefringence remained steady during stress relaxation [6] whereas in the tests reported here a modest drop in birefringence was recorded. This change in behaviour cannot be attributed to weathering in the case of the unexposed samples, but these had been stored for more than two years at room temperature before testing, whereas the specimens were tested within four weeks of moulding in the studies reported by Qayyum and White [6]. Hence it seems that the change in birefringence behaviour during stress relaxation is not specifically promoted by outdoor exposure.

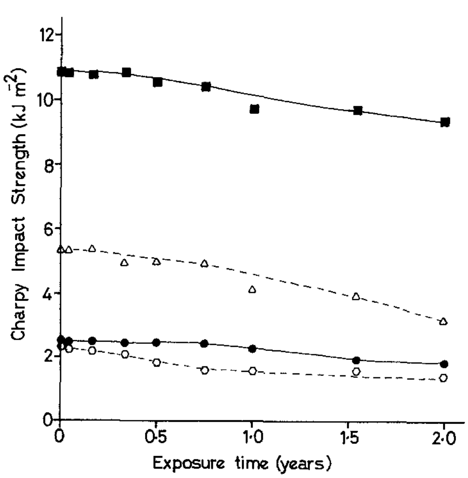


Figure 7 Charpy impact strength as a function of exposure time. (a) PMMA ●; (b) PS ○; (c) PC ■; (d) PVC △.

3.4. Scanning electron microscopy

3.4.1. PMMA

3.4.1.1. As-moulded surface. The as-moulded surface did not show any marked change in appearance even after weathering for 52 weeks. Both unexposed and weathered surfaces damaged

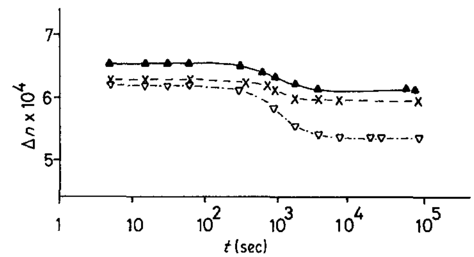


Figure 9 Birefringence as a function of time during stress relaxation tests for PC weathered for 0 weeks ▲; 8 weeks ×; 52 weeks ▽.

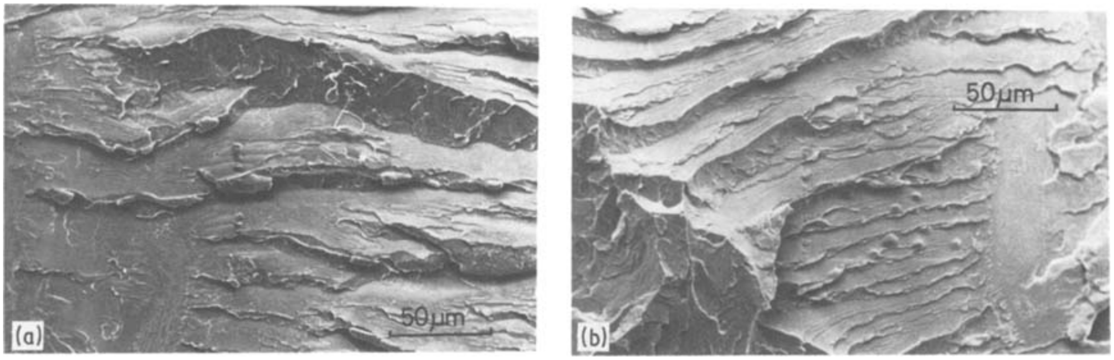


Figure 10 Uniaxial tensile fracture surfaces from PMMA (a) unexposed, (b) weathered for 52 weeks.

readily in the beam, developing picture frames and other visible damage.

3.4.1.2. Fracture surface. No marked differences were found on comparing uniaxial tension fracture surfaces obtained using specimens which had not been weathered and which had been exposed for 52 weeks respectively (see Fig. 10). No skin-core effect was found for exposed or unexposed samples; an area which includes the surface of a sample broken in uniaxial tension after 52 weeks weathering is shown in Fig. 11. There is no indication how the surface has influenced fracture either as a result of fabrication or weathering-related depth-dependent properties. This contrasts with the results obtained with PS (see below). The Charpy impact fracture surfaces showed typical ribbed structures [13] over much of the section. The ribbed structure did not develop until a depth of approximately 0.1 mm inside the notch root in the case of weathered samples, whereas the ribbed pattern commenced at the notch root in the unexposed sample (Fig. 12).

3.4.2. PS

3.4.2.1. As-moulded surface. Fig. 13 compares the as-moulded surface of an unexposed sample with a similar moulding after 52 weeks exposure. The unexposed surface is typically smooth, but weathering has produced a network of cracks which are tens of microns in length and, on examination at higher magnification, were found to be up to 2 μm wide.

3.4.2.2. Fracture surface. A common feature in fracture surfaces was a skin-core boundary of the order of 0.2 mm wide, dividing a region of very rough fracture near the surface and a region of much smoother fracture. Fig. 14 shows an example obtained by testing a sample weathered for 8 weeks in uniaxial tension. Although a skin-core morphology is normally associated more with injection-moulded crystalline polymers for which very distinct crystal morphologies develop near to the surface and within the interior of the moulding respectively (see [11] for a bibliography), non-crystalline polymers also show a marked variation in molecular orientation leading to large changes in birefringence near to the surface [14, 15]. The skin and core material have been found to have different thermal properties [16]. Thus, an explanation for the fracture morphology may be sought in terms of (a) the skin-core morphology of injection mouldings; (b) a plane stress/plane strain effect [17] or (c) residual stresses, which change very rapidly near to the surface [11, 18]. An explanation in terms of weathering can be ruled out because this characteristic is found in unexposed samples for which ultra violet degradation of

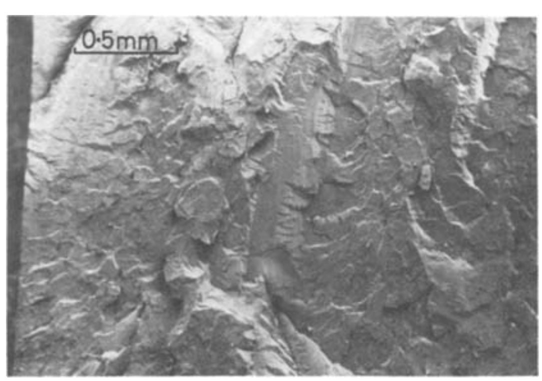


Figure 11 PMMA uniaxial tensile fracture surface from a specimen weathered for 52 weeks. There is no skin–core boundary visible near to the surface.

