Slow strain-rate testing of polymers with ultraviolet exposure

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Injection-moulded bars made from polypropylene, polystyrene and polycarbonate have been tested in tension at slow strain rate (mainly $1.1–1.4 \times 10^{-7} s^{-1}$). In some cases, the bars were exposed to ultraviolet irradiation (UV) simultaneously. Notched bars were used and were found to fail earlier when exposed to UV. The maximum load attained in the slow strain-rate test was found to be a suitable characteristic to represent the extent of the degradation caused by UV exposure. Pre-exposure to UV caused further reduction in performance during the slow strain-rate test. Of the materials tested, polycarbonate was least affected by UV exposure.

1. Introduction

The slow strain-rate test pioneered by Parkins [1, 2] is well established in the study of environmental stress cracking of metals and metal alloys. It involves subjecting a testpiece to a slow strain-rate test ($\sim 10^{-6}$ s^{-1}) in uniaxial tension while surrounded by a corrosive environment. In metals, the actual strain-rate is quite critical and it is likely that strain-rate effects will also be found in polymers, but even if this is not so, the use of this procedure with notched samples has strong potential. This paper discusses the design of equipment suitable for slow strain-rate testing of polymers and describes a preliminary study into the behaviour of polymers under slow strain-rate tensile deformation.

The purpose of the investigation presented here was to develop a test procedure that will provide a better guide to the weatherability of polymers than those currently in use. There are several critical reviews of the relationship between natural and artificial weathering [3–8]. There is general agreement that no correlation exists between natural and artificial weathering, and this view is even expressed in some of the Standards [9]. Even accelerated outdoor weathering, using mirrors to provide enhanced exposure, has been found to give contradictory information on polyolefins [10]. Marks and Butters [11] express doubt that data obtained in an extreme climate can give reliable prediction of performance in a temperate climate.

There are several reasons for the disagreement between outdoor service behaviour and the behaviour of polymer testpieces in the laboratory. Acceleration of testpiece failure is often achieved by using elevated temperatures. There are many chemical reactions involved in weathering-related failure of a polymer component. Some are sequential and most of them rely on diffusion of reactants, some of which are themselves products of reaction. As a consequence, the various reactions do not accelerate to the same extent when the temperature is elevated and the result may be that failure occurs by a different mechanism to that in outdoor conditions. The laboratory test is then unlikely to provide reliable data for the prediction of outdoor performance. Another way to accelerate degradation is to use ultraviolet irradiation that is more intense than that contained in solar radiation and/or to use artificial sources that contain lower wavelengths than are present in solar radiation at the Earth's surface. The low wavelength component is more energetic than terrestrial solar radiation and may promote chemical reactions that do not occur in polymers when they are exposed naturally. It is common in laboratory tests to conduct exposures for 24 h per day. This may again modify the failure mechanism. This is because the photo-oxidation rate is usually limited by the availability of oxygen and, under normal laboratory exposure conditions, the oxygen is consumed before it penetrates very far into the material [12, 13]. Under natural conditions, oxygen levels in the interior of a component may recover somewhat during the hours of darkness and some degradation can recommence the next day in regions much deeper within the body than is possible under uninterrupted exposure in the laboratory. The concentration of degradation into a thin surface layer that occurs in some laboratory tests may cause rapid weakening, with failure nucleating in the embrittled surface zone.

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If the testpiece is subjected to longer exposures, the surface may become so degraded that multiple cracks form in it, resulting in mutual unloading, or the surface layer may even begin to flake off. When this happens, the cracks that form easily in the surface are no longer able to form critical flaws that propagate into the less degraded material underneath and some recovery of properties occurs. The failure mechanism is then likely to change as the exposure period changes and may do so in a way that does not follow the same sequence as in outdoor exposure [14].

It is an almost inevitable consequence of acceleration that, in laboratory tests, the testpiece fails by a different mechanism to that which occurs in service. Thus, one of the long-term aims of this research is to establish laboratory conditions that can provide failure by similar mechanisms to those which occur in natural weathering without extending the test period unreasonably.

A departure of laboratory tests from service conditions is that the sample is usually subjected to a conditioning programme, then is given a short-term mechanical test to failure, whereas in service the component will normally be subjected to loading periodically or continuously throughout the time that it is exposed to photodegradation. Under the normal test procedure, the time taken to develop a critical condition cannot be identified more precisely than within the sampling period.

The tests examined here involve simultaneous irradiation and the application of steadily increasing deformation. Notched samples are used, giving accelerated cracking. In addition, it was expected that the stress concentration at the tip of the crack would accelerate the photo-oxidation there, giving further crack-growth acceleration. This kind of synergistic interaction between stress and photo-oxidation is believed to occur in many service situations but is not very faithfully reproduced in the most popular artificial weathering tests. One objective is, therefore, to introduce acceleration without adopting conditions that do not occur naturally. The tests are designed to be monitored continuously so that the development of a critical level of damage is indicated early on.

2. Equipment

2.1. Slow strain-rate rigs

Three types of slow strain-rate rig were designed and built for evaluation. The first design was based upon the well-tried Parkins test rig for the study of environmental cracking of metals but with detailed differences to allow for the lower loads and higher deformations expected with polymers. These rigs use a.c. motors and multi-stage reduction gears. Two rigs were built using variable speed d.c. motors that simplified the gear layout. The third design was built around a pneumatic loading device. The advantages of this design are that it is compact, reasonably inexpensive to build and run, and easier to adapt for computer control than the electric motor rigs. If the slow strain-rate test is to be adopted for general accelerated testing then it is essential that the rigs are inexpensive and compact, for multiple examples would normally be required.

The load was measured using a load cell connected in line with the testpiece and recorded either on to a chart recorder set at a very low speed, or into files in a PC. The crosshead displacement rate was checked at intervals during each test: it was found to be constant. Tests were normally run with a strain-rate in the range 2×10^{-8} to 7×10^{-7} s^{-1} though the rigs are designed to run even slower if required, giving a strain rate of 4×10^{-9} s^{-1} (based on a guage length of 100 mm). Temperature measurements were recorded and stored in PC data files. Tests were conducted in a room designed to remain at a constant temperature (30 °C) but some experiments were run at slightly higher temperatures after it was discovered that the air circulation equipment was inadequate to cope with solar heating during a sustained period of hot sunny weather.

All of the different rig designs performed satisfactorily. Breakdowns occurred in the drive trains of two a.c. rigs and one d.c. rig during a 2 year period. Reliability is an essential feature in tests that run for up to a month and this has caused a reappraisal of the choice of motor and the way in which the motors are run. The a.c. motors are relatively easy to dismantle and the gears can be replaced and the machines do not need to be out of service for an unreasonable length of time. Therefore, the problem is confined to the risk of failure during a long-duration test; it could be avoided by using a heavier duty motor though the original choice of motor proved entirely satisfactory as long as the material tested did not generate large stresses on deformation and as long as the crosshead speed was slow, keeping the torque low. D.c. motor failures are probably avoidable with proper routine maintenance.

