Plastic fracture in weathered polymers

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Injection-moulded bars made from several thermoplastics have been weathered for extensive periods in Saudi Arabia. With many of the polymers multiple diamond cavities were found to develop at the surface during uniaxial tensile testing, leading to the ultimate fracture, sometimes after coalescence of neighbours to form a dominant flaw. This did not occur with unexposed specimens tested under the same conditions and the formation of multiple cavities appears to be a consequence of weathering. Examples are presented and an explanation is offered to account for this plastic fracture phenomenon in weathered polymers.

(Keywords: plastic fracture; polymer weathering; poly(vinyl chloride); nylon-6,6; polycarbonate)

INTRODUCTION

Plastic fracture in which a diamond-shaped cavity nucleates and grows, spreading in all directions until a critical condition for fast fracture is reached, has been studied in a number of polymers by Haward, Hay and coworkers[1–6]. The diamond cavity may nucleate spontaneously during the course of a mechanical test, usually a uniaxial tensile test, but some observations were made in which the diamond was nucleated at a chosen site by making a nick in the surface using a scalpel point. It was found possible to promote this mode of fracture at room temperature in ductile polymers including poly(vinyl chloride) (PVC), polycarbonate (PC), poly(methyl methacrylate) (PMMA), poly(ether sulphone) (PES), poly(ethylene terephthalate) (PET), and high density polyethylene (HDPE). If no deliberate nucleating 'nick' was made, diamond cavities were usually observed to develop from surface flaws which formed during the earlier part of the uniaxial deformation. These flaws were described as crazes, though with some of the materials studied it was not obvious that the flaw had the generally accepted craze morphology (as described by Kambour[7], for example). In some cases several diamonds were found on the same surface, often at different stages of development[1,2,4].

In studies of injection moulded polymers weathered in Jeddah, Saudi Arabia, we have discovered that a form of failure is common in which multiple formation of diamond cavities occurs, leading to a somewhat modified ductile fracture process. The purpose of this paper is to report some of these observations.

EXPERIMENTAL

Specimen preparation and weathering

The results presented here were obtained during a study of the weathering behaviour of the following polymers: polystyrene (PS), PMMA, PC, PVC, nylon-6,6 (N-6,6), polyacetal (POM), and polypropylene (PP). Specimens were injection moulded into end-gated cavities to produce tensile test bars with gauge length cross section of 12.7 mm × 3 mm. Moulding conditions were chosen to give bars with good visual characteristics, free from sink marks etc., and the principal parameters are shown in *Table 1*.

The bars were exposed outdoors in Jeddah, Saudi Arabia, for periods of up to three years. The climate in Jeddah is hot and humid (with temperatures often above 40°C) but with almost no rainfall; more details, including measurements of u.v. dosage, are given in earlier publications[8,9]. Wind-borne particles are a further hazard[9].

Mechanical testing

Most of the results reported here were obtained during tensile tests conducted in uniaxial tension at room temperature. A crosshead displacement rate of 10 or 20 mm/min was used, corresponding to strain rates of approximately $1.5\times10^{-3}\,s^{-1}$ and $3\times10^{-3}\,s^{-1}$ respectively and specimens were normally tested to failure. Load–deformation characteristics have been presented previously[8,10]. After the discovery of the multiple cavity mode of failure a series of tests was conducted on PVC tensile test bars which had been weathered in Jeddah for three years. This type of specimen gave very pronounced multiple cavity failure and the experiments were designed to investigate the early stages in the development of the diamond cavities. We were not equipped to follow the process dynamically with the aid of a microscope plus video recorder in the manner described by Walker, Haward and Hay[5], but chose instead to terminate tensile tests at selected instants after yield and prior to failure, then view the specimens in the scanning electron microscope (SEM). The load–deformation curves for PVC specimens exposed for three years were found to be remarkably reproducible, and the positions at which tests

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Table 1 Moulding grades and conditions

Polymer	Grade	Mould temperatures (°C) Moving/fixed plate	Injection temperatures (°C) Nozzle/Zone 3/Zone 2/Zone 1	Injection pressure (MPa)
Poly(vinyl chloride) PVC	ICI: Welvic ZR18/1734/854	40/40	185/185/180/170	133
Polycarbonate PC	Bayer Makrolon 2603	89/85	325/335/335/335	95
Polystyrene PS	Hoechst Hostyrene N4001	33/30	215/200/200/190	114
Poly(methyl methacrylate) PMMA	ICI Diakon MG102	60/60	245/230/220/210	114
Nylon-6,6 N-6,6	ICI Maranyl A101 Black 936	55/60	300/275/265/260	106

