Effect of Water Absorption and Temperature Gradients on Polycarbonate Injection Moldings

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SYNOPSIS

Polycarbonate injection moldings have been conditioned for various times in (i) hot water (40, 60, 80, and 100°C) or (ii) in a temperature gradient (with hot surface/cold surface temperatures 80/25, 100/25, 120/35, and 140/60°C). Water absorption occurred in hot water and caused the formation of disc-shaped flaws, which were located at all depths within the bars and at all orientations. The presence of the flaws caused severe embrittlement and cracks were nucleated by them during uniaxial tensile testing. Residual stress levels were found to be diminished by hot water conditioning more than those in bars conditioned at the same temperatures in air. The sense of the residual stresses reversed in a bar that was allowed to cool slowly in the water bath, an observation attributed to desorption. It was generally found that the flaws near the surface healed on allowing the bars to stand in air at room temperature. Temperature gradient conditioning caused reversal of the sense of the residual stresses near to the hot surface at the two higher temperatures used and significant reduction in magnitude at the lower temperatures. Fracture nucleated at this surface during uniaxial tensile testing.

INTRODUCTION

The experiments described here were conducted to investigate the environmental degradation of polycarbonate under controlled laboratory conditions. The conditioning procedures investigated are (i) immersion in hot water and (ii) the imposition of a temperature gradient across the molding in the thickness direction. Water absorption is known to cause serious deterioration of mechanical properties and has been the subject of several studies.[1-15] Hydrolysis reactions cause molecular breakdown but, although this contributes to the observed degradation, other factors may also play a part. In the study of Ram, Zilber, and Kenig[14] the residual stresses present in the moldings were measured after various conditioning procedures including immersion in hot water and the authors deduced that the changes in residual stresses were responsible for the reduced

toughness in polycarbonate following water absorption. A temperature gradient can also be expected to modify the residual stress distribution in a molding,[16] generally with deleterious effect. As far as we are aware, the only previous report of the effect on the residual stresses in polycarbonate of a temperature gradient applied after molding is that made in an earlier study of weathered polymers.[17] Here we speculated that changes that occurred in the residual stress distribution were caused by the temperature gradient that will often be present during outdoor exposure.[17]

Residual stresses form in injection moldings as the result of the temperature gradients that exist during solidification.[18-23] Under normal molding conditions the stresses that form in the interior of the molding are tensile and fairly weak, and those at the surface are compressive and can be quite strong. Post-molding conditioning can cause large changes to occur in the residual stress distribution and studies have been made of the effects of aging and annealing,[24-28] a temperature gradient,[16] weathering,[17,29] and water absorption.[14,30-32] Polycarbonate has featured in several of these stud-

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ies[14,17,27] and the observation by Ram, Zilber, and Kenig that the stress distribution reversed after hot water conditioning, producing tensile stresses at the surface, led them to attempt to explain the reduction in toughness in terms of the changes in residual stress distribution.[14] This follows an earlier idea of Broutman and co-workers, who studied polycarbonate samples with different thermo-mechanical histories.[33-36] The various thermomechanical preparation procedures and conditioning treatments alter other properties of the material in addition to the residual stress distribution, including the molecular orientation and the density. These may also influence the mechanical and fracture properties of the material and it is not possible to attribute the changes in behavior simply to the changes in residual stress without considering the effect of changes in the other characteristics.

The experiments described here were part of a laboratory investigation designed to complement studies of the effects of natural weathering conducted by the authors.[17,29,37] One objective was to attempt to reconcile the results obtained by Ram, Zilber, and Kenig[14] with moldings weathered outdoors in Israel with those obtained by ourselves in an earlier study.[17] Ram et al. discovered that their moldings developed tensile stresses at the surface after weathering for 1 year, though they found that the readiness of samples to change the residual stress distribution with their several conditioning procedures differed considerably from one material grade to another. Qayyum and White used only one grade of polycarbonate and found that 1 year of weathering in Jeddah, Saudi Arabia, caused a considerable reduction in the residual stress levels, but the stresses did not reverse sense. Tensile stresses were observed to form at the surface of bars made from polystyrene and unplasticized poly(vinyl chloride) exposed at the same time. Extending the exposure time to 4 years still did not produce reversal of the stress sense with the grade of polycarbonate used by Qayyum and White.[37] The difference in behavior of polycarbonate and the other glassy polymers studied by Qayyum and White might be explained by the difference in their glass transition temperatures (T_g), which is much higher for polycarbonate than for polystyrene or poly(vinyl chloride). This is unlikely to account for the differences in residual stress development found by Ram et al. and by Qayyum and White. It was shown by Thompson and White that reversal of the sense of stress occurred near the warmer surface of a molding when subjected to a temperature gradient[16] and it was suggested that the same mechanism may occur during outdoor exposure in a hot climate, for it is known that the side that faces the sun reaches quite high temperatures.[17] The laboratory temperature gradient experiments of Thompson and White did not include polycarbonate and this has been remedied in the work described here.

EXPERIMENTAL

Materials and Specimen Preparation

The material used was Bayer Makrolon 2603 and was predried before injection-molding on a Stubbe 76-110 reciprocating screw machine at RAPRA (Shawbury, Shrewsbury, UK) into test pieces of two kinds: (i) ASTM D638 tensile test bars 190 mm long with gauge-length cross section ~ 12.7 × 3.2 mm using a single end-gated cavity; and (ii) Charpy test bars measuring 127 × 12.7 × 12.7 mm, also single end-gated. The moldings were drawn from the batches made for the studies reported before[17,37] and were molded in a single run with processing conditions kept constant throughout. The bars were aged indoors for several years prior to commencement of the laboratory tests described here.

Hot Water Treatment

Samples were immersed in deionized water held at 40°C for up to 97 days, at 60°C for up to 90 days, at 80°C for up to 21 days, and at 100°C for up to 15 days. At the end of the conditioning period, the bars were normally removed from the bath, dried using a soft tissue, and allowed to cool in laboratory air. One batch of specimens that were conditioned in water at 100°C for 7 days were allowed to cool in the water bath which was simply switched off at the end of the chosen time. Some specimens were immersed in deionized water at room temperature (~ 25°C).

Air Oven Treatment

Batches of specimens were heat-treated in an air oven at the same temperatures and for similar periods of time as those conditioned in hot water.

Temperature Gradient Treatment

Bars were subjected to a temperature gradient in pairs sandwiched between two plates kept at different constant temperatures, as described before.[16] The warmer plate was heated by poly(ethylene gly-

col) supplied by a recirculating constant temperature bath, which was connected to copper tubes attached to the plate. The hot plate temperatures chosen were 80, 100, 120, and 140°C. The cold plate tubes were supplied with water from a similar recirculating bath, with a target temperature of 25°C. The cooling arrangement was inadequate for tests with the two highest hot plate temperatures and the cold surface temperature drifted up to 30–40°C when the hot plate was set for 120°C and 55–65°C when it was set for 140°C. The temperature gradient was maintained for periods up to 1 h. The bars were lightly clamped during the temperature gradient treatment and were prevented from bending in response to differential thermal expansion or nonuniform relaxation during the conditioning process.