2.2. Crack-growth monitoring

Most tests were performed on notched samples and it was desirable to follow the crack-growth dynamics. The crack was photographed at intervals using a 35 mm camera with a macrolens giving a slightly magnified image on the negative. Overnight monitoring of crack development during critical stages of growth was conducted using timer-operated exposures at pre-set intervals. Crack and craze lengths and the crack-opening displacement were measured from the photographs.

2.3. Exposure conditions

The studies described here relate to photo-oxidation of polymers and the testpieces were exposed to ultraviolet irradiation (UV) during the slow strain-rate tests. The rigs could be modified to allow exposure of the testpieces to other aggressive environmental hazards either singly or in combination. For the current work, the UV was provided by fluorescent tubes type *UVA*-340 (*Q-Panel Company*). The tubes used were chosen because their output in the UV matches the spectrum of solar radiation at the Earth's surface fairly closely and because they have been used in complementary studies in this laboratory [15, 16]. The supplier's own data show that the match is extremely

close in the wavelength range below 360 nm down to the cut-off at approximately 295 nm [17]. This has been verified by measurements of the spectral output of the UVA-340 tubes made using a *Bentham Instruments* spectroradiometer based on a double grating monochromator [16].

The tubes are approximately 1.2 m long with a fairly uniform output over the central metre. They are used in pairs and one pair serves up to three slow strain-rate rigs placed side by side. Measurements have shown that the illumination falling on to a flat testpiece with its axis perpendicular to the tube axes is fairly uniform over the gauge-length. The separation between the testpiece surface and the plane containing the tube axes is approximately 100 mm and gives an intensity of 2.5–4 $W m^{-2}$ in the wavelength range 295–320 nm, that is the total radiation below 320 nm wavelength. This corresponds closely to the midsummer intensity at noon in Jeddah, Saudi Arabia, which has one of the most severe climates in which polymer weathering trials have been conducted [18–26]. The daily dose for samples exposed in the laboratory under these conditions is therefore 60–96 W h m^{-2} compared to the daily UV dose within this wavelength range in Jeddah in midsummer of 20 W h m^{-2}.

The illumination provided by the tubes is checked regularly using the Bentham Instruments spectroradiometer. The calibration of the instrument is checked every 3–4 months using a standard lamp delivering wavelengths in the range 250–3000 nm (Bentham Instruments model CL2).

Some samples were exposed with the broad moulded face towards the UV source so that the exposure levels on that face were as given above ("side-on" exposure). Other samples were exposed with the edge containing the notch facing the UV source ("edge-on" exposure). Because the tubes provide an extended source, significant illumination fell on to the broad faces during the edge-on exposures. The level of illumination was measured using appropriate positioning of the spectroradiometer detector and was found to be of the order of 25% of that falling on to a plane facing the source and located at the same distance from it.

3. Experimental procedure

3.1. Materials and sampling preparation

Samples were made in the form of tensile test bars, measuring approximately 190 mm × 12.7 mm × 3 mm, by injection moulding into a single end-gated mould. They were made in large batches with the moulding machine cycling under constant conditions. The materials chosen for study were all provided free of charge by the manufacturers and were: (a) polystyrene (PS), BP H101, (b) polypropylene (PP), ICI GWM22, (c) polycarbonate – unstabilized (PC), Bayer Markrolon 2600.

Samples were stored in the dark for at least 1 month prior to conducting a slow strain-rate test. Notches were cut using a broaching tool giving one of the notch profiles specified in BS and ISO standards: notch depth = 2.7 ± 0.1 mm; radius of root of notch = 0.25 mm; included angle between notch faces = 45°.

3.2. Pre-exposure

Some samples were exposed to UV in open frames using similar tubes and similar intensities prior to conducting the slow strain-rate test. Half of these samples were exposed "side-on" and the other half were exposed "edge-on". The pre-exposure time chosen for the preliminary studies was 12 weeks, and some further experiments were conducted using a pre-exposure time of 5 weeks.

3.3. Slow strain-rate tests

Slow strain-rate tests were conducted on samples of three types: (a) unexposed, (b) pre-exposed side-on, (c) pre-exposed edge-on. Similarly, there were three options for the exposure condition during the slow strain-rate test: (a) no UV, (b) side-on exposure, (c) edge-on exposure. Thus there were nine possible combinations without even considering the effect of changing the pre-exposure time prior to the slow strain-rate test. In addition, some un-notched samples were run.

The slow strain-rate rigs have a manual drive facility that was used when setting up the test prior to engaging the motor. This was used to remove any backlash in the drive train at the beginning of each test, giving the sample a slight pre-tension (~20 N). Once the test had commenced it was left unchanged (same strain-rate, same exposure conditions) until the sample failed. Failure normally meant fracture, but in some cases extensive drawing occurred (even with notched samples) and the test was terminated when it was judged that no more useful information would be gained.

Photographs of the sample were recorded periodically, at a frequency determined by the crack-growth rate.

3.4. Fractography

Selected samples were inspected in the scanning electron microscope (SEM) after failure in the slow strain-rate test. They were gold-coated prior to insertion in to the SEM to minimize charging and problems associated with radiation damage in the microscope. Some samples were inspected in the light optical microscope; a limited series of experiments was conducted in which a dye was used to increase the contrast of surface cracks. The purpose of these studies was to determine the deformation and fracture characteristics of the different materials during slow strain-rate testing so that an informed assessment could be made of the generality of the observed behaviour.

4. Results

4.1. Un-notched samples/no UV exposure

Some preliminary investigations were made into the behaviour of samples which were not pre-exposed and which were deformed at slow strain rate in the absence

of UV irradiation. Tests were made both with bars containing a notch and bars in the un-notched state. With ductile polymers it was observed that the deformation was spread over a much larger volume during neck formation than is the case in samples that are tested at normal rates, giving a gentler transition between the drawn and the undrawn regions on either side of the neck. It later became much more localized.

4.2. Polystyrene

Load–deformation curves for notched polystyrene (PS) samples are given in Figs 1 and 2. These tests were performed before the procedure to reduce backlash was developed, which accounts for the low load generated in the early stages of the tests (deformation <0.2 mm). The sample that was tested without UV exposure reached the highest load and the greatest deformation before failing. The effect of UV exposure during the test was to produce failure at a slightly lower load and at a slightly smaller deformation. When samples were pre-exposed edge-on before testing with edge-on UV illumination during the slow strain-rate test, the failure occurred much sooner (Fig. 1). Side-on pre-exposure followed by side-on exposure during the slow strain-rate test also gave earlier failures, but the effect was not as large as with the edge-on samples (Fig. 2, cf. Fig. 1). The difference between samples pre-exposed for 5 and 12 weeks, respectively, was not large, though in both cases the sample pre-exposed for the longer period recorded a lower maximum load (Figs 1 and 2 and Table I).