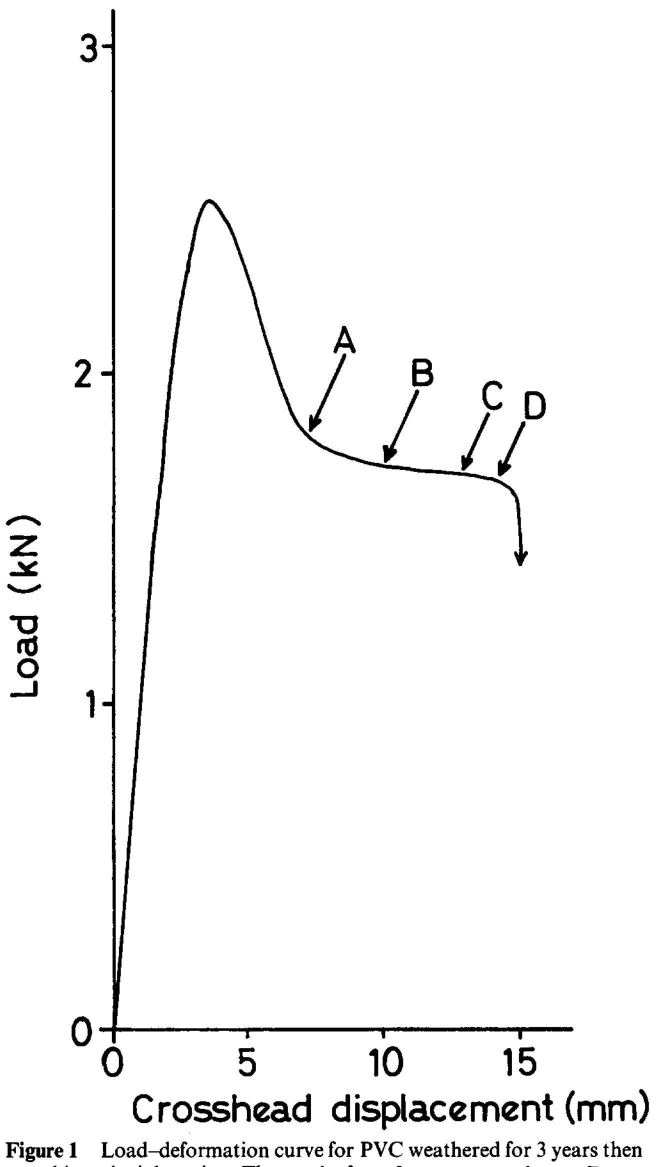

Figure 1 Load–deformation curve for PVC weathered for 3 years then tested in uniaxial tension. The results from four tests are shown. D was continued to fracture, whereas A, B and C were terminated before fracture at the positions indicated

were terminated are indicated on a single characteristic (*Figure 1*).

Molecular weight measurement

Molecular weight measurements were made on samples prepared from near the directly exposed surface by milling material away from the back. Measurements were made by gel permeation chromatography using a Waters Associates ALC200 operating at room temperature with a flow rate of 1 ml/min using tetrahydrofuran as solvent. The results are summarized in *Table 2*.

Table 2 Molecular weight data

Material	Exposure period (Years)	$\bar{M}_w \times 10^{-3}$	$\bar{M}_n \times 10^{-3}$	M_w/M_n
PVC	0	126	53	2.4
	1	74	37	2.0
	2	53	27	1.9
	3	40	19	2.1
PC	0	43.4	24.0	1.8
	1	40.2	22.2	1.8
	2	28.2	12.7	2.2
	3	24.4	13.7	1.8
PS	0	365	163	2.2
	1	185	58	3.2
	2	99	35	2.8
	3	78	30	2.6
PMMA	0	87	44	1.9
	1	62	32	1.9
	2	45	25	1.8
	3	31	14	2.2

Scanning electron microscopy

Specimens were cut 5–10 mm back from the fracture surface, mounted on SEM stubs with the fracture surfaces upwards, and gold-coated by evaporation using a planetary specimen holder to ensure that the coating covered the moulded surfaces as well as the fracture surface. Some specimens had a network of fissures on the surface, preventing the formation of a satisfactory continuous gold coating, and required an additional coating of carbon to avoid serious charging problems. In the case of tests terminated prior to fracture the specimens were cut from the necked region. Observations in the SEM were made using the secondary electron image at fairly low voltage, usually 7.5 kV, but lower for very sensitive polymers such as POM, and higher if the material was sufficiently resistant to electron beam damage (e.g. PS).

RESULTS

Although plastic fracture appears to be a quite general phenomenon in severely weathered polymers, it is convenient to deal with each material separately. The results obtained with PVC will be presented first because this is the material in which plastic fracture has been most extensively studied, both by ourselves and by others. N-6,6 will be considered next, to illustrate plastic fracture with a crystallizing polymer, then some examples of the phenomenon with other polymers will be given for comparison. In the following discussion we will refer to the 'moulded surface' to distinguish it from the fracture surface, even for specimens which have suffered large deformations that have caused the appearance to be quite different from the as-moulded state. We will use the terms 'face' and 'side' to distinguish the broad and narrow surfaces of tensile bars (*Figure 2*) and, when relevant, 'upper' to indicate the surface facing the sun during weathering and 'lower' to indicate the underside.

Poly(vinyl chloride)

Figure 3 shows part of the fracture surface of a PVC tensile bar weathered for 1 year then fractured in uniaxial tension. The specimen necked and displayed considerable drawing before fracture. Fracture occurred at several sites along the axis of the bar and failure was completed by axial cracks which are easily formed in a drawn polymer. Another view at lower magnification is found in ref. 8. Two features of special interest are the site of crack nucleation near the bottom left hand corner of *Figure 3*, and the apparent smoothness of the moulded surface visible nearby. These characteristics are found also in unexposed PVC mouldings tested in the same way, and contrast with the appearance of bars weathered for longer times before tensile testing.

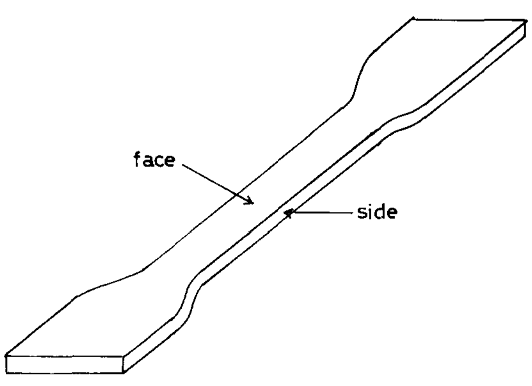

Figure 2 Schematic diagram of a moulded test bar, showing the surfaces referred to in the text as 'face' and 'side'

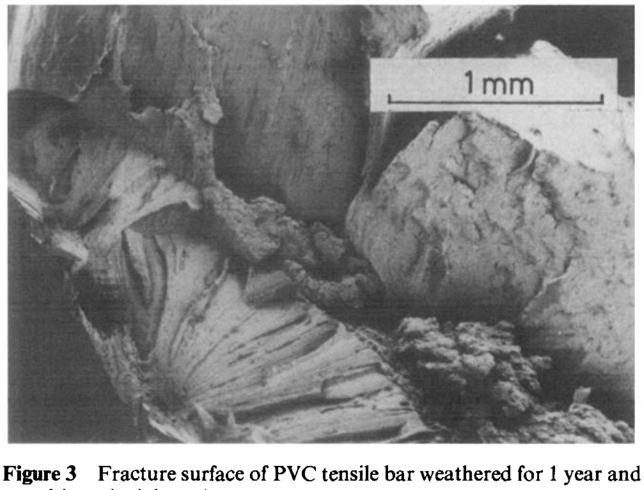

Figure 3 Fracture surface of PVC tensile bar weathered for 1 year and tested in uniaxial tension