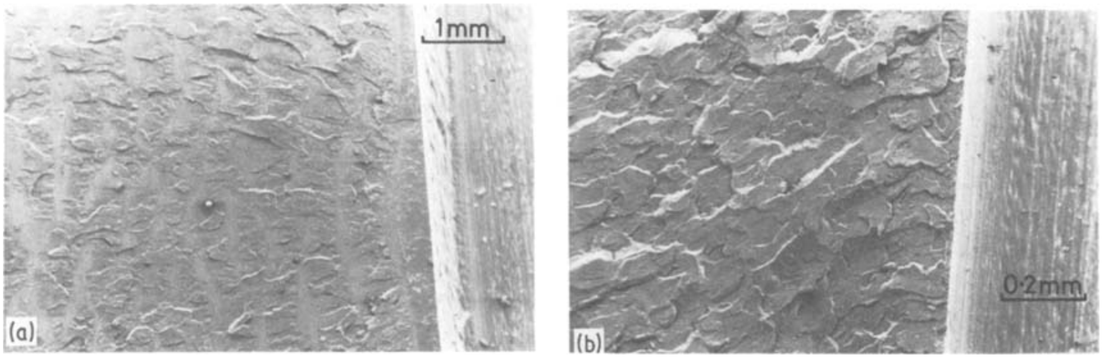


Figure 12 PMMA Charpy impact fracture surfaces (a) unexposed, (b) weathered 52 weeks.

the surface cannot have occurred. The morphological explanation seems the more likely, and futher evidence is provided by three-point bend specimens in which the skin-core appearance is shown near to the edge which was at the convex (tensile) surface in the three-point bend test. An example is shown in Fig. 15a for an unexposed sample. The part of the fracture surface adjacent to the compressive surface in three-point bend tests shows gross deformation, disguising the skin/core morphology. The skin/core appearance is less clear with specimens weathered for longer periods because the fracture surface is much rougher in the interior, as shown in Fig. 15b, which corresponds to a uniaxial test conducted on a specimen exposed for 16 weeks.

Smooth fracture covered much of the surface with unexposed specimens and with some exposed for only 8 weeks (Fig. 16). Evidence of crazing was visible even at low magnification ($\lesssim \times 50$) with such specimens (see, for example, Fig. 14), but for specimens weathered for 16 weeks and 52 weeks crazing was only clearly visible at higher magnifications ($\gtrsim \times 200$), as illustrated by the fracture surface from a specimen weathered for 52 weeks and broken in three-point bending (Fig. 17). Thus, the development of large planar crazes appears not to have occurred in specimens weathered for 16 weeks or more.

A feature found primarily with specimens weathered for 16 weeks was the production of long fibrils measuring tens of microns in length and a fraction of a micron in diameter (Fig. 18). These fibrils were found on specimens tested both in uniaxial tension and in three-point bending. Similar features were seen on a sample exposed for 8 weeks, then broken in three-point bending.

3.4.3. PC

3.4.3.1. As-moulded surface. PC showed no noticeable surface deterioration after 52 weeks weathering (compare Figs. 19a and b). Some picture frame damage occurred during exposure.

3.4.3.2. Fracture surfaces. PC showed considerable ductility and significant area reduction took place in uniaxial tension for all exposures. Prominent shear lips can be seen on samples which were

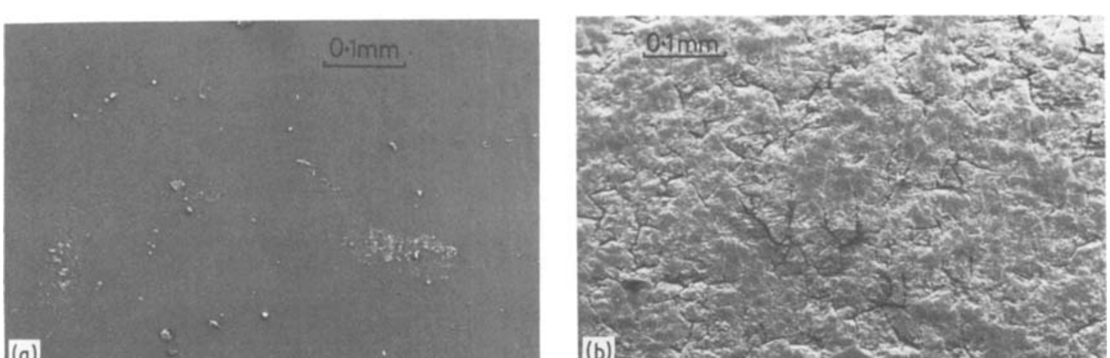


Figure 13 PS surfaces (a) unexposed, (b) weathered 52 weeks.

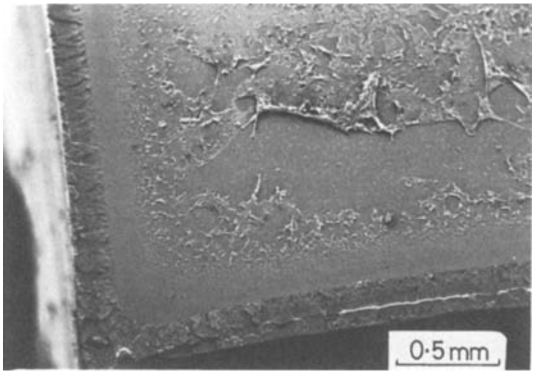


Figure 14 PS uniaxial tensile fracture surface from specimen weathered for 8 weeks.

unexposed and weathered for 52 weeks respectively (Fig. 20a and b). A network of lines is seen on the fracture surfaces of both samples. These have not yet been explained. A number of examples of wavy ribbons of a kind seen on fracture surfaces before [19–21] were found; Fig. 21 is from a specimen exposed for 8 weeks. Such features are believed to occur when cracks develop simultaneously on different planes, then eventually coalesce. Evidence for the operation of similar mechanisms was found for a sample weathered for 52 weeks.