A complex pattern of crazes developed during the slow strain-rate tests on PS samples that were exposed edge-on (Fig. 3). In the sample shown in Fig. 3 a family of crazes formed in front of the notch and arched crazes formed further away from the fracture plane but fairly close to the notch tip. The visibility of the crazes on the photographs recorded during the test was quite good, and measurements were made of the distance of the tip of the main craze from the root of the notch. Results for the development of the craze in

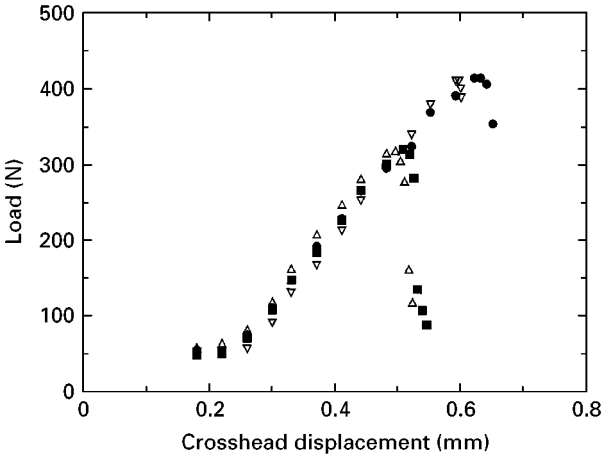

Figure 1 Load–deformation relationships for polystyrene samples pre-exposed edge-on for (▽) 0, (■) 5 and (△) 12 weeks and tested at slow strain-rate with edge-on UV exposure. Results for a sample tested without UV exposure and no pre-exposure are shown (●) for comparison.

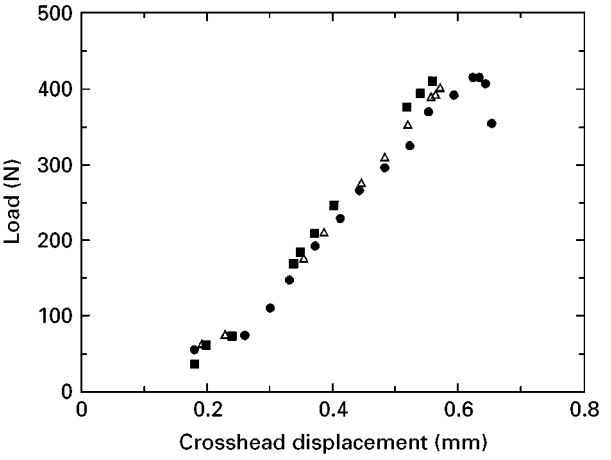

Figure 2 Load–deformation relationships for polystyrene samples pre-exposed side-on for (■) 5 and (△) 12 weeks and tested at slow strain-rate with side-on UV exposure. Results for a sample tested without UV exposure and no pre-exposure are shown (●) for comparison.

TABLE I Maximum load in slow strain-rate tests, after pre-exposure (p.e.) and test exposures

	Maximum load (N) at test exposures								
	p.e.: none			p.e.: side (= S)			p.e.: notch (= N)		
	None	S	N	None	S	N	None	S	N
PP	535	500	510	328	290[a]	298			
	520	508	490	320	295[a]	290			
PE	238[b]	199	201				150	124	121
	230[b]	202	201				167	125	122
								141	126
PC	1591	1401	1361						
[c]	1461	1390	1492						
		1448	1444						
PS	440				414[d]				404[d]
[e]					352				326

[a] Test exposure applied to opposite face to pre-exposure.
[b] Test terminated before fracture: load still climbing slowly at time of termination.
[c] High temperature (33–35 °C).
[d] 5 weeks pre-exposure (all other pre-exposures 12 weeks).
[e] Low crosshead speed (ca. 2.2×10^{-6} mm s^{-1}).

samples exposed edge-on are given in Fig. 4. The craze-growth rate increased rapidly once it had been initiated and it is convenient to plot the craze length logarithmically. From the load–deformation data and the craze–time data, the craze length can be plotted versus the load (Fig. 5). The plots in Fig. 5 can be used to estimate the corresponding threshold craze initiation load. Thus for a bar tested without UV pre-exposure and without UV during the test the threshold craze stress was approximately 350 N. For bars tested with edge-on UV exposure the threshold stress was 270 N for 5 weeks pre-exposure and 225 N for 12 weeks pre-exposure.

The fracture surface of the PS samples tested with no UV exposure showed that the craze grew smoothly to about 5 mm long (Fig. 6). It then became unstable and the craze/crack grew rapidly across the remainder of the bar section to complete fracture within about a second, producing a rougher surface (Fig. 6). A much longer smooth zone was obtained with samples that were pre-exposed and tested with edge-on UV exposure (Fig. 7). On a microscopic level, the fracture surface of samples exposed edge-on was found to contain two distinct zones (Fig. 8). That immediately adjacent to the notch root was smoother than the other one,

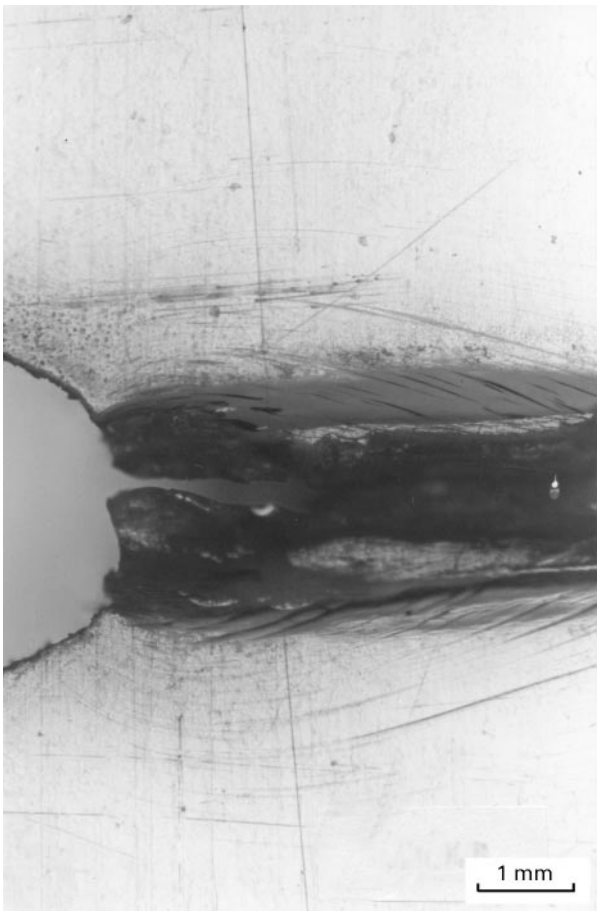

Figure 3 Light optical photograph of the craze zone ahead of the notch of a PS sample exposed edge-on in the slow strain-rate test.