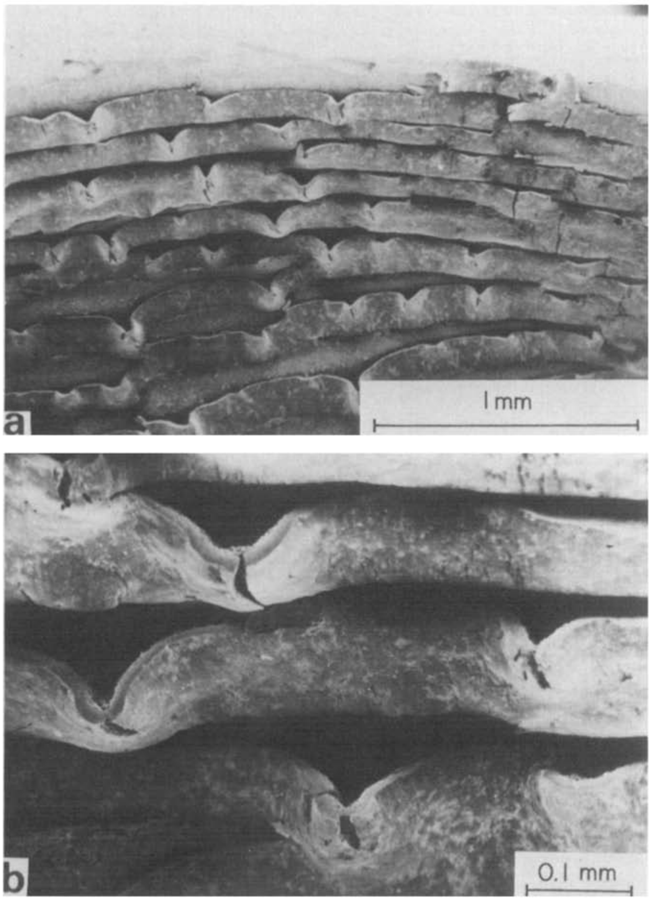

Figure 4 Moulded face of PVC specimen weathered for 2 years, after uniaxial testing to failure (a) general pattern of surface cracks; (b) higher magnification image showing surface layer beginning to peel away

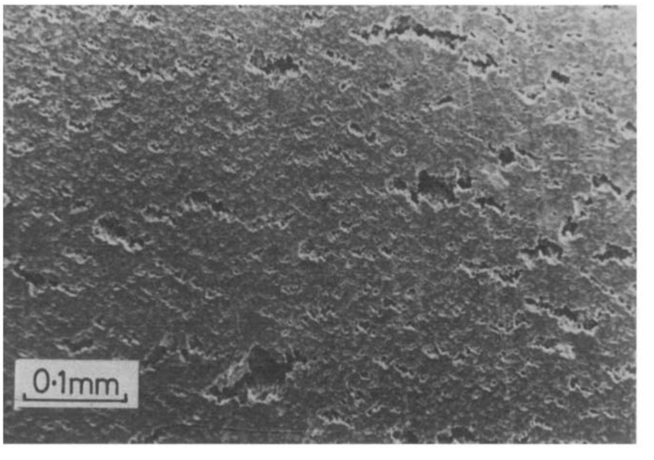

Figure 5 Lower face of the specimen shown in *Figure 4*, showing less severe damage than the direct exposed upper face

Figure 4 was obtained from a specimen weathered for 2 years prior to uniaxial testing and shows part of the upper moulded face near to the fracture surface. Surface cracks have formed perpendicular to the tensile axis and in places a surface skin (*ca.* 4 μm thick) appears to be coming detached from the underlying material. The lower face has a quite different appearance but shows considerable damage with voids and fissures up to 75 μm in diameter (*Figure 5*). *Figure 6* shows the upper moulded face of a specimen weathered for 3 years. The appearance is basically similar to that from the specimen exposed for 2 years, except that the surface skin fragments

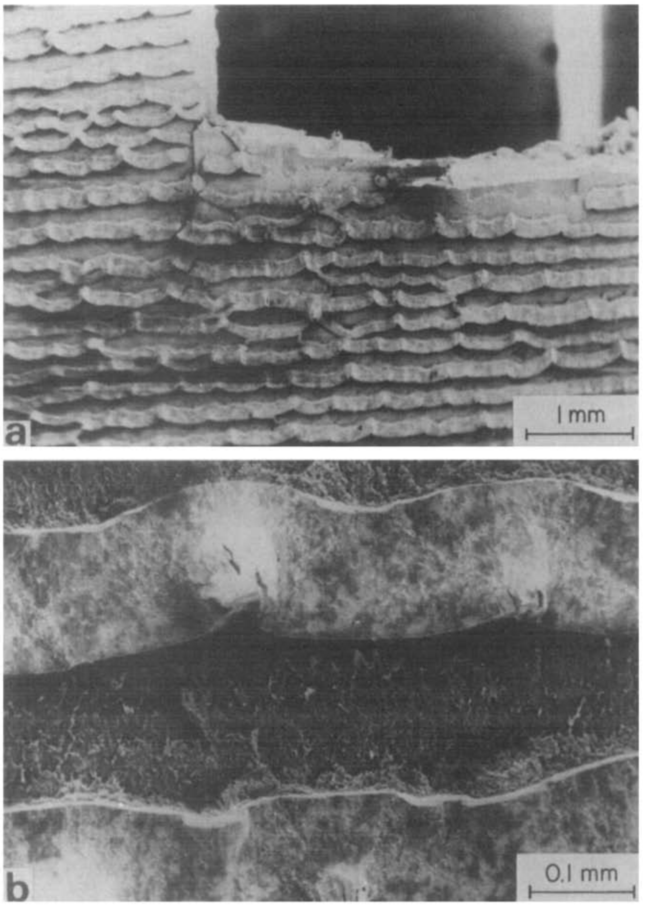

Figure 6 Upper moulded face of PVC specimen weathered for 3 years, after uniaxial testing to failure. (a) General view; (b) higher magnification