3.4.4 PVC

3.4.4.1. As-moulded surface. The moulded surface showed considerable deterioration after 52 weeks exposure (compare Fig. 22a and b). On examining the specimens at higher magnification it was found that the unexposed surface had a speckled appearance, showing nodules of 1 μm or less in diameter (Fig. 22c), whereas the surface weathered for 52 weeks had a generally much rougher appearance, but with many features of similar scale (Fig. 22d). It is of interest to note that PVC preparations often show particles in the same size range (see [22] for discussion of the possible interpretations of these features).

3.4.4.2. Fracture surface. Considerable deformation was found to occur before fracture even with specimens which had been weathered for 52 weeks. Fig. 23 shows that some drawing occurred prior to fracture and reveals very coarse fibrillation with some axial cracking. The crack initiation site was usually identifiable and coincided with a second-phase particle (Fig. 24a). Local fibre drawing was found in some extensive regions (Fig. 24b). No significant differences in appearance were found on Charpy impact fracture surfaces from unexposed and weathered specimens, respectively.

3.5. Residual stress analysis

The results of the layer removal analyses are shown in Figs. 25 to 28. In each case specimens weathered for 8 weeks and for 52 weeks, respectively, are compared with unexposed specimens by presenting both the plots of curvature against material removed and the residual stress profiles derived from these plots assuming uniform modulus. Although the tensile tests indicate that a small fall in stiffness occurs on weathering the same value for the modulus was used in the Treuting and Read analysis for a particular material independent of the state of weathering. The values of Young's modulus, E, and Poisson's ratio, ν, used for the analyses are given in the figure captions.

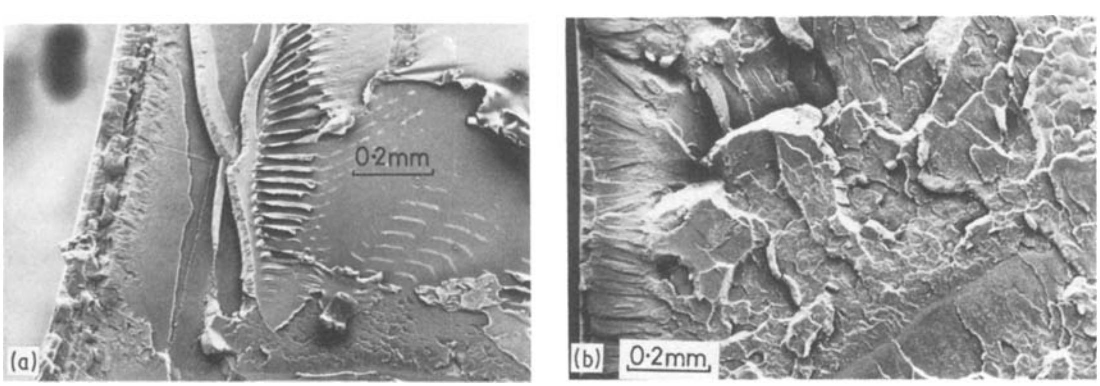


Figure 15 Part of PS uniaxial tensile fracture surfaces form (a) unexposed specimen, (b) specimen weathered for 16 weeks.

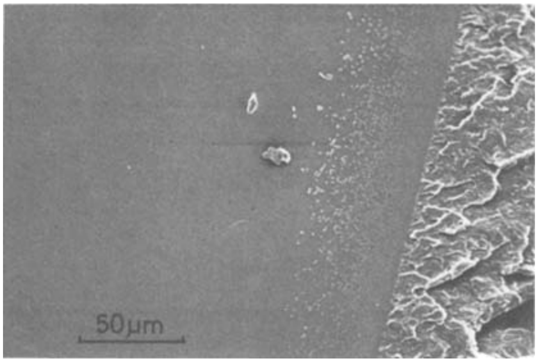


Figure 16 Smooth fracture region of an unexposed PS sample broken in three-point bending.

3.5.1. PMMA
The unexposed bar shows the usual nearly parabolic stress distribution with compressive stresses near the surface and fairly low ($< 2\,\mathrm{MN\,m^{-2}}$) tensile stress in the interior. Weathering is seen to reduce the magnitude of the stresses both near the surface and in the interior (Fig. 25), but the effect is fairly modest.

3.5.2. PS
The residual stresses in unexposed PS are also nearly parabolic, and after two months weathering the stress magnitude is again found to diminish at most locations, falling to very low levels (but still tensile) in the interior ($< 0.5\,\mathrm{MN\,m^{-2}}$ near the bar centre), Fig. 26. The results for 52 weeks exposure show a marked change for now the bar is found to curve in the opposite sense when layers are removed, an immediate indication that the sense of the stress distribution must be reversed. The computed residual stress distribution shows a significant tensile residual stress has developed near the surface, balanced by a small nearly constant compressive stress ($\lesssim 0.5\,\mathrm{MN\,m^{-2}}$) over most of the interior of the bar.

3.5.3. PC
Higher stresses were found to be present in the unexposed PC bar than in either PMMA or PS (Fig. 27). The stress magnitudes diminished considerably on weathering for 8 weeks, and a further marked change took place on extending the weathering period to 52 weeks. Although for PC the stress at the surface has not actually reversed and become tensile after 52 weeks weathering, the remaining compressive stress is very small indeed.

3.5.4. PVC
The residual stress levels in unexposed PVC are fairly small and have diminished still further after 8 weeks weathering (Fig. 28). After 52 weeks weathering the bar had developed a permanent curvature and on conducting the layer removal procedure it was found that the side of the bar which had been exposed had developed tensile stresses near to the surface.