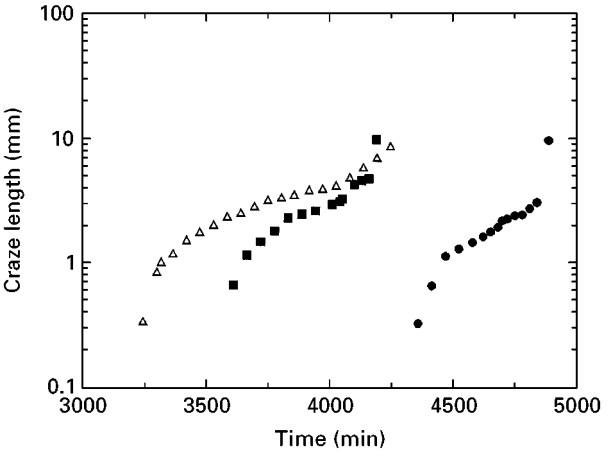

Figure 4 Craze-length development during slow strain-rate tests on PS samples with (■, △) edge-on UV exposure following edge-on pre-exposure for (●) 0, (■) 5 and (△) 12 weeks. ((●) No exposure in test.)

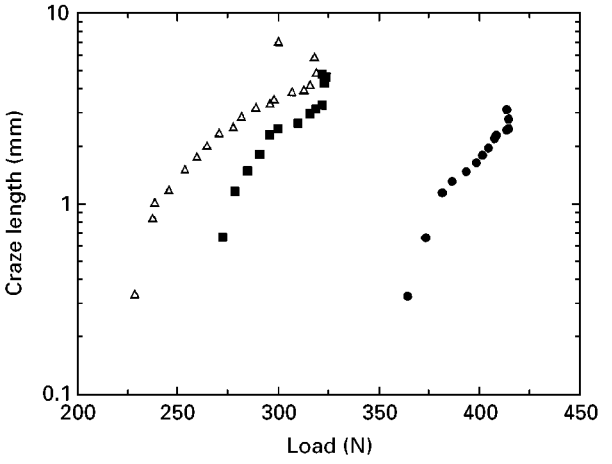

Figure 5 Craze length versus load during slow strain-rate tests on PS samples (same tests as for Fig. 4).

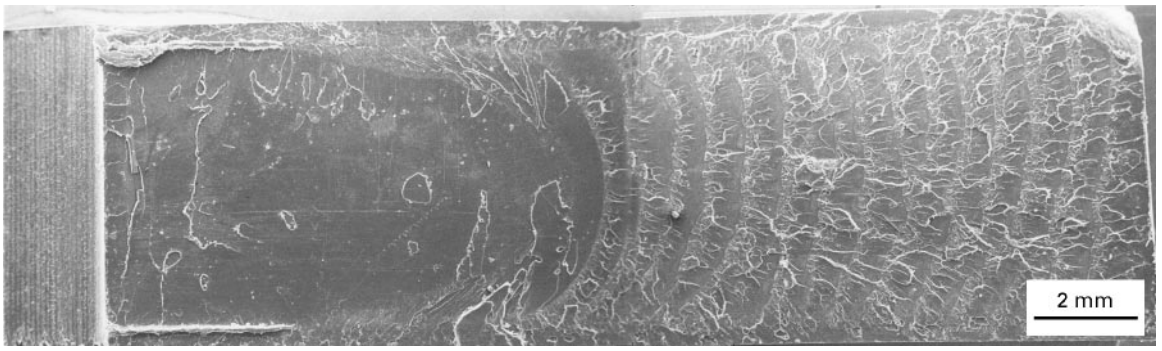

Figure 6 Fracture surface of a notched PS bar broken at slow strain-rate with no UV pre-exposure and no UV exposure during the test. The notch is to the left. The surface of the notch contains lines parallel to the notch root, left by the broaching tool.

Figure 7 Fracture surface of a notched PS sample broken in a slow strain-rate test with edge-on UV exposure following 5 weeks edge-on UV pre-exposure.

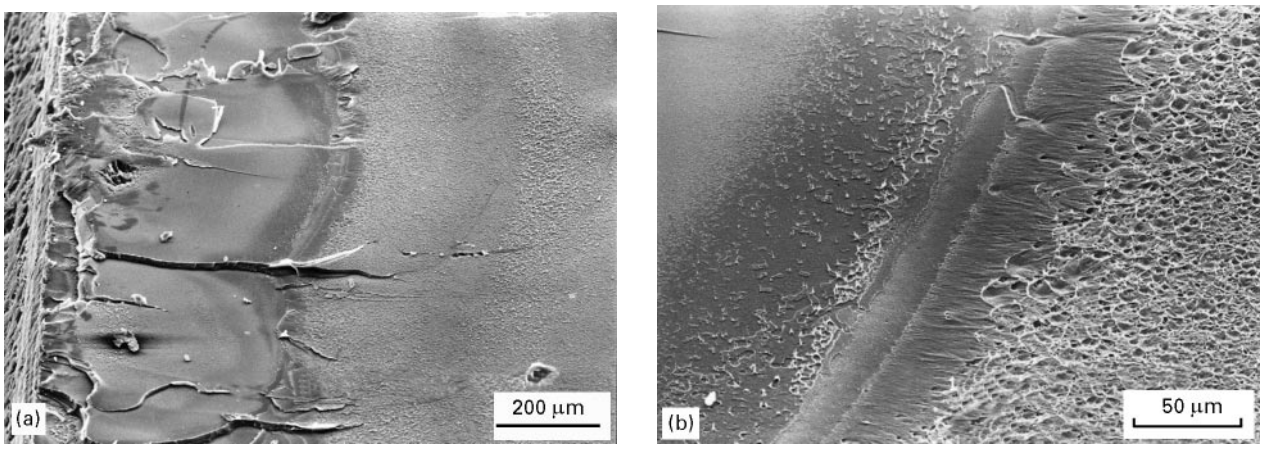

Figure 8 High-magnification images from the area near to the notch root in Fig. 7. (a) The initiation zone immediately adjacent to the notch root (on the left). (b) Magnified detail from the centre of (a) showing the transition from the initiation zone to the flat featureless zone that covers the rest of the fracture surface.