Molecular Weight Measurement

Samples were cut from bars treated in hot water and analyzed by gel permeation chromatography using a Waters Associates ALC 200 operating at room temperature with a flow rate of 1 mL/min using a 0.2% solution in tetrahydrofuran. It was not expected that the relatively short temperature gradient treatments would produce significant molecular weight degradation and no molecular weight measurements were made on them.

Mechanical Testing

Uniaxial tensile tests were conducted using a crosshead speed of 20 mm/min and were used to find the upper yield stress, the tensile strength, and the extension to fracture. Impact tests were made on Charpy test bars into which were cut notches to a depth of 2.5 mm with a tip radius of 0.25 mm and a 45° entrance angle. The tests were conducted on an Avery-Denison 6709U machine using a striking velocity of 3.46 m/s.

Dynamic Mechanical Thermal Analysis

A Polymer Laboratories DMTA with the standard head was used to perform dynamic mechanical analyses on samples machined, respectively, from the skin and the core of moldings after hot water conditioning. The heating rate was 4°C/min and the temperature scans were made from −100 to +170°C. All of the results presented below were obtained at a frequency of 1 Hz. Specimens were vibrated in cantilever bending mode and the results are presented uncorrected for clamping errors. Thus the Young's modulus values quoted are too low by

an unknown amount, but the data are perfectly adequate for internal comparisons. The position of the tan δ peak was taken as the glass transition temperature.

Residual Stress Measurement

Residual stress distributions were determined at the end of the various conditioning treatments using the layer removal procedure described by Treuting and Read[38] and adopted for use with polymers by several groups.[14,16,20-31,34] Thin uniform layers are removed from one surface of the bar by high speed milling using a single point cutter with fly cutting action. The bars were fastened to the machine bed using double-sided adhesive tape and care was required when removing them from the machine bed to avoid introducing nonrecoverable deformation.

On releasing the bar from the machine bed, it is found to be curved because of the imbalance in residual stress caused by removing a layer that had itself been stressed. The curvature was measured at each layer removal using the optical lever principle with a laser as the light beam source.[20,22,24] Plots of curvature ρ ($= 1/$radius) versus depth of material removed were thus generated and were used to compute the residual stress distributions using the following formula taken from Treuting and Read[38]:

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

This represents the stress in the bar axis ($x-$) direction as a function of distance z_1 from the central plane (before layer removals are made) of a bar of thickness $2z_0$ and assumes that the Young's modulus E and Poisson's ratio v are uniform throughout the bar. This form of the Treuting and Read formula corresponds to the case where the curvature transverse to the bar axis direction is zero. This value is difficult to measure in a narrow bar but visual observation confirmed that it was small in the specimens studied here. The error incurred by using this formula rather than the complete biaxial form[22,38] is small.[20] The errors resulting from depth-dependent variations in modulus can likewise be neglected to a first approximation.[31,39] Layers were removed until just over half of the bar had been removed, permitting analysis of the stresses in one half of the bar. This is all that is needed as long as the stresses are symmetrical about the central plane. For the

specimens subjected to a temperature gradient, the stresses are not expected to be symmetrical and pairs of bars treated together were used, one machined from the side that was kept warm during conditioning and the other from the side that was kept cool. The two analyses were then conducted separately as usual, but the results from one of them are presented with the distance from the surface plotted from right to left. By placing these results to the right of those from the other bar and adjusting the positions corresponding to the two surfaces of the bar so that the center of the bar is coincident in both halves, the stress distribution is obtained through the whole thickness of the bar.

Scanning Electron Microscopy

Fracture surfaces were gold-coated and examined in a scanning electron microscope using the secondary electron image. The molded surfaces near the fracture surface were also inspected.

RESULTS

Visual Observations

Bars conditioned in hot water developed flaws that had the appearance of thin disc-shaped cracks or crazes up to 2 mm in diameter and occasionally even larger. They were present throughout the bar thickness and apparently did not possess any preferred orientation. After removing the bar from the water bath and drying the surface, it was found that the flaws located near to the surface began to heal almost immediately and eventually disappeared altogether to the naked eye, whereas those in the interior did not show any tendency to alter their appearance.

Molecular Weight Measurement

Values for the number average molecular weight M_n, and the weight average molecular weight M_w, obtained by gel permeation chromatography, are given in Table I. It is evident that the rate of molecular scission is much higher in water than in air. After 7 days at 100°C in air the values of M_n and M_w had fallen by 12 and 2%, respectively, whereas in water at 100°C M_n fell 27% and M_w 22%. Extending the period of treatment in water at 100°C to 15 days caused the fall in M_n to increase to 42% and that in M_w to 35%. Less damage was recorded at 60 and 80°C both in air and water than at 100°C, but at both temperatures the molecular weight degradation was considerably higher in water than in air. The results do not show conclusively whether 21 days at 80°C or 90 days at 60°C is more damaging for either environment.

Mechanical Testing

The load–deformation behavior of polycarbonate bars stored in water at 40 and 100°C for various periods is shown in Figures 1 and 2. Treatment in water at 40°C caused a reduction in extension to break but the bars retained considerable ductility even after 97 days. Strain hardening was observed with bars conditioned for 30 days or less but not with those conditioned for 97 days. The load–deformation curve for bars kept in water at room temperature for 7 months was almost indistinguishable from that shown in Figure 1 for the bar aged at room temperature in laboratory air. Bars conditioned in water at 60°C showed much more rapid deterioration than those treated at 40°C, with disappearance of the strain hardening phase even after as little as 2 days. Bars treated in water at 80 and 100°C failed without drawing even at the shortest dwell times (2