4. Discussion
It must be emphasized that the materials tested here were all commercial grades, presumed to be designed for European conditions; none of them were claimed to be suitable for the weather conditions in Saudi Arabia. The materials will inevitably have different amounts of protective additives of different kinds, and the remarks which follow must, therefore, be taken to refer

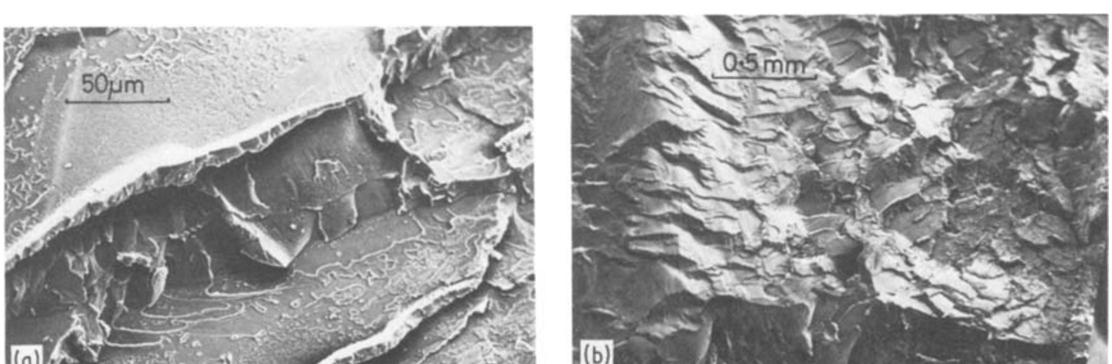


Figure 17 Three-point bending fracture surface from specimen weathered for 52 weeks. (a) Crazes clearly visible at high magnification, (b) same area at low magnification, showing no indication that crazing is present (compare Fig. 14).

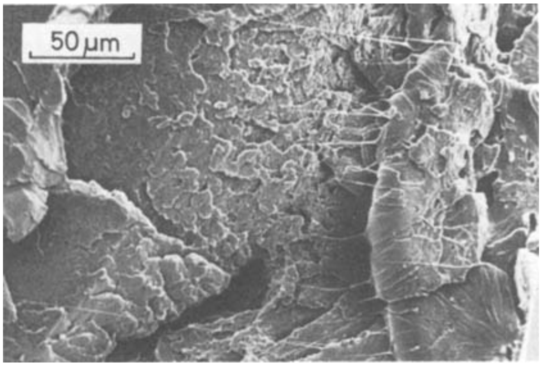


Figure 18 Fibrils on the three-point bend fracture surface of PS weathered for 16 weeks.

to the particular grades of material used. Nevertheless, behaviour of the materials is mainly controlled by the polymers used and the results will generally reflect their relative merits, but the results presented here cannot be taken as indicative of their performance in a less extreme climate. Similarly, relative changes in performance might be expected in grades compounded with additives chosen to optimize performance in the kind of climate employed in these studies.

From the results presented here PMMA and PC are least affected by weathering in almost every respect. They show the smallest reductions in molecular weight and glass transition temperature. No major changes were found in the moulded surface appearance or in the apparent fracture mechanism when the SEM was used to compare unexposed and weathered samples. Nevertheless, both materials showed a significant reduction in toughness, as assessed by the Charpy impact test. A reduction in ductility was found in uniaxial tension in PMMA and PC and a considerable reduction in the tensile strength was recorded for PMMA. Although changes in the magnitudes of residual stresses were found to occur with PMMA, the overall effect was not very different from what would be expected to be promoted by ageing at a (uniform) temperature slightly higher than room temperature and these changes do not appear to be as important as those found with PS and PVC (see later). With PC a substantial change was found with the specimen tested after 52 weeks exposure and will be discussed later.

PS and PVC both show marked reductions in both molecular weight and glass transition temperature on weathering. Both effects are consistent with significant chain scission having been promoted, and this would naturally lead to a lower resistance to fracture. Both materials show a marked reduction in toughness, with PVC displaying the greatest fractional drop of all the materials tested, and PS suffered a particularly large deterioration in tensile strength on weathering.

Both PS and PVC showed marked changes in the moulded surface appearance on weathering. In the case of PS a network of surface cracks were found to have developed after 52 weeks exposure. The uniaxial tension fracture surface appearance was different for PS specimens of different exposures, indicating detailed differences in fracture mechanism. Large planar crazes, a feature found on specimens exposed for short periods, were absent on specimens exposed for 16 weeks or more. Crazing could be seen only at high magnification on fracture surfaces from specimens weathered for long times, indicating that although crazing preceded fracture even for fast brittle failures the crazes were probably not as deep as in unexposed samples, and this, coupled with the

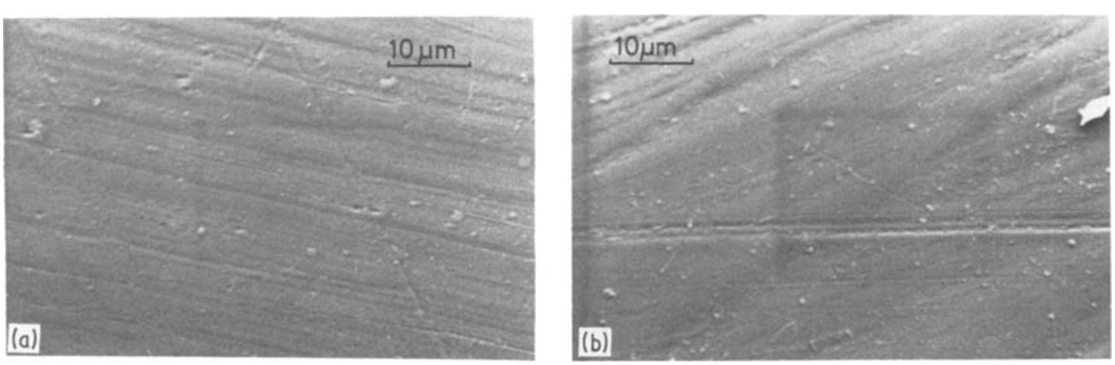


Figure 19 Moulded surface of PC (a) unexposed, (b) weathered 52 weeks.