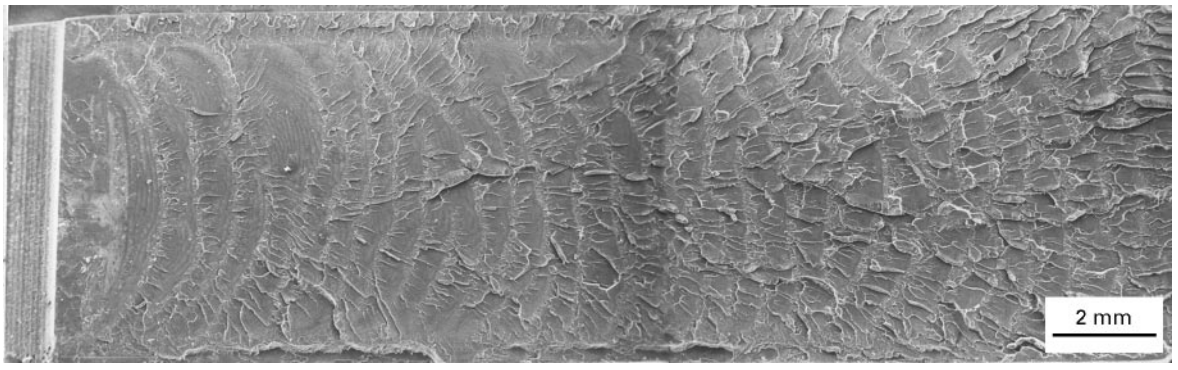

Figure 9 Fracture surface of a notched PS sample broken in a slow strain-rate test with side-on UV exposure following 5 weeks side-on UV pre-exposure.

which showed signs of localizing drawing. Bars which were pre-exposed side-on broke suddenly soon after the craze initiated, leaving behind a smooth zone less than a millimetre long (Fig. 9).

4.3. Polypropylene

An extensive investigation into the slow strain-rate behaviour of polypropylene (and polyethylene) has been made and will be described elsewhere [27]. The results presented here were made as part of a preliminary study and used mouldings from a different batch to those upon which the further study [27] is based.

Fig. 10 shows the effect on the load–deformation behaviour of UV exposure during the test and of the effect of pre-exposure for edge-on UV exposure . Exposure to UV during the slow strain-rate test reduced the load for a particular deformation and caused premature failure. Pre-exposure caused failure to occur even earlier, though in the tests for which results are given here the sample that had received 16 weeks pre-exposure survived longer than that which was pre-exposed for 12 weeks. Similar behaviour was observed when side-on exposure was used instead (Fig. 11). One apparently anomalous result is shown in Fig. 11 where the load–deformation characteristic

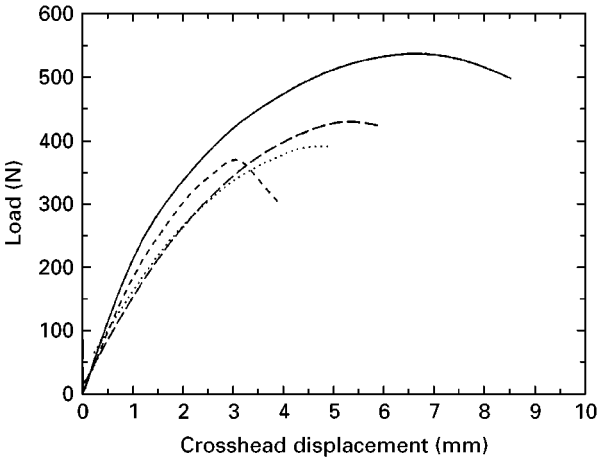

Figure 10 Load–deformation relationships for polypropylene samples pre-exposed edge-on for (———) 0, (- - -) 12 and (···) 16 weeks and tested at slow strain rate with edge-on UV exposure. Results for a sample tested without UV exposure and no pre-exposure are shown (——) for comparison.

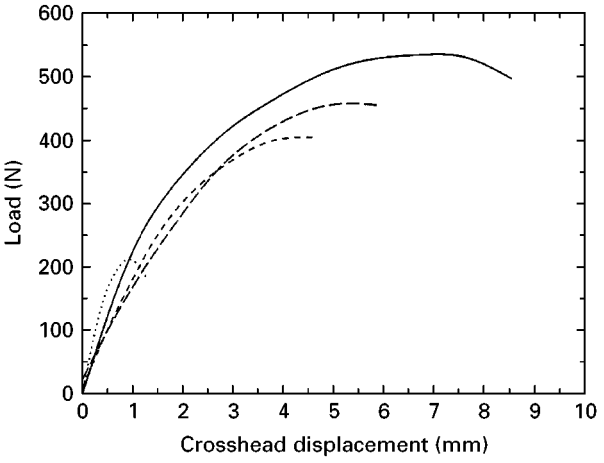

Figure 11 Load–deformation relationships for polypropylene samples pre-exposed side-on for (———) 0, (- - -) 5 and (···) 16 weeks and tested at slow strain rate with side-on UV exposure. Results for a sample tested without UV exposure and no pre-exposure are shown (——) for comparison.

for 16 weeks pre-exposure is steeper than any of the others. Tensile tests at conventional strain rates on un-notched polypropylene bars exposed to UV for varying periods up to 24 weeks confirmed that they first became stiffer then began to lose stiffness again [28].

The maximum load recorded in slow strain-rate tests with ductile polymers seems to be a promising simple parameter to use to compare different samples and the effects of edge-on and side-on pre-exposure are shown in Fig. 12 (see also Table I). For short pre-exposure times there is not much difference in the maximum loads, but at longer pre-exposures (12 and 16 weeks) the deterioration caused by side-on exposure is much greater than that caused by edge-on exposure. By measuring the area under the load-deformation curve the energy dissipated during the failure of the sample can be determined and when this is plotted, the effect of the direction of pre-exposure is even more apparent (Fig. 13). Some further results for

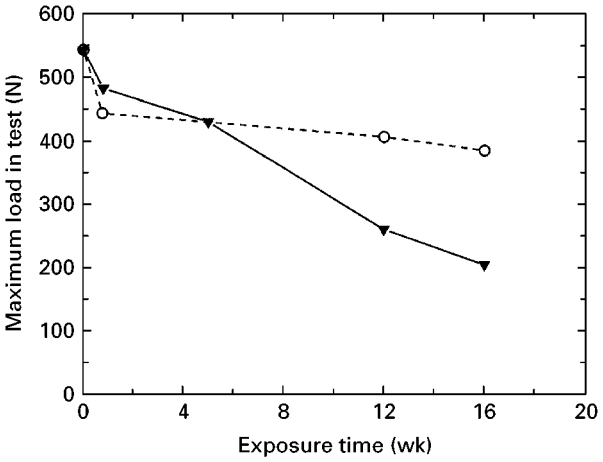

Figure 12 Maximum load recorded in slow strain-rate tests on PP after various pre-exposures: (–▼–) side-on, (- -○- -) edge-on.