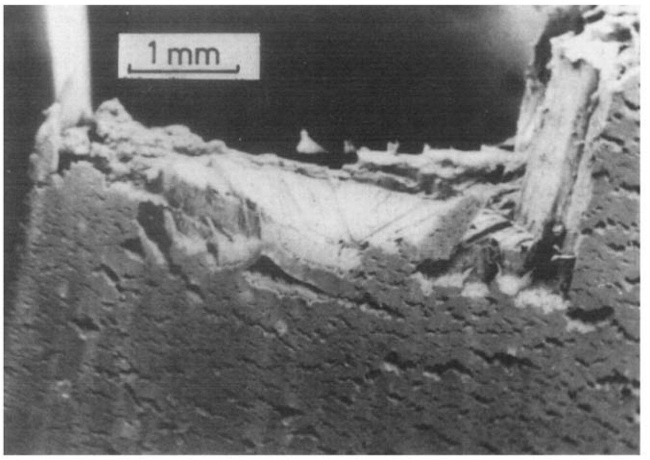

Figure 7 Lower moulded face of the specimen shown in *Figure 6*

have become separated to reveal the underlying material. The lower moulded face (*Figure 7*) also resembles that obtained with the specimen exposed for 2 years except that the voids and fissures are larger, and appear to be related to features on the fracture surface. Damage was also visible in the necked/drawn region on the moulded side surfaces and *Figure 8* illustrates this for specimens weathered for 3 years prior to testing. Note the corner cracks opening up along the line of intersection with the moulded face of the bar. There is a clear resemblance to the 'diamond' ductile fracture mode of failure.

To investigate the development of these surface features a series of tests were conducted on PVC samples weathered for 3 years and tested in uniaxial tension, interrupting the test at different stages, as described in the section on mechanical testing. *Figure 1* shows the stage at which each test was interrupted in terms of the load–deformation characteristic. It was found that for the specimens in which the test was interrupted soon after yield ('A' in *Figure 1*) the upper moulded face showed a series of narrow cracks lying perpendicular to the tensile axis (*Figure 9*). *Figure 10* shows a later stage ('B') with the cracks widened considerably. At one site near the centre of *Figure 10a* the widening is much more pronounced and this area is shown at higher magnification in *Figure 10b*; it should be noted that this example of significant widening is the only one found in an area much more extensive than that shown in *Figure 10a*. Further extension ('C') caused further progression towards the surface appearance already shown for fractured specimens (*Figure 11*, cf. *Figure 6a*) and again a dominant flaw seemed to be developing. Although the dominant flaw was thus not 'typical' it is included in the area presented as *Figure 11*, and by this stage it has taken on an appearance very similar to that of a diamond fracture. Note the large difference in size of this flaw compared to the one shown in *Figure 10*; the seemingly modest progression from stage B to stage C has given a flaw more than three times larger.

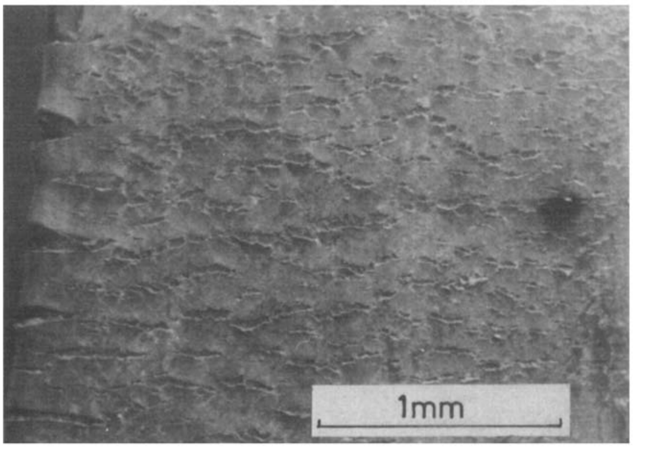

Figure 8 Side surface of a PVC specimen weathered for 3 years and tested in uniaxial tension, showing fissures. Fissures at corner sites have developed to greater depth

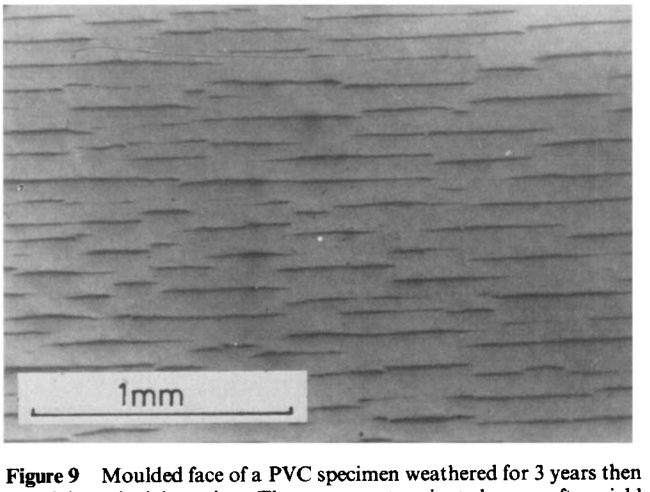

Figure 9 Moulded face of a PVC specimen weathered for 3 years then tested in uniaxial tension. The test was terminated soon after yield (position 'A' in *Figure 1*)