Table I Molecular Weight Measurements

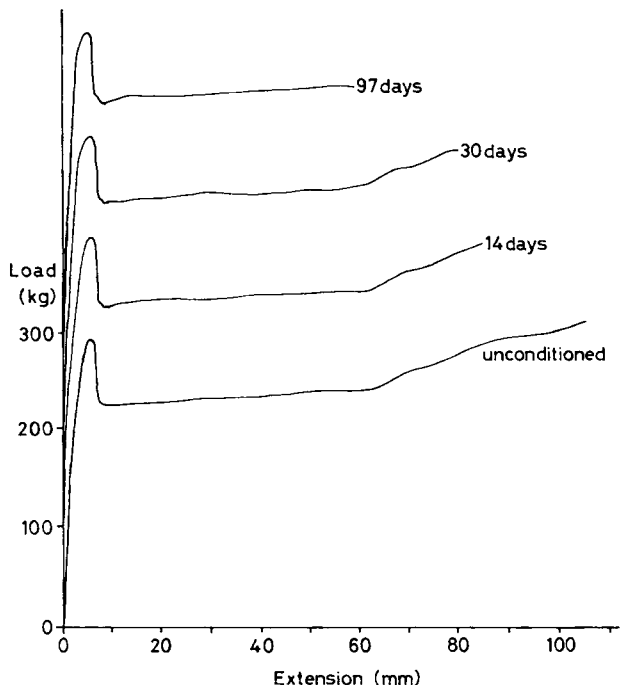| Code	Temperature (°C)	Time (days)	Air or Water	$M_n/10^3$	$M_w/10^4$	M_w/M_n
PC U A	RT[a]	—	Air	7.73	1.76	2.28
PC 60 W	60	90	Water	6.30	1.56	2.47
PC 80 W	80	21	Water	6.91	1.53	2.21
PC 100 W 1	100	7	Water	5.61	1.37	2.44
PC 100 W 2	100	15	Water	4.45	1.15	2.58
PC 60 A	60	90	Air	7.12	1.74	2.44
PC 80 A	80	21	Air	6.82	1.68	2.46
PC 100 A	100	7	Air	6.77	1.73	2.55

[a] RT = room temperature.

Figure 1 Tensile load–deformation curves for polycarbonate bars that had been conditioned in water at 40°C for different periods of time prior to testing. Each curve is displaced upwards by 100 kg relative to the one below. The lowest one is for a bar that had been aged at room temperature and not given a water treatment.

days at 80°C or 8 h at 100°C); no yield drop was found with specimens treated for 8 days at 80°C or 1 day at 100°C (see Fig. 2). The most sensitive pa-
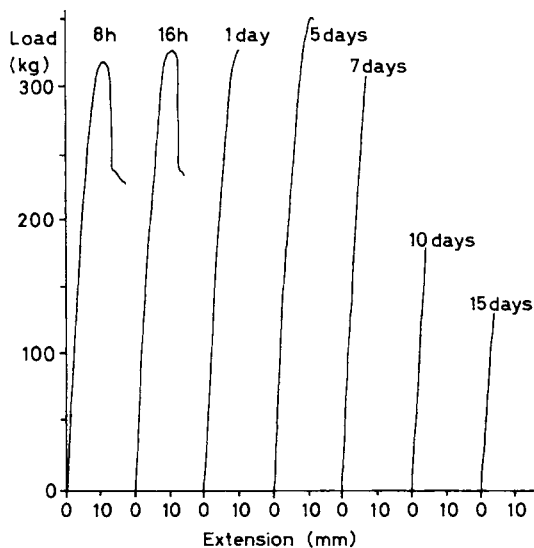
Figure 2 Tensile load–deformation curves for polycarbonate bars that had been conditioned in water at 100°C for different periods of time prior to testing.
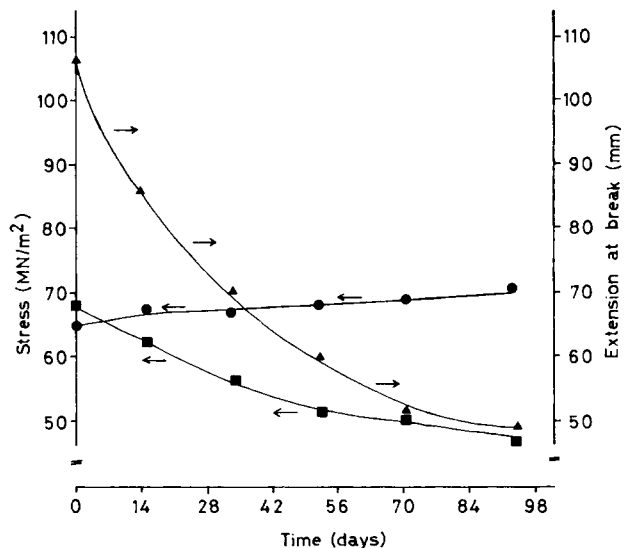
Figure 3 Summary of the tensile properties of bars conditioned in water at 60°C: (●) upper yield stress; (■) stress at fracture; (▲) extension at break.

rameter that can be extracted from these tests is the extension to break, and the variation of this with treatment time is shown together with the (engineering) yield strength and (engineering) fracture strength for tests conducted at 60 and 80°C in Figures 3 and 4. Only the extension to break is plotted for tests conducted on samples conditioned in water
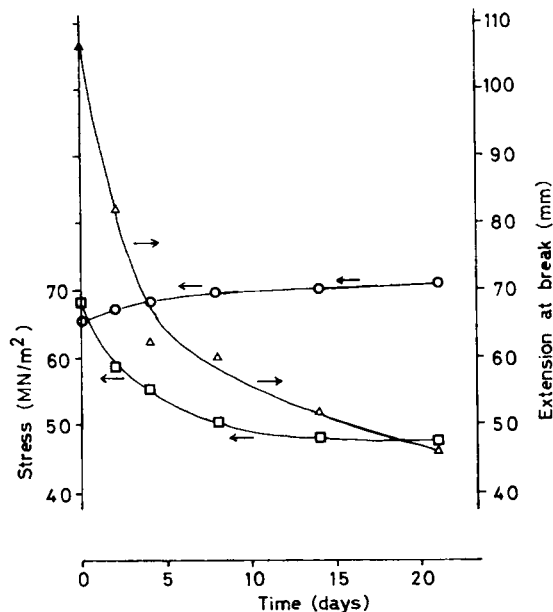
Figure 4 Summary of the tensile properties of bars conditioned in water at 80°C: (○) upper yield stress; (□) stress at fracture; (△) extension at break. Note that the scale of the time axis is different from that in Figure 3.

at 100°C (Fig. 5). At both 60 and 80°C the yield strength increased slowly with increased exposure whereas the fracture stress fell considerably and quickly became lower than the yield stress, the specimens showing little or no strain hardening even when drawing substantially.

The reductions in properties were much less severe for specimens heat treated in air. After heat treatment at 40°C the bars still showed considerable drawing and strain hardening even for 81 days dwell. Drawing was still obtained after 90 days conditioning in air at 60°C but fracture occurred much sooner and without strain hardening. Strain hardening was not observed with specimens conditioned for a week or more at 80 and 100°C. The fall-off in property for bars conditioned at 60 and 80°C is summarized in Figures 6 and 7 and shows similar trends to those obtained with water-conditioned specimens.

The Charpy impact energy for specimens conditioned in water fell progressively at all temperatures, with very rapid deterioration at the highest temperatures (Fig. 8). The reduction in property was less pronounced with specimens conditioned in air (Fig. 9).