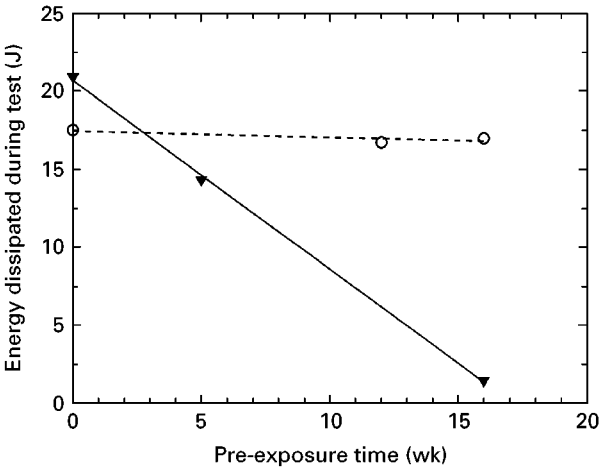

Figure 13 Energy dissipated in tests conducted on PP after various pre-exposures: (–▼–) side-on, (- - ○- -) edge-on.

both PP and PE are given elsewhere [27] and a set of results for a linear low-density poly(ethylene) (PE) are shown in Table I for comparison.

The fracture surface of a bar tested without UV exposure prior to or during the test is shown in Fig. 14a. The region immediately after the notch root is highly deformed with a great deal of drawing in evidence for about 5 mm. Thereafter the fracture surface is much smoother. The general characteristics of the fracture surface of a sample tested with side-on exposure (but no pre-exposure) were rather similar [28]; the main effect of 5 weeks side-on pre-exposure was to shorten the highly deformed ductile zone to about 3.5 mm (Fig. 14b). Longer pre-exposures resulted in larger zones with a ductile appearance [28] (Fig. 14c). Further discussion of the fracture of polypropylene during slow strain-rate tests with UV exposure is given elsewhere [27].

4.4. Polycarbonate

Only one series of tests was conducted on polycarbonate, on samples with no pre-exposure. The load–deformation behaviour was not very different for the three

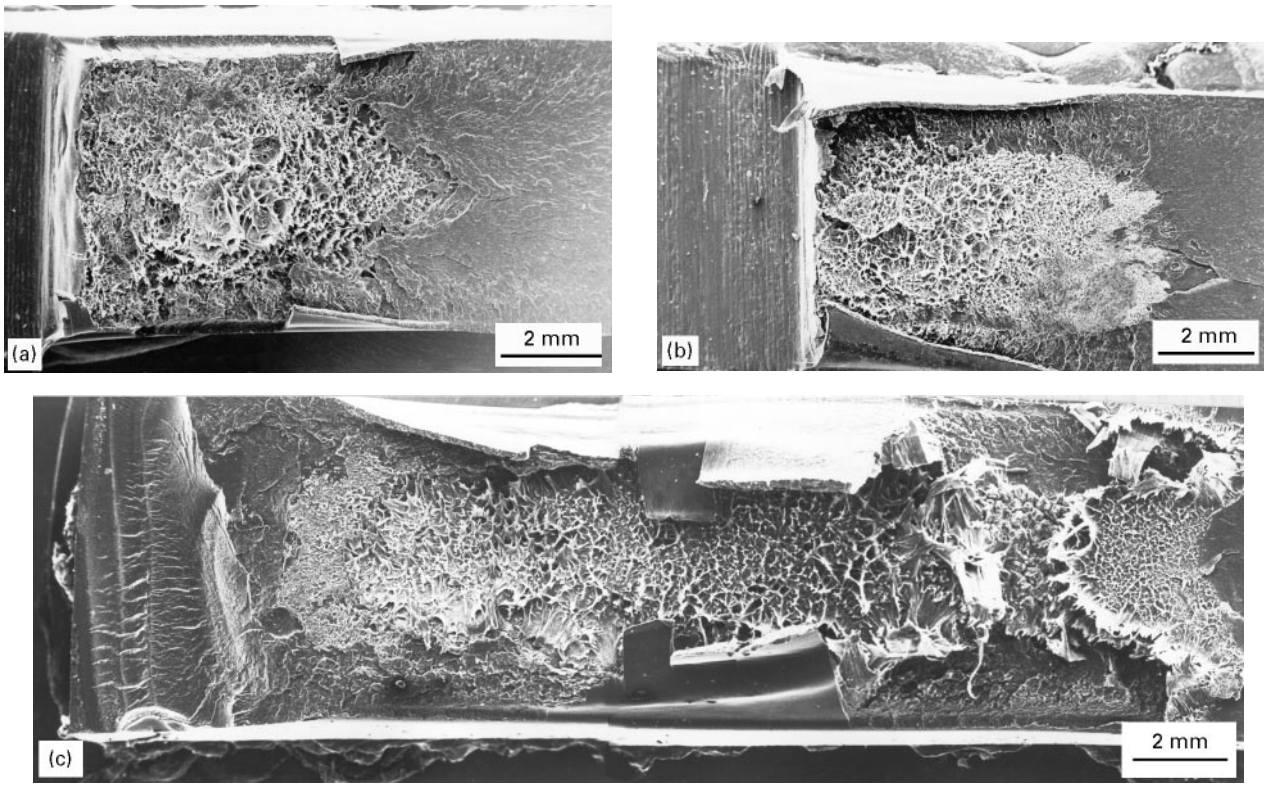

Figure 14 Fracture surfaces of notched PP samples broken in slow strain-rate tests, (a) with no UV pre-exposure and no UV exposure during the test, (b) 5 weeks side-on pre-exposure, side-on exposure during test (exposed side at the bottom of the picture); (c) 12 weeks edge-on pre-exposure, edge-on exposure during test. Note that in (c) the notch is to the right and the crack growth direction is right to the life.

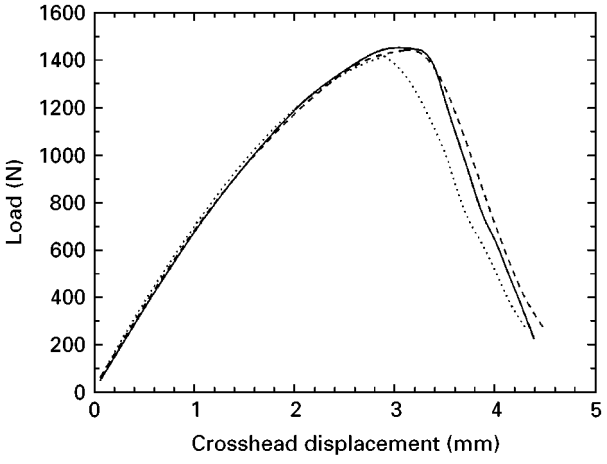

Figure 15 Load versus crosshead displacement for polycarbonate samples tested at a strain rate of 1.33×10^{-7} s^{-1}, (——) no UV in test, (···) side-on exposure, (- - -) edge-on exposure.

different test conditions (Fig. 15). The examples shown in Fig. 15 are representative only, and the repeat tests did not superimpose exactly for any particular condition. In the examples shown in Fig. 15, the results for the sample tested in the absence of UV and for that tested with edge-on UV exposure were almost inseparable, though those for the sample tested with side-on exposure departed from them slightly, registering the maximum load slightly earlier and therefore of slightly lower value.