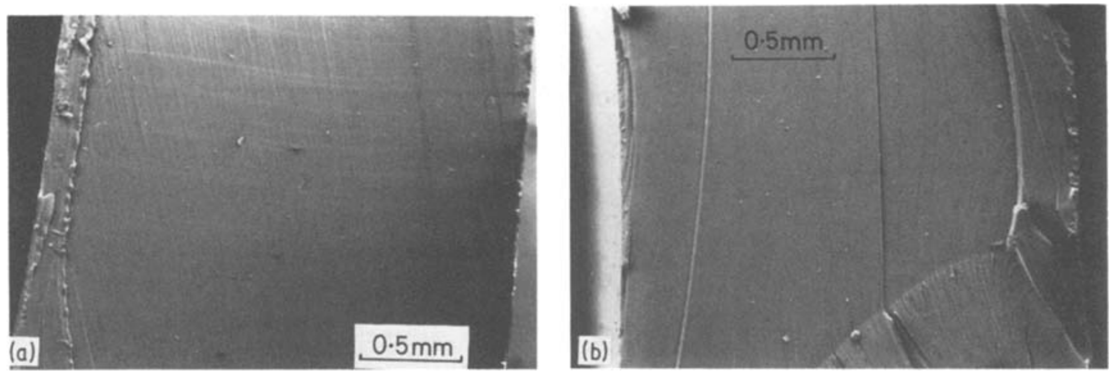


Figure 20 Uniaxial tensile fracture surfaces from PC (a) unexposed, (b) weathered 52 weeks.

large departures from planarity of the fracture path, rendered the crazes less visible.

With both PS and PVC which had been weathered for 52 weeks the bars showed significant curvatures, with the exposed surface becoming concave. The magnitudes are recorded on the relevant ρ against $(z_0 - z_1)$ plots (Figs. 26 and 28) at $(z_0 - z_1) = 0$. On performing the layer removal analyses it was found that tensile stresses were present near to the surface. The analysis was conducted in such a way that the stress distributions presented in Fig. 26 and 28 correspond to the bars in their self-stressed (curved) attitudes prior to machining; if the bars were to be straightened by the application of external forces the tensile stress at the exposed surface would increase still further. It should be noted that the layer removal analyses presented above were all conducted using data obtained when machining layers from the exposed surfaces and the computed stress distributions, therefore, correspond to that side of the bar. To determine the stresses in the other side of the bar a similar analysis is required, machining away from the "unexposed" side. It is reasonable to expect that the stresses in the half of the bar away from direct sunlight would be intermediate between those found in an unexposed bar and those found in the exposed half of the bar. This is confirmed in the example obtained with PC exposed for 52 weeks shown in Fig. 29. This imitates the behaviour found to occur when specimens are conditioned in a temperature gradient [23]. The imbalance in the stresses causes the bar to bend. Distortion is, of course, an important cause of failure of polymeric components and this aspect of weathering is therefore of interest for its own sake. Possibly of even greater importance is the combination of several factors which change on weathering and which together can be expected to make the component more vulnerable to fracture. With both PS and PVC it has been found that after 52 weeks weathering (i) the residual stresses have reversed their sense, becoming tensile near the surface; (ii) visible surface degradation has developed; and (iii) significant reductions in molecular weight have occurred. Components which fail by breaking often do so by means of a crack which begins at a surface flaw. Thus the normal residual stress distribution which has compressive stresses at the surface will tend to inhibit or retard this mode of failure since the externally applied stresses must first overcome the residual compressive stresses before crack propagation can occur. The weathered specimens have lost this measure of protection and have developed residual stresses which will assist the process of crack growth from a surface flaw.

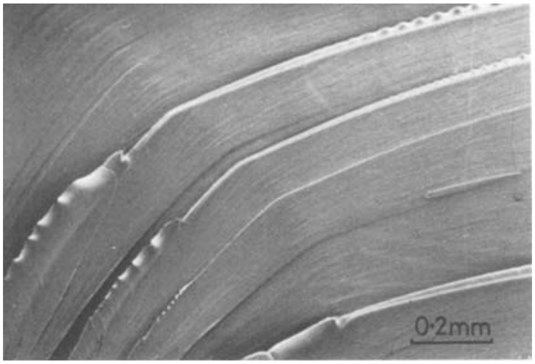


Figure 21 Part of uniaxial tensile fracture surface from PC weathered for 8 weeks.