Samples heat-treated in a temperature gradient showed much less reduction in fracture strength, and the yield stress increased slightly (Fig. 10). This
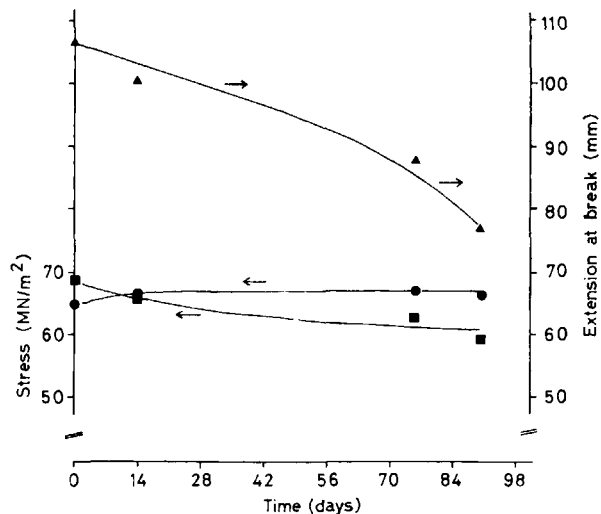

Figure 6 Summary of the tensile properties of bars conditioned in air at 60°C: (●) upper yield stress; (■) stress at fracture; (▲) extension at break.

increase was accompanied by a loss in ductility and the extension at break fell, with very large drops for samples having the hot surface at 120 or 140°C.

Dynamic Mechanical Thermal Analysis

Skin samples gave higher values for the storage modulus E' than the core for all conditioning states (e.g., Fig. 11). The values of E' for samples taken from the skin of bars aged at room temperature and those conditioned in water at 100°C for 15 days were almost indistinguishable at all temperatures except
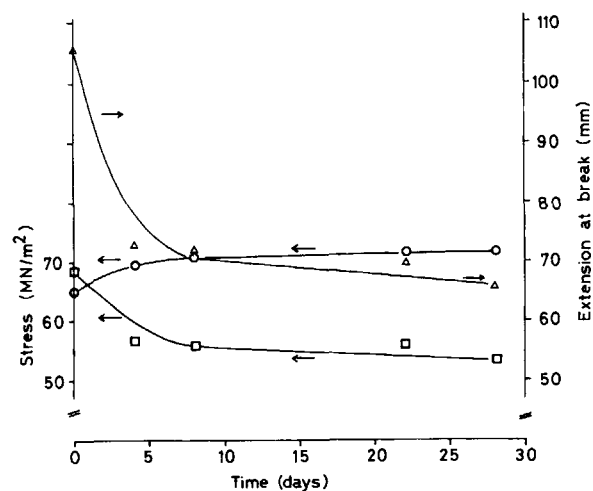

Figure 5 Extension at break of bars conditioned in water at 100°C.

Figure 7 Summary of the tensile properties of bars conditioned in air at 80°C: (○) upper yield stress; (□) stress at fracture; (△) extension at break.
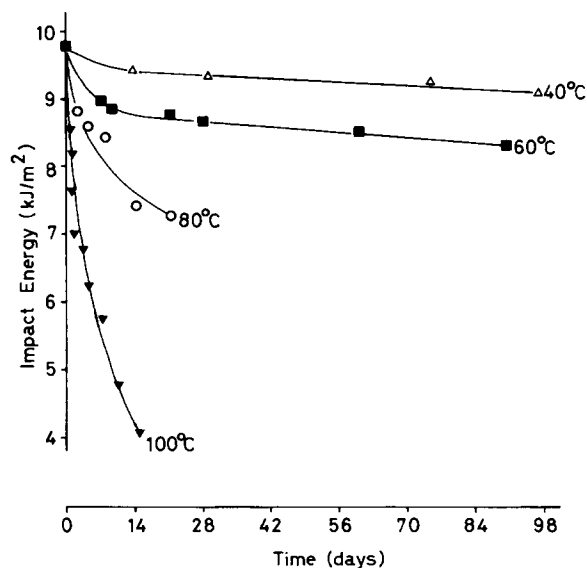
Figure 8   Charpy impact energy of polycarbonate after conditioning in water at various temperatures, plotted versus conditioning time.

close to the glass transition temperature. A slight displacement seems to be present between the E' traces for the corresponding core samples, but we do not regard this as significant given the level of reproducibility obtained with the DMTA with specimens of this kind. The drop in E' at the glass transition occurred at a lower temperature with the water-conditioned samples. A corresponding shift in the tan δ peak was evident and the temperature at the maximum was recorded as the T_g. T_g values read in this way from DMTA traces obtained with specimens conditioned in water at 100°C for various times are given in Figure 12 and show that the shift is progressive as the dwell time increases.

The major secondary relaxation has been designated as the γ-transition[40] and is located between
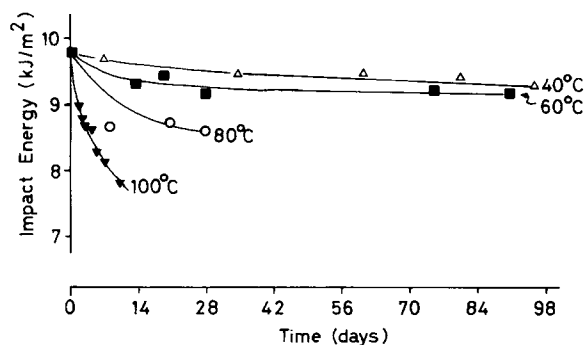

Figure 9   Charpy impact energy of polycarbonate after conditioning in air at various temperatures, plotted versus conditioning time.
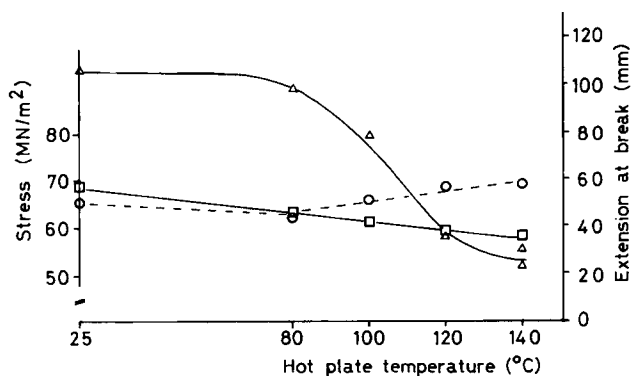

Figure 10   Summary of the tensile properties of bars conditioned in a temperature gradient, plotted versus the hot surface temperature (the cold surface was nominally at 25°C): (○) upper yield stress; (□) stress at fracture; (△) extension at break.