Fig. 16 consists of a sequence of photographs taken during a slow strain-rate test with side-on UV exposure. No significant change in appearance occurred until the crosshead displacement was nearly 2 mm, when short bright shear bands were visible growing away from the notch tip (Fig. 16b). The shear bands then proceeded to develop, reaching well across the width of the bar before any significant crack growth occurred (Fig. 16c). Finally, a sharp crack propagated through the drawn region that developed between the shear bands (Fig. 16d). The appearance of the test pieces at similar stages during tests with edge-on UV exposure and with no UV exposure was virtually identical.

As might be expected from the observations made of the crack appearance, the plots of crack length or of COD versus the crosshead displacement were insensitive to the UV condition during the test. Even though the appearance of the notch and of the shear bands and crack that grew from it were fairly similar over the range of strain rates employed in this study, the crack length and the COD were quite sensitive to the strain rate. Fig. 17 gives data for the crack length versus crosshead displacement and clearly shows that the crack grew most rapidly at the highest strain rate (1.33×10^{-7} s^{-1}) whereas at the slowest rate (1.12×10^{-7} s^{-1}) the crack grew at less than half the speed. Note that the ratio of these strain rates is less than 1.2. The results for the intermediate strain rate ($\sim 1.23 \times 10^{-7}$ s^{-1}) fell between those for the other two strain rates. A similar partition of results for different strain rates was obtained with the COD measurements (Fig. 18).

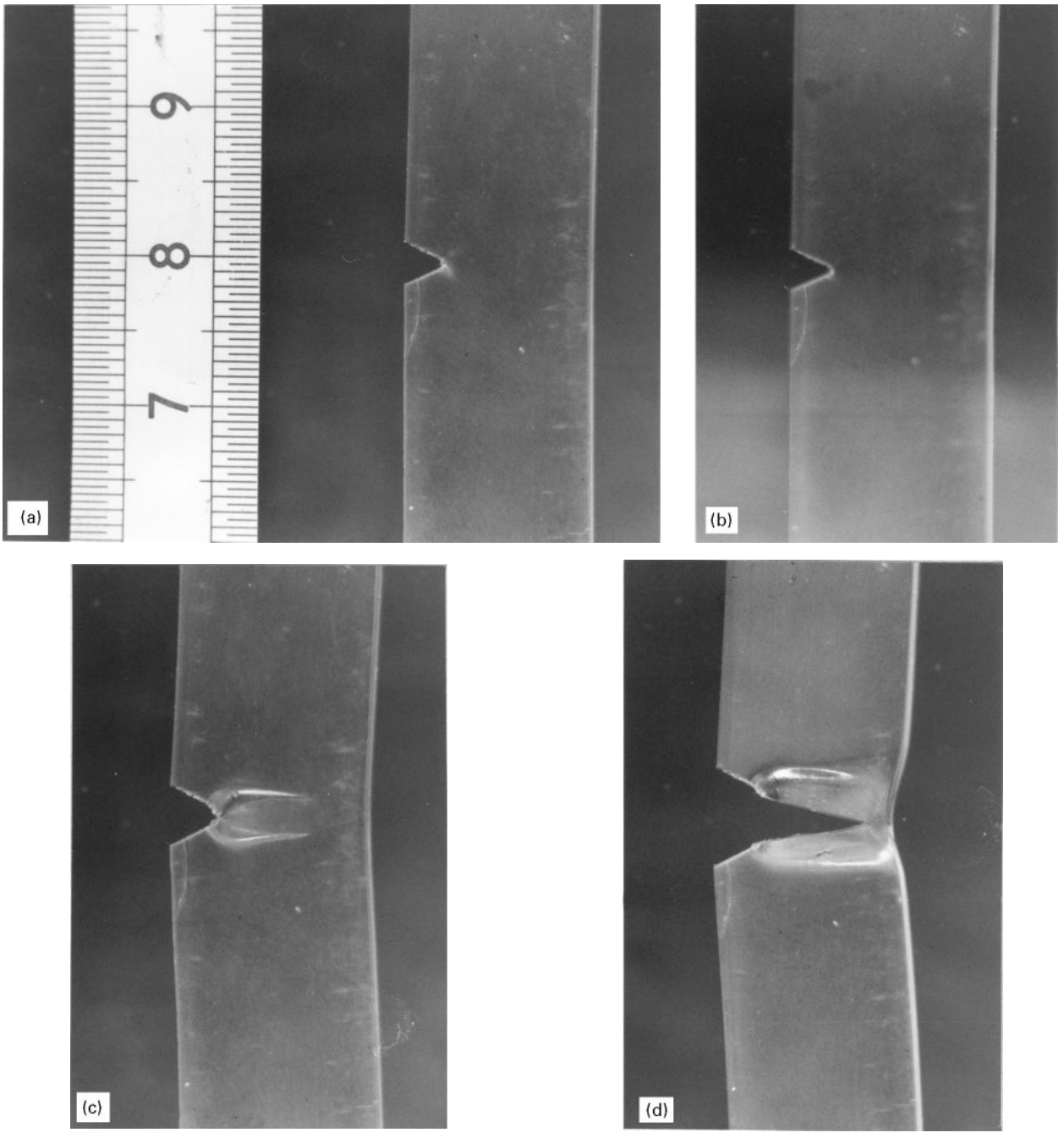

Figure 16 Polycarbonate bar during a slow strain-rate test ($1.33 \times 10^{-7}\ s^{-1}$) with side-on exposure. Photographs taken at crosshead displacement of (a) 0.8 mm, (b) 1.97 mm, (c) 3.10 mm and (d) 4.28 mm.

5. Discussion

The behaviour of all of the materials tested in tension at slow strain rate changed when UV irradiation was applied during the test and/or when UV pre-exposure was applied prior to the test. The effect of UV exposure was least with polycarbonate, which showed only small changes in the load–deformation characteristic and no apparent modification to the failure mechanism. Polycarbonate has a better reputation for outdoor exposure in service than the other polymers included in this study and it is important that any test designed to determine the relative weatherability of the materials should indicate this. It is also interesting to observe the strong strain-rate dependence of the results recorded with polycarbonate. This had a much greater influence than the presence or absence of UV during the slow strain-rate test.