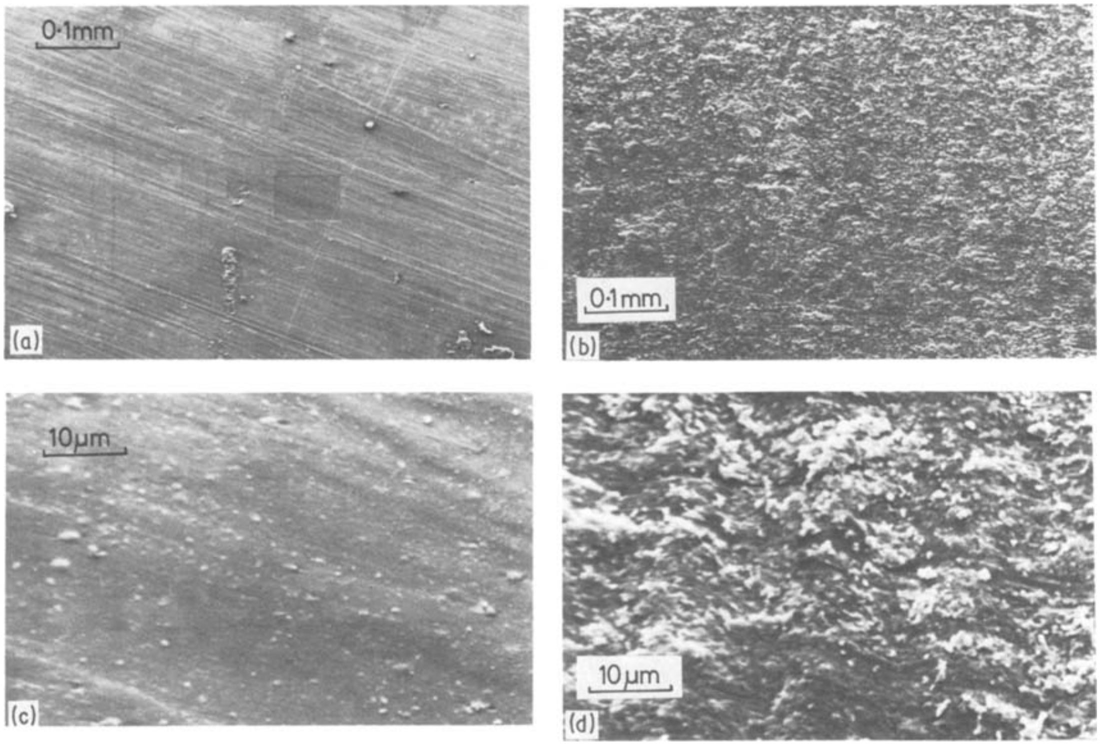


Figure 22 Moulded PVC surface (a), (c) unexposed, (b) and (d) weathered 52 weeks.

Then it should be noted that surface flaws have developed during weathering, and finally that the material in which the crack is to initiate and grow has been weakened (molecular weight reduction). It would seem that all of these changes are important in reducing the fracture resistance of polymers and that attempts to improve the outdoor performance of polymeric components should not be confined to the introduction of additives which inhibit molecular changes. Such protection is, of course, of vital importance, and we do not yet know to what extent the changes referred to above are interactive. One question which needs to be answered is whether in the absence of serious molecular weight degradation large changes in residual stresses may still occur. On the evidence provided by PC, for which significant distortion developed after 52 weeks exposure during which only a modest reduction in molecular weight occurred, it would seem that these two effects are, or at least can be, independent. The same conclusion can be drawn from the behaviour of moulded bars in a temperature gradient [23]. Note that although the residual stresses in PC did not actually reverse, the compressive stresses at the surface of the specimen weathered for 52 weeks were negligible and the surface would have been put into considerable tension simply by restoring the target dimensions of the bar (i.e. by straightening it).

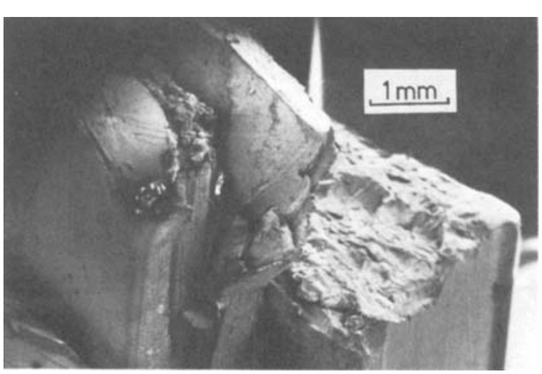


Figure 23 Low magnification image of PVC broken in uniaxial tension after 52 weeks.

The source of surface cracking in PS is not yet explained, but we can speculate that thermal cycling may contribute. The skin and core of injection mouldings have different thermal expansion coefficients [16] and the residual stress levels will, therefore, change with temperature even if the specimen temperature remains always

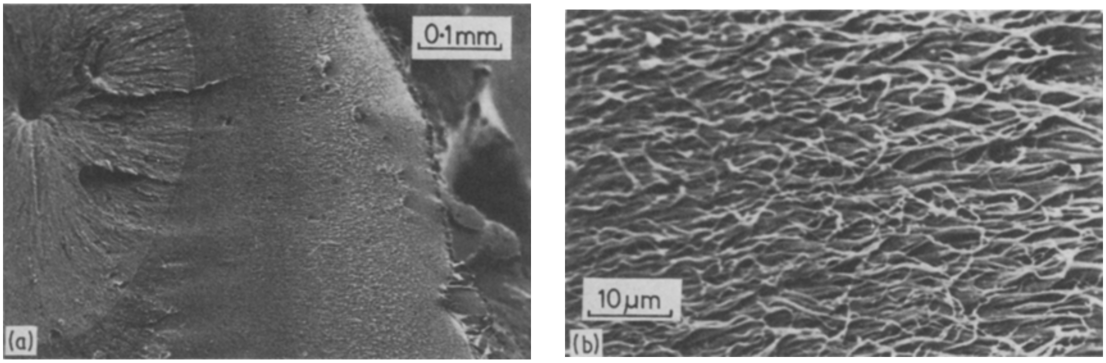


Figure 24 (a) Probable fracture initiation site (on left of picture) from specimen shown in Fig. 23. (b) High magnification image from the centre of (a).

uniform. The shear stresses associated with differential thermal expansion will be greatest in the skin or at the skin-core boundary where the steepest property gradients exist. Again it is noted that it is in this region that the material becomes weakened as a consequence of weathering processes that cause molecular weight reduction.

An explanation for the reversal of the sense of residual stresses in bars annealed in a temperature gradient was advanced by Thompson and White [23] and may apply to the present investigation. It is not unreasonable to expect a temperature gradient to exist in the bars when placed in the attitude used for these studies. The residual stresses will then begin to relax, predominantly near the exposed surface, and to understand the argument developed here it is convenient to suppose that the stresses are removed completely within a region adjacent to the surface. When the bar returns to a uniform (lower) temperature, differential thermal contraction causes the exposed side to shrink more than the unexposed, putting the region near to the surface into tension.

The discovery that during weathering residual stresses may develop that are detrimental to the moulding leads naturally to the quest for means of controlling the residual stress distribution. In other studies it has been found that fillers have a strong influence on the levels of residual stress and the extent to which they can be modified by ageing or annealing [24]. It is anticipated that the effect of weathering on polymers containing fillers may be strongly influenced by filler type and shape and that considerable advantage may be achieved by choosing the appropriate composite.