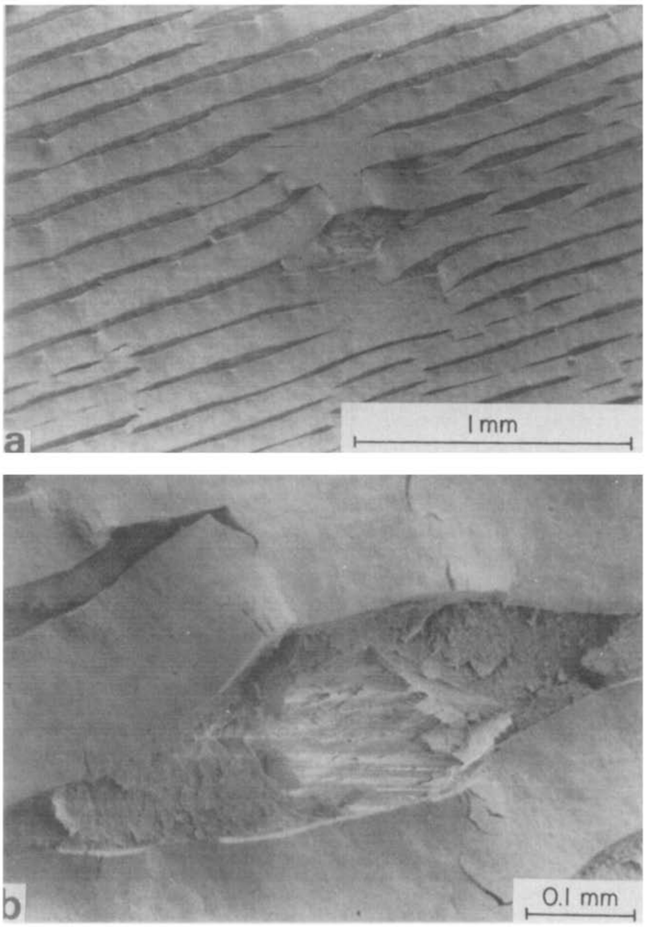

Figure 10 Moulded face of a PVC specimen weathered for 3 years then tested in uniaxial tension. The test was terminated at 'B' in *Figure 1*. (a) General view; (b) higher magnification image of a surface crack that had opened out as a result of ductile fracture in the material underneath. No other similar example was found on this surface

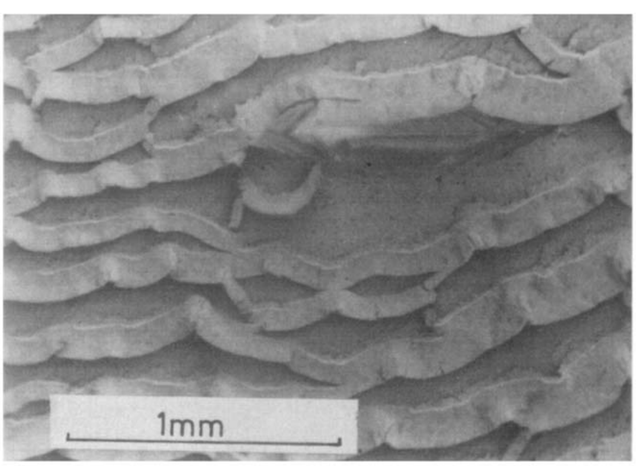

Figure 11 Moulded face of PVC specimen weathered for 3 years then tested in uniaxial tension. The test was terminated at 'C' in *Figure 1*

Nylon-6,6

Many of the features noted above with PVC have been observed previously with N-6,6[10]. No diamond cavities were found with unexposed specimens tested in uniaxial tension, but specimens weathered for as little as 8 weeks showed characteristic diamond cavities, though they did not develop extensively[10].

On comparing the results obtained with PVC and N-6,6 it seems that with PVC cracks grow in the (degraded) surface skin before significant ductile fracture occurs whereas with N-6,6 diamond cavities nucleate and grow independently. This can lead to a very dense population of cavities (*Figure 12*). Neighbouring cavities may merge on impingement giving rise to an uneven connected fissure (*Figure 12b*). As a result the fissure pattern with N-6,6 is not as regular as that found with PVC, though some similarities do exist (*Figure 13*).

Polycarbonate

Unexposed PC necked and then displayed considerable cold drawing[8]. After failure it was found that

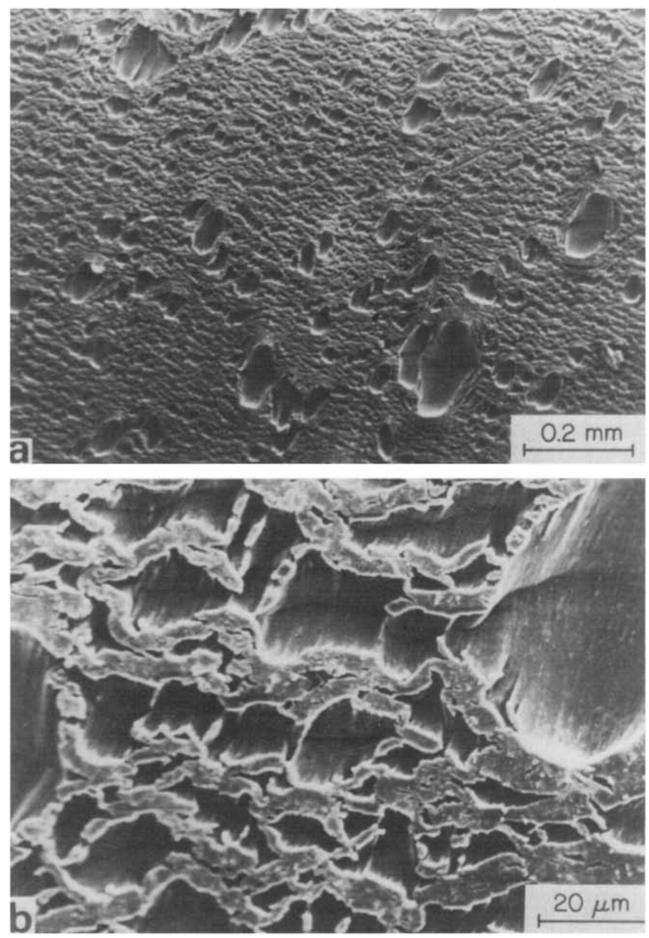

Figure 12 Moulded face of a N-6,6 specimen weathered for 3 years in the shade then tested in uniaxial tension. (a) General view; (b) higher magnification