−80 and −90°C in the DMTA traces. This peak also shifted as the result of conditioning in water and data obtained from DMTA traces recorded with specimens treated in water at 100°C are shown in Figure 13. Curiously the peak temperature for skin samples climbed whereas that for core samples fell. In the untreated state the γ-transition of the skin was 3.5° lower than that for the core whereas after 15 days in water at 100°C it was 3° higher.

Residual Stress Measurement

Even after the long aging period at room temperature, the polycarbonate bars contained significant residual stresses, approaching 2 MN/m² (tensile) in the interior and 6 MN/m² (compressive) near the surface (Fig. 14). The sense of the stresses was thus that normally found with newly made injection moldings produced under conventional processing conditions. After heating in air for 7 days at 100°C the stresses remained roughly the same over the central 1.0–1.5 mm of the bar but stress magnitudes were reduced at other locations (Fig. 14). Conditioning for a week in water at 100°C caused a significant reduction in stress levels; this is shown in Figure 14 in which the example presented was obtained from a bar which was allowed to stand in ambient air for 6 months before conducting the layer removal test. Presumably this will have allowed some desorption of water. The residual stress levels measured in a bar which was allowed to stand in air at 30°C for only 2 days after conditioning in water at 100°C for 7 days were lower still (Fig. 15) and it appears that desorption is accompanied by partial recovery of residual stresses. In another experiment
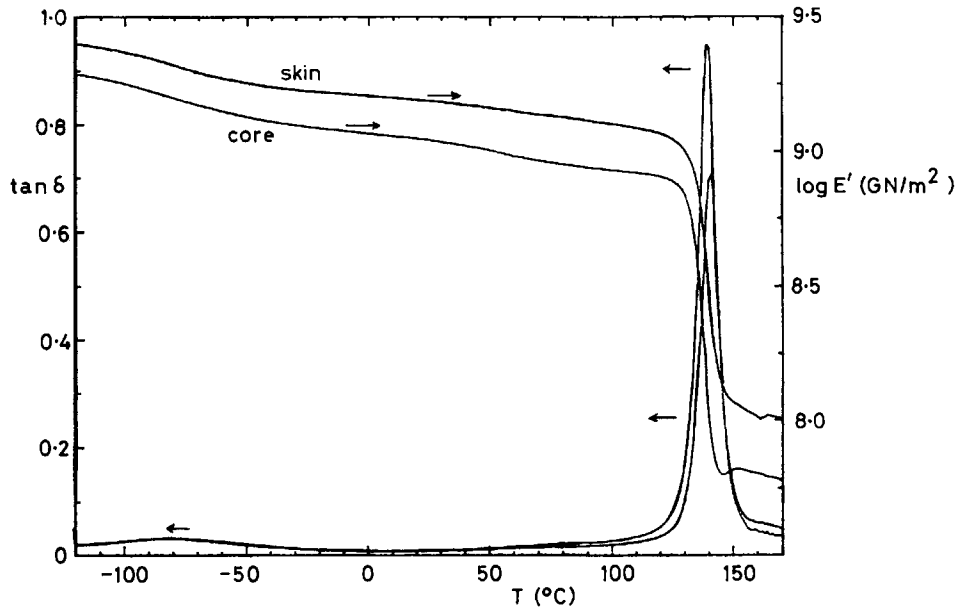
Figure 11   Storage modulus (E') and tan δ obtained for skin and core samples taken from bars aged in water at 100°C. The measurements were made over a wide temperature range using the DMTA.

bars were allowed to cool slowly in the water bath, the power to which was simply switched off at the end of the 7-day conditioning period. The stresses in this type of specimen were very small indeed, most likely the consequence of a very slow cooling rate preventing large temperature gradients from developing (Fig. 15). Measurement of curvatures as low as those obtained with this sample is not very accurate, but there does appear to be a strong indication that the curvature fell for the first three layer removals, indicating that the stress near the surface was tensile. This might be caused by desorption of water after removal from the water bath if desorption occurs preferentially from the surface regions.

This explanation is in apparent contradiction to that advanced above concerning stress recovery and will be discussed further later on.

Examples of stress distributions measured in bars after temperature gradient treatment are shown in Figures 16–18. With a hot surface/cold surface temperature combination of 80°C/25°C, the bars had compressive stresses near to both surfaces with lower magnitudes at the hotter surface than at the cooler one. A generally similar distribution seems apparent for 100°C/25°C (Fig. 16), though in this case there is an indication that the curvature reduces on the first layer removal from the hot face which, if it is a true result, would mean that the residual
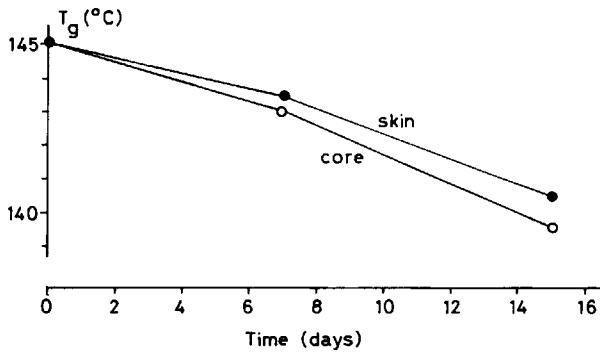

Figure 12   Glass transition temperature measurements made on samples conditioned in water at 100°C plotted versus conditioning time.
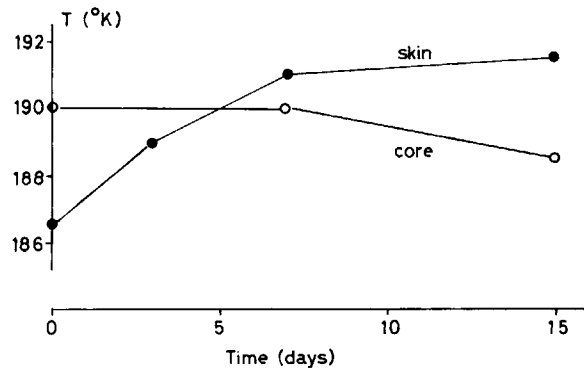