5. Conclusions

The most important piece of new information that

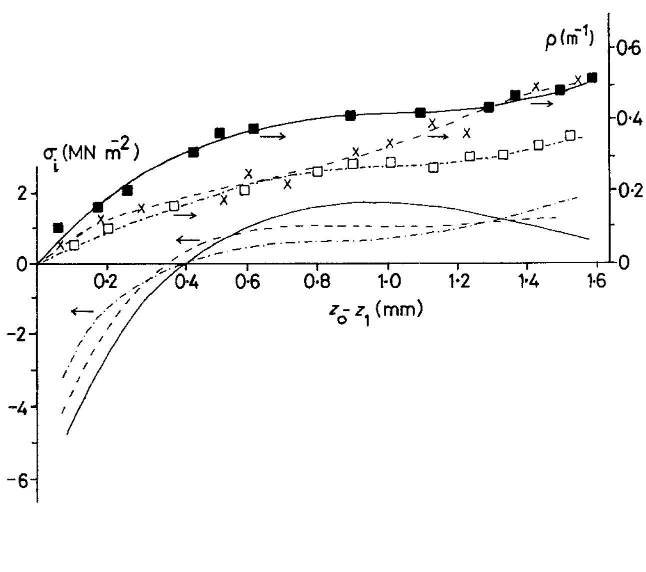
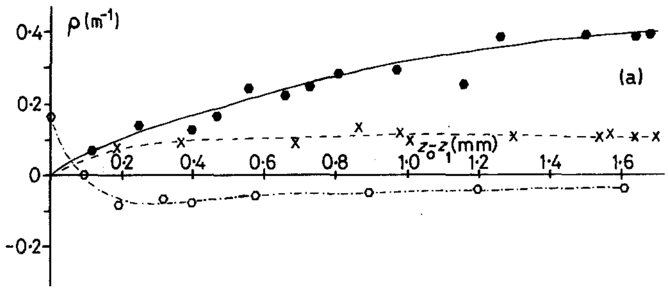


Figure 25 Layer removal analyses for PMMA, showing both curvature (ρ) plotted against amount of material removed ($z_0 - z_1$) and the computed residual stress distributions in the exposed half of the bar. Results are for specimens exposed for 0 weeks ▪ —; 8 weeks × – – –; 52 weeks □ –.–.–. The elastic constants used to compute the results were $E = 3.3\,\mathrm{GN\,m^{-2}}$, $\nu = 0.35$.



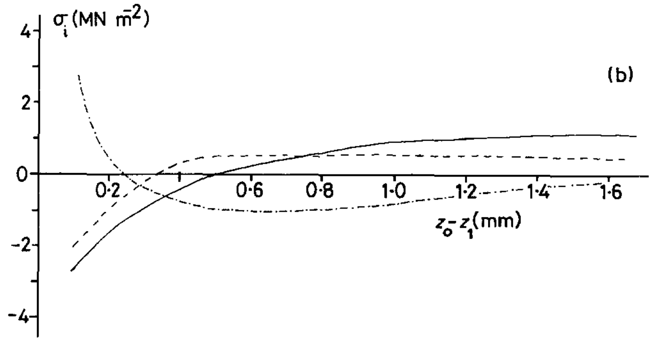


Figure 26 (a) Curvature plotted against depth of material removed for PS. (b) Residual stress distributions in the exposed half of the bar. Results are for specimens exposed for 0 weeks ● —; 8 weeks × ---; 52 weeks ○ -·-·-. $E = 3.4$ GN m^{-2}, $\nu = 0.33$.

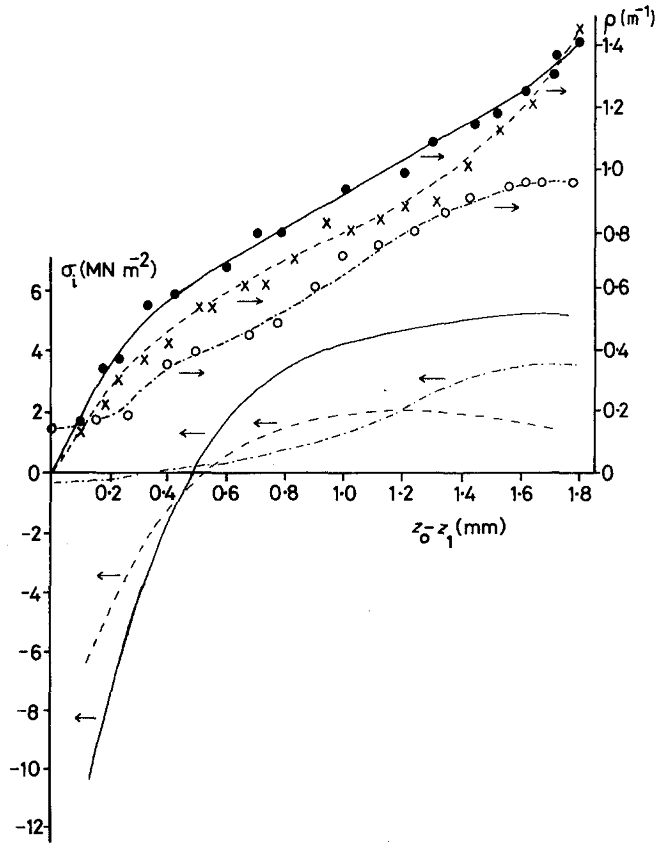


Figure 27 Layer removal analyses for PC, showing curvature as a function of depth removed and residual stress distribution in the exposed half of the bar for specimens weathered for 0 weeks ● —; 8 weeks × ---; 52 weeks ○ -·-·-. $E = 2.6$ GN m^{-2}, $\nu = 0.38$.