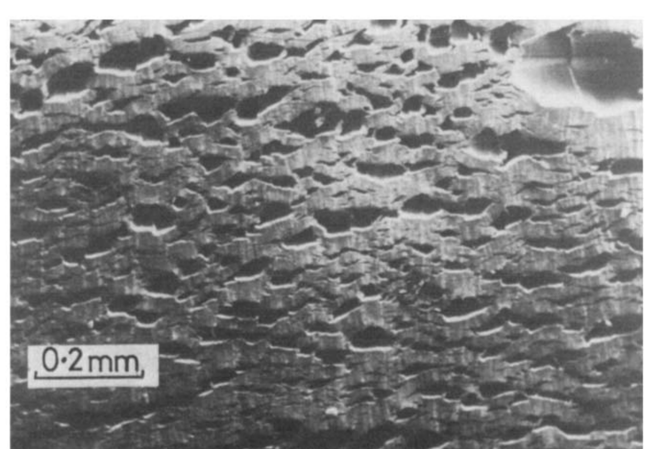

Figure 13 Moulded face of N-6,6 specimen weathered for 3 years then tested in uniaxial tension

a small number of well separated diamond cavities had developed. A specimen which had been weathered for 8 weeks formed a high concentration of cavities on the upper face, and a very much lower concentration on the lower face. After longer times the pattern of surface cracking on the moulded surface was intermediate between that displayed by PVC and by N-6,6 respectively (*Figure 14*). The appearance of a specimen tested in uniaxial tension after 3 years weathering seems to indicate that surface cracks probably came first (as with PVC) but that diamond cavities began to develop from them before

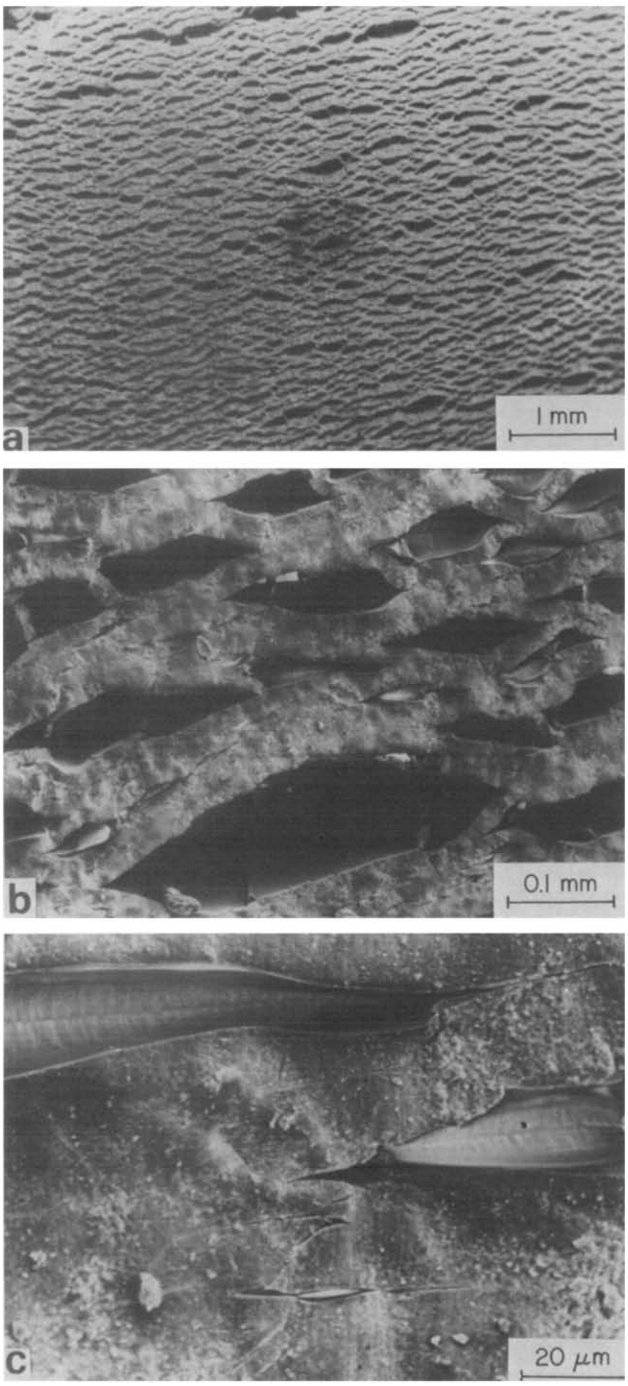

Figure 14 Upper moulded face of PC specimen weathered for 3 years then tested in uniaxial tension. (a) General view; (b) intermediate magnification showing diamond cavity development beneath the surface layer; (c) high magnification showing surface cracks which have not developed, presumably because of local stress relief provided by cavities developing from adjacent cracks

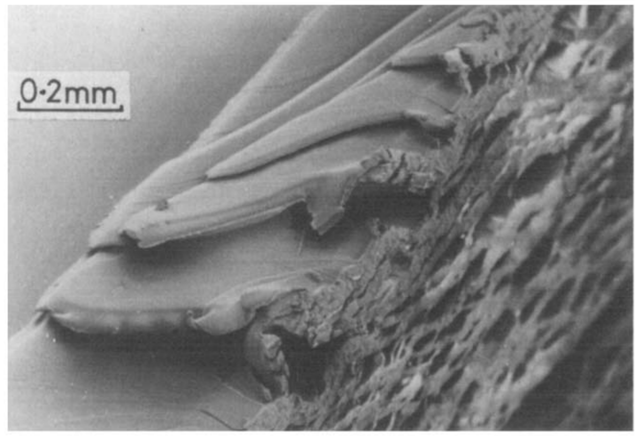

Figure 15 Part of the intersection of the fracture surface and upper moulded face of a PC specimen weathered for 2 years then tested in uniaxial tension. The fracture path follows cracks which have developed from the surface