Figure 13   γ-peak temperatures for samples conditioned in water at 100°C for various treatment times.
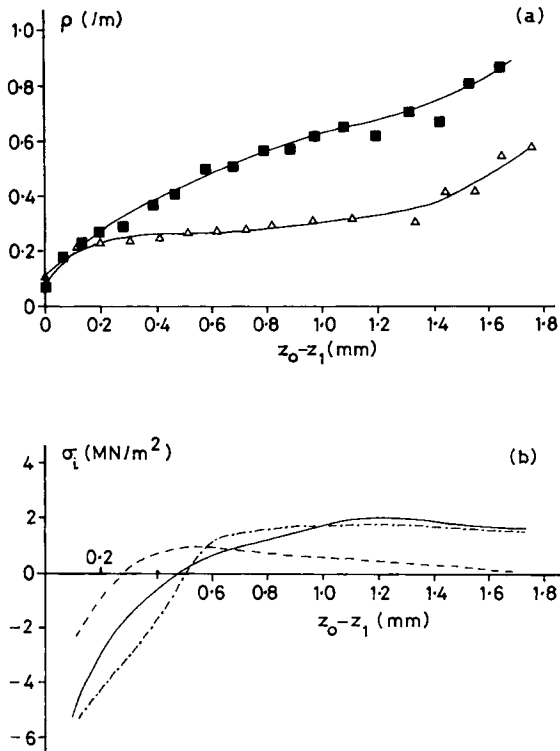
Figure 14 (a) Curvature ρ versus depth removed, (z_0 − z_1), for bars conditioned for 7 days at 100°C in air (■) and conditioned for 7 days at 100°C in water, dried in ambient air, and tested six months later (△). (b) Residual stress analyses from the curves in (a): bars conditioned in air (———) and in water (− − −). Shown for comparison is the distribution obtained with a bar aged at room temperature (− · − · −).

Figure 15 (a) Curvature versus depth removed for bars conditioned for 7 days at 100°C in water: dried at 30°C for 2 days before testing (■); sample cooled slowly in water bath (○); dried in ambient air and tested six months after water conditioning (———) [repeats one of sets (△) of results shown in Figure 14]. (b) Residual stress analyses from the curves in (a): bars dried at 30°C in air for 2 days before testing (———); cooled slowly in water bath (− · − · −); dried in ambient air and tested 6 months after water conditioning (− − −).

stress at the surface is tensile on this side. For 120°C/35°C the presence of tensile stress near to the surface held at the higher temperature during gradient annealing is positively confirmed (Fig. 17) and the same is also true of bars treated for much shorter times with a 140°C/60°C combination (Fig. 18).

Scanning Electron Microscopy

The flaws observed by eye in the bars conditioned in hot water acted as crack nuclei. Large disc-shaped flaws with the normal to the disc face directed parallel to the bar axis were most likely to reach the critical fracture condition and this is evident on the fracture surfaces. Figure 19 shows the fracture surface from a sample tested in uniaxial tension after conditioning in water at 60°C for 9 days. The initial disc-shaped cavity is shown with radial fracture markings running from it. In some cases the density
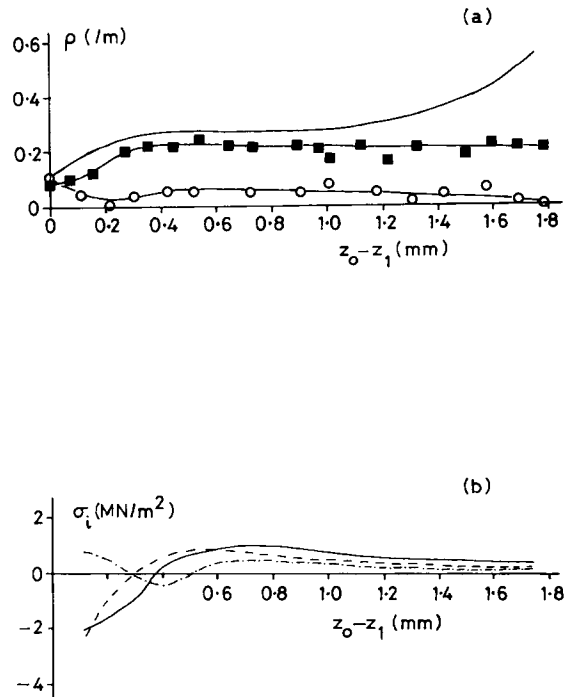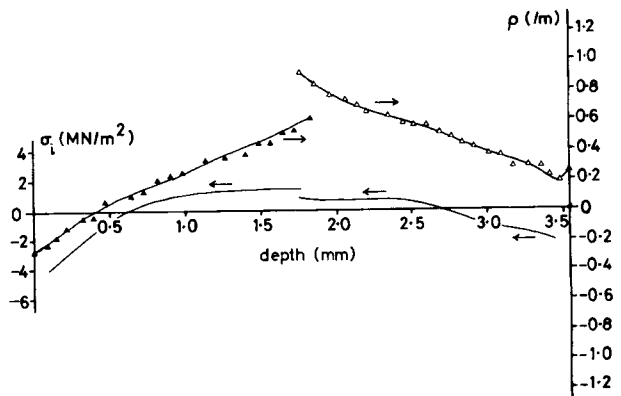

Figure 16 Curvature plots and residual stress analyses for a pair of bars conditioned in a temperature gradient for 1 h with hot/cold face temperatures of 100/25°C. The left-hand axis corresponds to the cold surface and the right-hand axis to the hot surface and the two axes are separated by the bar thickness so that the bar center position for both analyses is coincident.

of flaws was so high that the fracture surface contained two or more, and it appeared that the fracture path had diverted to include cracks growing on different planes. Figures 20(a) and (b) show two large flaws on the fracture surface from a bar conditioned in water at 60°C for 90 days. The one shown in Figure 20(b) is located on a region of the fracture surface inclined quite steeply to the area shown in Figure 20(a), which is in the plane normal to the bar axis [Fig. 20(c)]. Flaws with their normals inclined to the bar axis were a common feature, as noted above in the section on visual observations, and they frequently appeared on fracture surfaces as in Figure 20(b). Other smaller flaws were also found on the fracture surfaces, and radial markings running from them indicated that they influenced cracking in the vicinity.

The molded surfaces of bars conditioned in hot water were found to contain shallow cracks after uniaxial tensile testing (Fig. 21). The surface cracks run perpendicular to the tensile stress direction and are reminiscent of the features formed during uniaxial testing of weathered polycarbonate.[37] Another feature in common with weathered samples tested in tension is the appearance of diamondlike cavities within the pattern of surface cracks [Fig. 21(b)]. Such cavities nucleate plastic fracture in weathered samples.[41]

Failure of temperature-gradient annealed bars in uniaxial tensile tests generally occurred by the growth of a crack nucleated at the surface that was held at the higher temperature during conditioning (Fig. 22), often at a corner site (Fig. 23).