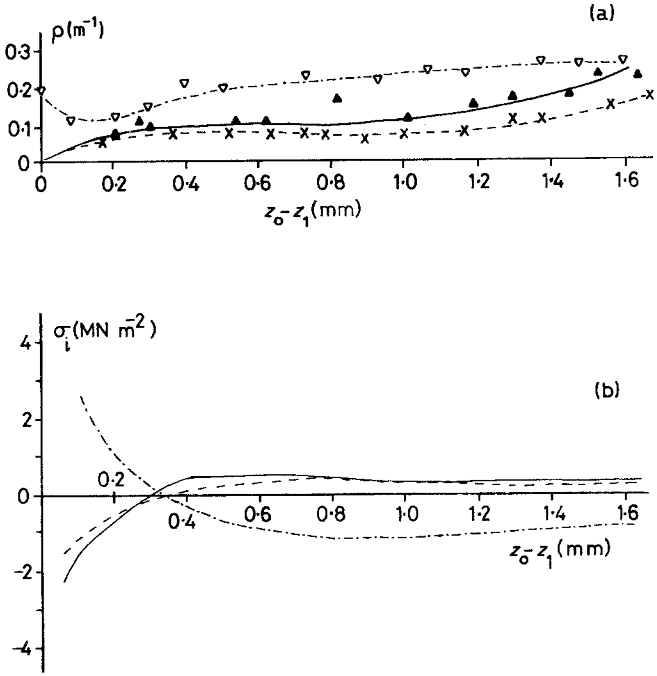


Figure 28 (a) Curvature as a function of depth removed for PVC. (b) Residual stress distributions in the exposed half of the bar. Results are for specimens weathered for 0 weeks ▲ —; 8 weeks × ---; 52 weeks ▽ -.-.-. $E = 2.6\ \mathrm{GN\,m^{-2}}$, $\nu = 0.38$.

has come from this work is the discovery that weathering may cause a significant change in the residual stress distribution within a moulded bar. This can cause distortion but may also have an important influence over the fracture properties of the moulding. It can be concluded that it is necessary to know about physical changes that are promoted by weathering as well as chemical changes in order that long term serviceability may be predicted. Similarly measures to control such changes may be sought in order to act along with chemical degradation inhibitors such as ultra violet stabilizers to prolong the lifetime of plastic articles.

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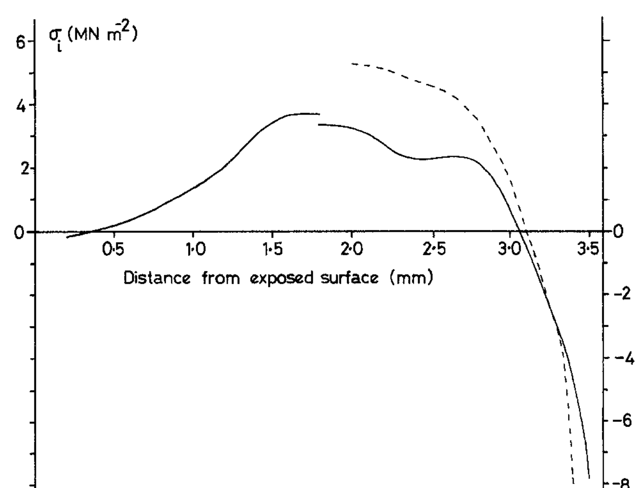

Figure 29 Residual stress distribution in PC weathered for 52 weeks. The two solid curves show the results of analyses using bars machined from the exposed side (left-hand side), and the unexposed side (right-hand side), respectively. The vertical axes (σ_i axes) coincide with the bar surfaces. Note that the two curves almost match at the centre, as should be the case if both had identical stress profiles. The dashed line shows the stress profile in a totally unexposed bar (cf. Fig. 27) for comparison with the analysed stresses in the unexposed side of the specimen weathered 52 weeks.

References

1. A. DAVIS and D. SIMS, "Weathering of Polymers" (Applied Science, Barking, 1983).
2. M. M. QAYYUM and A. DAVIS, *Polymer Degrad. Stab.* **6** (1984) 201.
3. L. D. CARPENTER, MSc thesis, University of Newcastle upon Tyne (1979).
4. B. HAWORTH, MSc thesis, University of Newcastle upon Tyne (1979).
5. L. D. COXON and J. R. WHITE, *Polymer Eng. Sci.* **20** (1980) 230.
6. M. M. QAYYUM and J. R. WHITE, *Polymer* **23** (1982) 129.
7. *Idem, J. Polymer Sci. Polymer Lett. Ed.* **21** (1983) 31.
8. *Idem, J. Appl. Polymer Sci.* **28** (1983) 2033.
9. R. G. TREUTING and W. T. READ Jr, *J. Appl. Phys.* **22** (1951) 130.
10. P. SO and L. J. BROUTMAN, *Polymer Eng. Sci.* **16** (1976) 785.
11. B. HAWORTH, C. S. HINDLE, G. J. SANDILANDS and J. R. WHITE, *Plast. Rubb. Proc. Applic.* **2** (1982) 59.
12. J. R. WHITE, *Polymer Testing* **4** (1984) 165.
13. R. P. KUSY, H. B. LEE and D. T. TURNER, *J. Mater. Sci.* **11** (1976) 118.
14. H. JANESCHITZ-KRIEGL, *Rhelol. Acta* **16** (1977) 327.
15. M. R. KAMAL and V. TAN, *Polymer Eng. Sci.* **19** (1979) 558.
16. C. S. HINDLE, A. V. IACOPI, C. K. LAM, M. J. RICHARDSON and J. R. WHITE, unpublished results, 1980–1984.
17. J. G. WILLIAMS, *Polymer Eng. Sci.* **17** (1977) 144.
18. G. J. SANDILANDS and J. R. WHITE, *Polymer* **21** (1980) 338.
19. F. PAREDES and P. FRIAS, *J. Mater. Sci. Lett.* **1** (1982) 394.
20. R. J. BIRD, J. MANN, G. POGANY and G. ROONEY, *Polymer* **7** (1966) 307.
21. J. R. WHITE and T. W. TEH, *ibid.* **20** (1979) 764.
22. C. J. SINGLETON, T. STEPHENSON, J. ISNER, P. H. GEIL and E. A. COLLINS, *J. Macromol. Sci. Phys.* **B14** (1977) 29.
23. M. THOMPSON and J. R. WHITE, *Polymer Eng. Sci.* **24** (1984) 227.
24. C. S. HINDLE, K. THOMAS and J. R. WHITE, to be published.

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