For many samples, the load–deformation characteristic during the slow strain-rate test went through a maximum before failure occurred, as the bar continued to deform for some considerable time after reaching the peak value. This was true even for polystyrene with no pre-exposure or with edge-on pre-exposure, but not for side-on pre-exposure. The changes in the behaviour of polypropylene did not always follow a monotonic progression. This is probably a consequence of the presence of several contributions to the ultimate failure. It has been observed that exposure to UV causes the formation of a brittle layer on PP and that this may fracture easily, nucleating the final failure of the bar. However, prolonged exposure may cause this layer to become so fragile that it can no longer transmit the stress concentration around a crack tip into the less-degraded material in

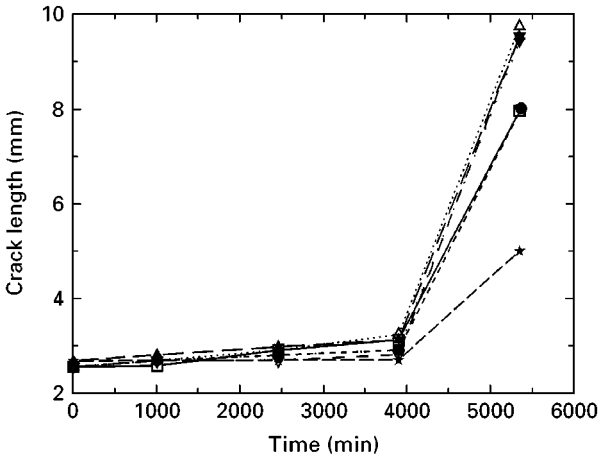

Figure 17 Crack length versus crosshead displacement for polycarbonate samples tested at different strain rates and under different exposure conditions. (□, ▽) No exposure, (★, ▲) edge-on exposure (towards the notch) (N), (●, ▼, △) side-on exposure(S). Strain rates ($nm\,s^{-1}$): (–□–)12.2, (–▽–) 13.2, (--★--) 11.2, (··▲··) 13.3, (—●—) 12.4, (—▼—) 13.1, (··△··) 13.3.

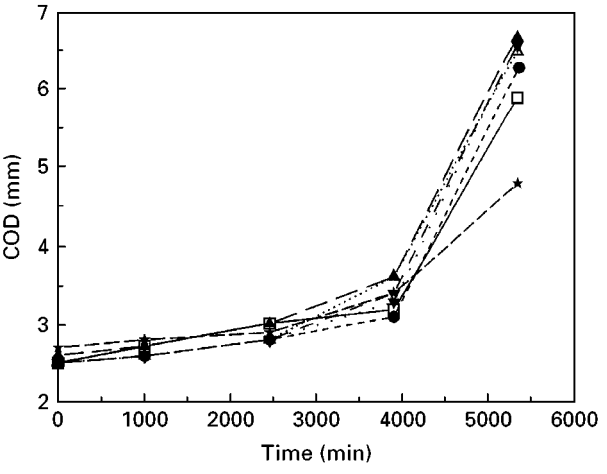

Figure 18 Crack opening displacement versus time for polycarbonate samples tested at different strain rates and under different exposure conditions. For key, see Fig. 17 caption.

the interior and instead flakes off or forms multiple cracks which mutually unload [14]. When the tensile test is conducted at slow strain rate with UV exposure, further subtle differences may arise that influence the response to the combination of pre-exposure and exposure during deformation. Chain scission promoted by UV irradiation during the deformation test may be preferentially focused on strained bonds so that embrittlement is less likely to develop during these circumstances than when UV is applied in the unstressed state, as in pre-exposure (ignoring here the influence of residual stresses).

Changes in slope are present in the load deformation graphs that correspond to the formation of crazes or shear bands, but none of the materials studied so far show a change of this nature that is sufficiently positive to use as a characteristic to represent the state of degradation of the material. Arnold has studied the response of polymers in slow strain rate tests when in contact with aggressive liquids and has found that there is a clear departure of the load–deformation behaviour from that obtained in the absence of the liquid [29]. The differences observed in the current work do not appear at such an early stage as in the examples of environmentally assisted cracking given by Arnold [29].

Pre-exposure was found to cause failure to occur earlier in the slow strain-rate test. The use of pre-exposure violates two of the ideal requirements of an improved weatherability test. Firstly, the addition of a pre-exposure increases the overall time required to assess a set of testpieces. Secondly, there is the problem identified in Section 1 whereby the use of a small number of discrete pre-exposure times may allow a critical condition to be missed. For example, with PP the strength versus exposure characteristic goes through a minimum (corresponding to the formation of a brittle surface layer that is sufficiently integral to promote propagation of a crack into the interior) but then recovers somewhat (corresponding to disintegration of the surface layer and the loss of its ability to form a crack that can propagate into the interior [14, 30]). If sampling occurs at pre-exposure on either side of the minimum, the strength will be greater than would be recorded at the minimum and will give a false impression of the worst state of the material. Thus although pre-exposure may speed up a slow strain-rate test and in some cases provide amplification of the differences between samples with different weatherability, it should be used with extreme caution, and preferably only after conducting a thorough investigation into the failure mechanism(s) during the test (and, if possible, during service), and into the sequence of major steps in the degradation pathway.

The critical load for craze formation in polystyrene was determined fairly accurately using a plot of log (craze length) versus load and extrapolating back, as in Fig. 5. This was found to be quite sensitive to pre-exposure and, in the case of polymer prone to crazing, might be used as a characteristic to describe the state of degradation in a sample that had been exposed for an unknown period. On considering the discussion here and that presented earlier relating to polycarbonate, it is clear that in some cases the interpretation of the results of the slow strain-rate tests may apply only to one particular polymer or generic group.

An effect of the direction of application of UV was apparent in many cases. Generally, side-on exposure caused greater deterioration in properties than edge-on exposure. This may simply be a consequence of the greater total energy absorbed with side-on illumination, following from the greater area presented to the UV. It should be recognized, however, that even this simplistic notion may require qualification because not all of the incident energy is absorbed and a greater fraction is transmitted and escapes when the direction of propagation coincides with the short ("thickness") dimension of the testpiece, as in "side-on" exposure.

6. Conclusion

Exposure of polymer samples to ultraviolet irradiation (UV) during a slow strain-rate tensile test accelerates

failure. The extent of the acceleration appears to rank polymers according to their resistance to outdoor exposure. The maximum load attained during the slow strain-rate test is a suitable characteristic to compare the degradation of samples photo-oxidized under different conditions. Pre-exposure to UV prior to the slow strain-rate test causes further acceleration of failure.

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