DISCUSSION

The results of the mechanical tests on samples conditioned in water confirm the vulnerability of polycarbonate to this kind of treatment. Such data have been published before by others and the reason for including them here is simply to enable comparison with the rest of the results. The same is true of the molecular weight data, which confirm that significant chain scission takes place as the consequence of hydrolysis when the material is placed in water at elevated temperatures. This causes a reduction in the glass transition temperature, shown by DMTA. A reduction in the temperature of the γ-relaxation peak was obtained with core specimens when the conditioning time was increased, an effect that might be anticipated to accompany a reduction in molecular weight. Curiously, the temperature of the γ-peak increased with conditioning time with
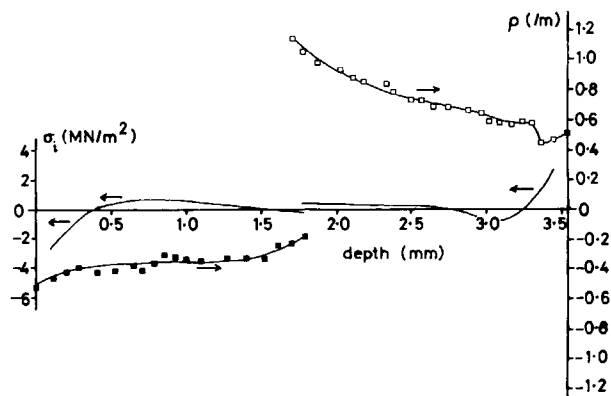

Figure 17   Curvature plots and residual stress analyses for a pair of bars conditioned in a temperature gradient for 1 h with hot/cold face temperatures of 120/35°C.

skin specimens. We speculate, without supporting evidence, that scission occurs preferentially at the most strained bonds and that in the skin, in which considerable molecular orientation already exists, this will allow closer packing of the molecules; this will naturally discourage secondary relaxations, causing the temperature at which they peak to increase. In the core the molecules possess more tightly coiled conformations, and the entanglements restrict rearrangement even when scission occurs, so that increased molecular packing is prevented, whereas the free volume associated with the newly created chain ends permits easier secondary relaxations and the peak temperature falls.

The residual stress levels fell in samples conditioned in hot water. This is partly a stress–relaxation effect, caused simply by the elevated temperature, as shown by the reductions in stress levels obtained with specimens conditioned in an air oven at the same temperatures. In water the changes in residual stress levels were significantly greater, however, as is to be expected, for it is almost inconceivable that the residual stresses remain unmodified by other effects of the water treatment, as listed below:

(i) Scission will provide stress–relaxation additional to that associated with molecular conformation changes, especially if scission is a stress-assisted process and therefore occurs preferentially at the most stressed bonds.

(ii) Swelling of the polymer will occur when water is absorbed and if absorption is nonuniform then residual stresses will result.[31]

(iii) If relaxation is promoted by the presence of water, this will be additional to that which
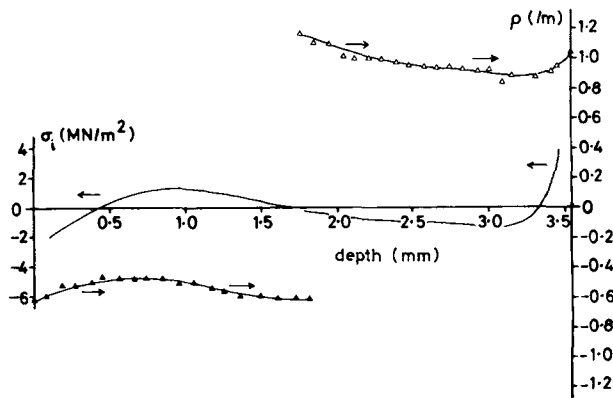
Figure 18 Curvature plots and residual stress analyses for a pair of bars conditioned in a temperature gradient for 15 min with hot/cold face temperatures of 140/60°C.

would occur at the same temperature in the dry state.

(iv) If water absorption alters the modulus of the material, this may alter the residual stress levels.[31]

The amount of water absorbed by bars conditioned in water at 100°C for 7 days was measured using a thermogravimetric analyzer in which the weight loss