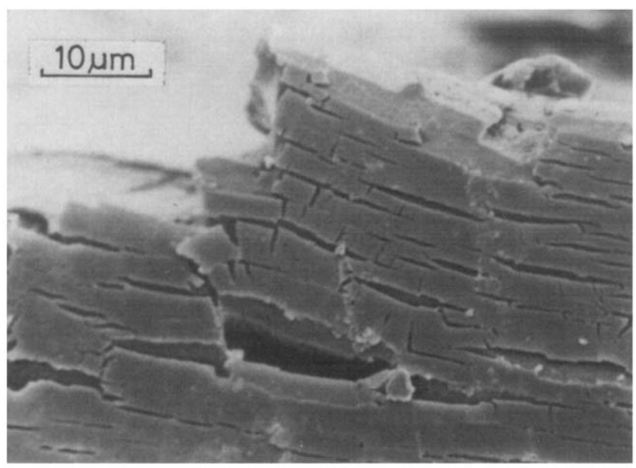

Figure 16 Moulded surface of a PS specimen weathered for 3 years in the shade then tested in uniaxial tension

the surface cracks had extended as much as is the case with PVC (cf *Figure 9*). Sharp narrow cracks were still visible on the moulded surface after the sample had been extended to fracture if the stress had been relieved locally by growing diamond cavities (*Figure 14c*). This behaviour is also indicated to be present on the lower face.

The extent of the influence of the surface damage on ultimate failure is indicated by *Figure 15* which shows that the fracture path follows the ductile cavities growing in from the surface.

PMMA and PS

PMMA and PS did not show the formation of diamond cavities at any of the weathering conditions tested here. A PS specimen weathered for 3 years in the shade developed surface cracks on the moulded face during uniaxial tension. These were located close to the intersection with the fracture surface and are shown in *Figure 16*. A surface film appears to be present, but in this case the surface cracks have not nucleated ductile fracture in the underlying material.

PE, PP and POM

Although fissure formation has been observed on a PP specimen tested in tension after 2 years weathering[10], this type of damage is less general with PP than with the other materials dealt with above. The fracture mechanism appears to be much more complicated and we are currently investigating this matter as part of a study of the effect of additives on outdoor performance of PE and PP. We have reported on weathering damage to the surface of POM previously[10], but SEM observations are difficult because of its extreme sensitivity to electron irradiation.

DISCUSSION

Earlier reports of plastic fracture place little emphasis on multiple diamond cavity development, and failure often seems to have been associated with a single cavity. The nucleation of a diamond cavity presumably requires the presence of a flaw, as provided by the scalpel nick by some experimenters. If no such artificial nucleation is applied, spontaneous nucleation of diamond cavities must occur at moulded-in flaws. Because of the statistical nature of the flaw size distribution the cavity that begins first (from the largest, most suitably-positioned, flaw) may well develop considerably before conditions make possible the formation of another one elsewhere, and the first cavity may thus dominate failure without any significant development of others. If no large flaw is present then at practical strain rates the test piece will acquire a high strain energy density before nucleation and development of the first cavity takes place. If there is sufficient strain energy to promote rapid fracture once a cavity starts to grow then again conditions do not favour the formation of a multiplicity of diamond cavities.

The observations reported here show that multiple cavity formation can occur in some polymers after weathering, whereas unexposed mouldings made from the same materials do not show the phenomenon when tested under the same conditions*. Before further discussion on why weathering should cause this change in failure mechanism it is worth listing some of the changes that have been found to be promoted in these materials by weathering.

(i) Chemical changes take place, mainly near to the surface, and may lead to chain scission, causing weakening. Molecular weight degradation was found to be significant with all of the polymers for which data was obtained (PVC, PC, PS, PMMA: *Table 2*). With most polymers this is caused primarily by u.v. irradiation.

(ii) The residual stress distribution becomes modified on weathering[8,10]. In the as-moulded bar the stresses are generally tensile in the interior and compressive near to the surface[11,12]. Weathering in Jeddah has been found to cause significant changes in stress distribution[8,10]. For all of the materials tested the magnitude of the compressive stresses near to the surface diminished and in many cases the sense of the stresses reversed, becoming tensile near to the surface, as, for example, with PS and PVC weathered for one year[8].

(iii) Surface damage, visible on microscopical examination, developed with most of the polymers studied and was particularly pronounced with PS and PVC.

* It should be noted that the strain rates used in the studies reported here are somewhat higher than those used by Haward and coworkers to promote diamond growth and this may account for differences in failure mechanisms in unweathered samples.

Consider now the possible consequences of these changes when a tensile test is performed. The as-moulded stress distribution is generally thought to be beneficial because the surface compressive stresses rise quite steeply in magnitude near to the surface and will tend to inhibit crack growth from a surface flaw, whereas the tensile stresses in the interior are rather modest (usually less than $2\,MN/m^2$ for unfilled polymers, depending on the polymer and the fabrication conditions) and are much smaller than the applied stress at failure in this region. On the other hand, after weathering, the stresses become tensile near to the surface and in some cases it is indicated that they rise quite steeply. It is conceivable that very close to the surface conditions may even develop that cause the failure of the (weakened) material there without application of external forces and may account for the network of fine crack like features that have been found to form on the surface of some polymer mouldings[8]. If an external force is applied, as is generally required to promote failure, the net stress at the surface becomes much higher on the addition of the residual stresses. If flaws exist at the surface, and, as has already been mentioned, these may themselves be formed during weathering, then failure is likely to occur in the surface region which, as noted above, may have become weakened during weathering through chain scission processes. The stress concentration thus becomes transferred to the material in the interior which remains almost untouched by weathering (*Figure 17*). Thus, the conditions may be such that cavities can nucleate and develop near to the surface before the bulk of the material in the interior has sufficient strain energy to promote fast crack growth.

In the as-moulded bar the flaws will usually be foreign particles, hence a large range of sizes is to be expected and it is very likely that a small number, possibly just one, will dominate. In the case of weathered bars, if flaws of sufficient size to nucleate diamond cavities have formed as

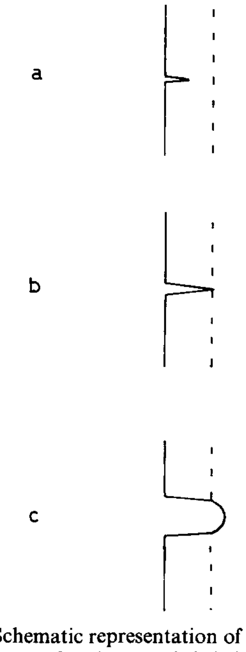

Figure 17 Schematic representation of crack development in a ductile polymer with a surface layer embrittled by weathering. (a) A fine crack initiates at a surface flaw and grows inwards as well as along the surface; (b) on continued testing the crack reaches the underlying undamaged material; (c) if the stress concentration is sufficient to cause yield a ductile fracture may begin to develop

a consequence of weathering it is to be expected that the size distribution will be much more uniform and that many visible cavities will develop within a fairly narrow range of (applied) strain. If the material beneath the surface retains some ductility and has not reached a critical level of strain energy when cavities first begin to appear, then the growing cavities will stabilize and develop in a slow, controllable manner, permitting others to nucleate and grow before fast fracture intervenes.

Although we have identified many examples of this mode of failure the behaviour is not general. A crack developed in a brittle surface layer may provide a critical flaw which leads to brittle fracture in the underlying material. So and Broutman conducted experiments on rubber-modified specimens and showed that under conditions normally producing ductile behaviour their materials could be made to fail in a brittle fashion when coated with thin films of polystyrene or styrene acrylonitrile to imitate the surface embrittlement caused by weathering[13].

Thus the notch sensitivity of the material in the interior is important and helps to dictate the failure mode. It should be noted that in the experiments described here, the weakened surface layer developed on PS bars during weathering did not lead to the intervention of ductile fracture when tested in tension because of the brittle nature of the unweathered polymer underneath. It seems unlikely that a brittle to ductile transition could be achieved by the provision of a brittle surface layer (i.e. the converse of the effect illustrated by So and Broutman[13]) and the rôle of the brittle layer in ductile failure is primarily that of causing multiple nucleation of diamond cavities. Compared with ductile failure in unexposed bars, the overall toughness is not enhanced by this process, but the decrease in toughness caused by weathering is less than would be the case if failure became totally brittle.

Finally, it should be noted that a related failure mechanism has been observed in PC by Sherman *et al.*[14]. For intermediate weathering periods they found that brittle failure occurred in the degraded surface layer and led to a reduction in overall ductility in tension. Their micrographs show some resemblance to those presented here. For longer periods of weathering the surface layer flaked off and was no longer effective in nucleating cracks to grow into the unweathered material beneath, and some ductility was recovered. Their material appeared to be more sensitive to weathering than the PC used in our studies, for the flaking off occurred with specimens weathered for one year in Israel (or shorter periods of artificial weathering).

CONCLUSIONS

The formation of a brittle surface layer is a common consequence of weathering with many polymers. This layer normally fractures early on during tensile testing, and this leads to ultimate failure. With some polymers cracks in the brittle surface layer provide flaws of sufficient size to cause brittle failure in the remainder. With certain ductile polymers the cracks in the surface layer nucleate ductile fracture instead, causing the formation of diamond cavities. If the surface layer is sufficiently fragile many such cavities may open up almost simultaneously over an extended area. Diamond cavities sometimes form along the line of a linear crack in the surface layer and coalesce after a period of growth. Eventually a dominant flaw may develop and lead to ductile failure of the remainder of the specimen. Polymers in which this mode of failure has been observed are PVC, PC and N-6,6. In each case unexposed mouldings of similar kind showed ductile behaviour when tensile tested under the same conditions. Multiple diamond cavity formation has been noted in specimens weathered in Jeddah for as little as 8 weeks (N-6,6) but the overall fracture mechanism did not become dominated by the development of these cavities until the weathering time was >1 year in the materials tested in this programme.

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REFERENCES

1 Cornes, P. L. and Haward, R. N. *Polymer* 1974, **15**, 149
2 Cornes, P. L., Smith, K. and Haward, R. N. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 955
3 Walker, N., Hay, J. N. and Haward, R. N. *Polymer* 1979, **20**, 1056
4 *idem., J. Mater. Sci.* 1979, **14**, 1085
5 Walker, N., Haward, R. N. and Hay, J. N. *ibid.*, 1981, **16**, 817
6 Mills, P. J. and Hay, J. N. *Polymer* 1985, **26**, 901
7 Kambour, R. P. *J. Polym. Sci. Macromol. Revs.* 1973, **7**, 1
8 Qayyum, M. M. and White, J. R. *J. Mater. Sci.* 1985, **20**, 2557
9 Qayyum, M. M. and Davis, A. *Polym. Degrad. Stab.* 1984, **6**, 201
10 Qayyum, M. M. and White, J. R. *J. Mater. Sci.* 1986, **21**, 2391
11 Haworth, B., Hindle, C. S., Sandilands, G. J. and White, J. R. *Plast. Rubb. Proc. Applics.* 1982, **2**, 59
12 White, J. R. *Polym. Testing* 1984, **4**, 165
13 So, P. and Broutman, L. J. *Polym. Eng. Sci.* 1982, **22**, 888
14 Sherman, E. S., Ram, A. and Kenig, S. *ibid.*, 1982, **22**, 457