in a run made at 4°/min and terminating at 200°C was 0.52%. A bar conditioned the same way showed a weight loss of 0.45% when heated at 100°C for 2 days directly after the water treatment. The weight loss of a similar bar was 0.34% when allowed to stand at 30°C for 2 days. Although we have no data on the depth dependence of water concentration for the various water conditioning treatments, it was observed that when internal flaws formed they were evenly distributed throughout the bar thickness at the end of the immersion period. Hence it might be deduced that water distributes fairly uniformly through the bar thickness, though the exact mechanism of flaw formation and its dependence on residual stress and water concentration are unknown so this cannot be certain. That the flaws appeared to heal preferentially near the surface on removal of the bar from the water bath suggests that redistribution of water occurs. This might be partly due to the residual stresses present. The preferential absorption of water in regions containing tensile stresses is understandable and the consequent swelling would reduce the stress levels. The formation of modest tensile residual stresses near the surface of the bar that was allowed to cool slowly in the water bath at the end of the conditioning treatment at elevated temperature has been attributed
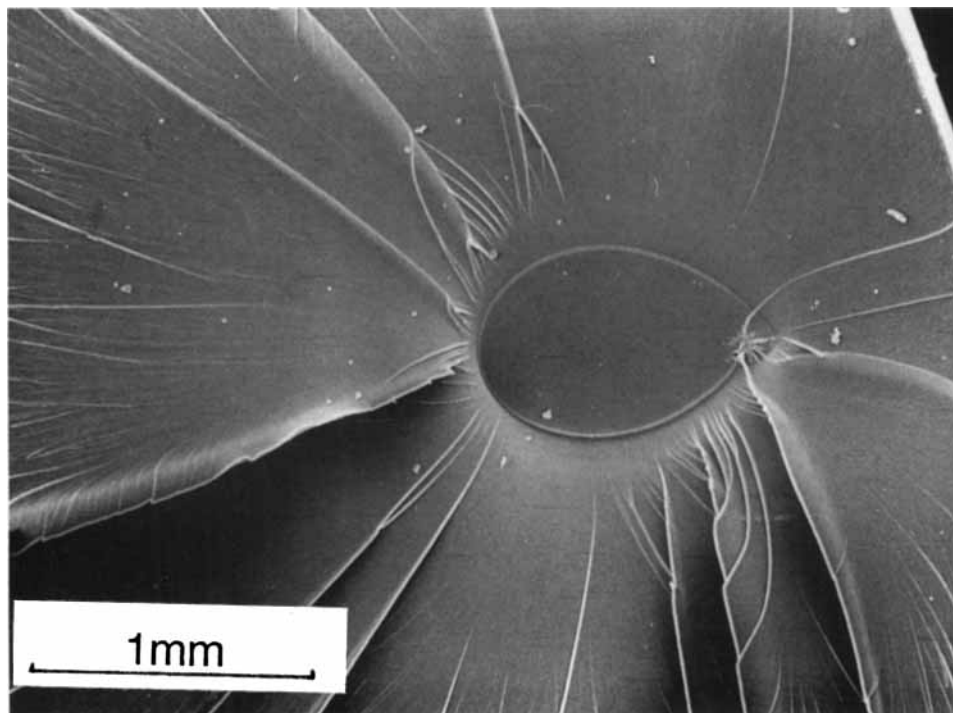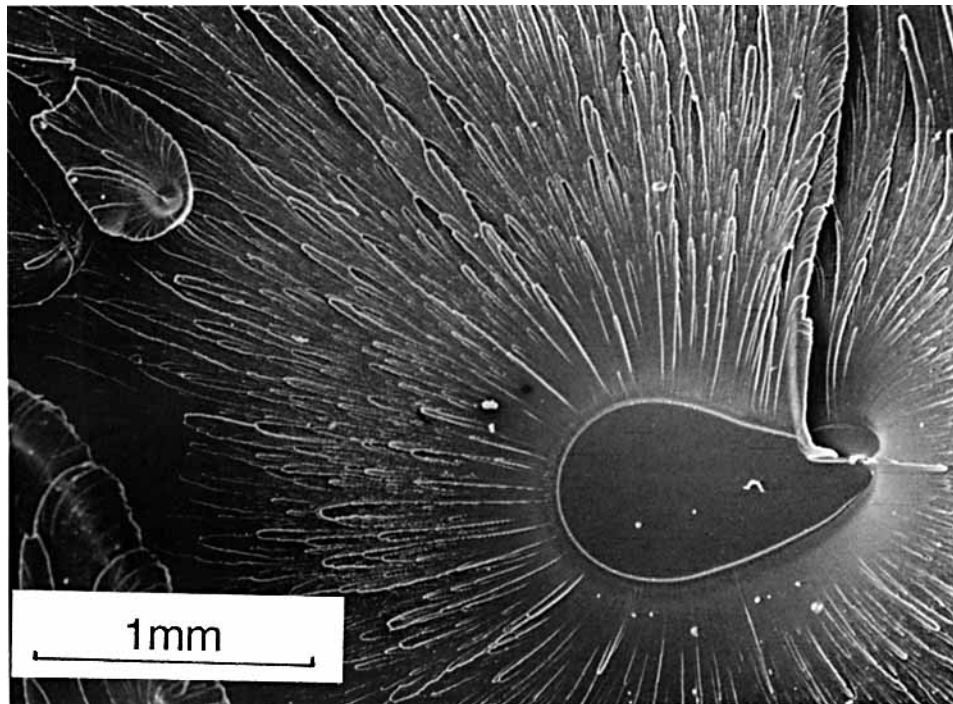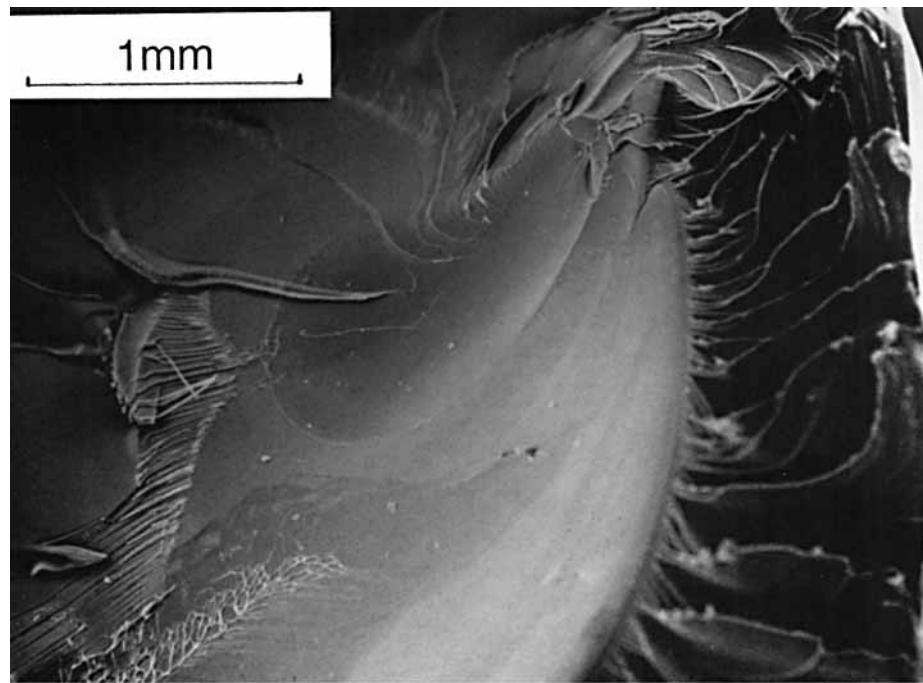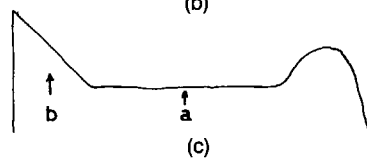

Figure 19 Secondary electron image (SEI) of the fracture surface of a bar tested in uniaxial tension after conditioning in water at 60°C for 9 days.
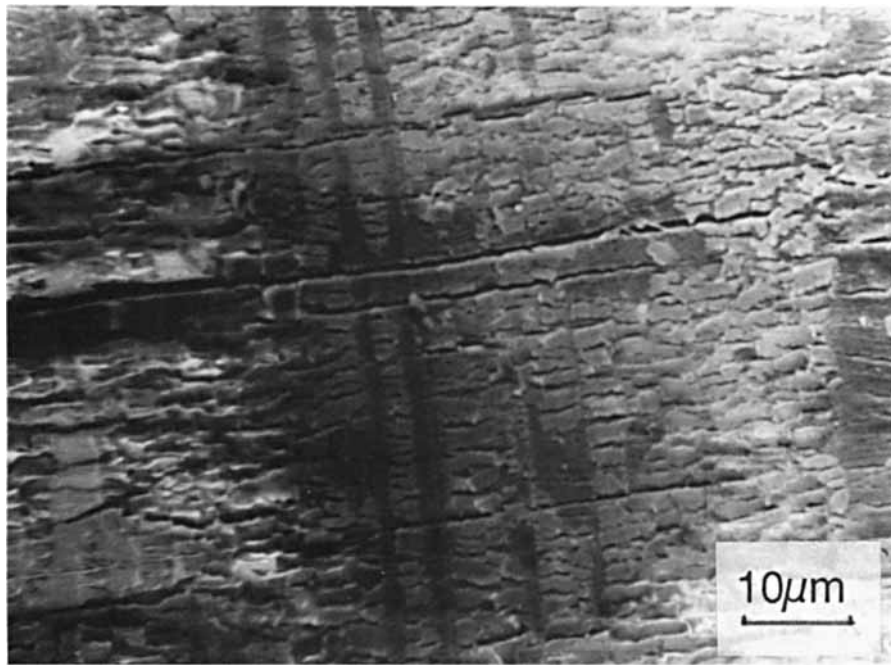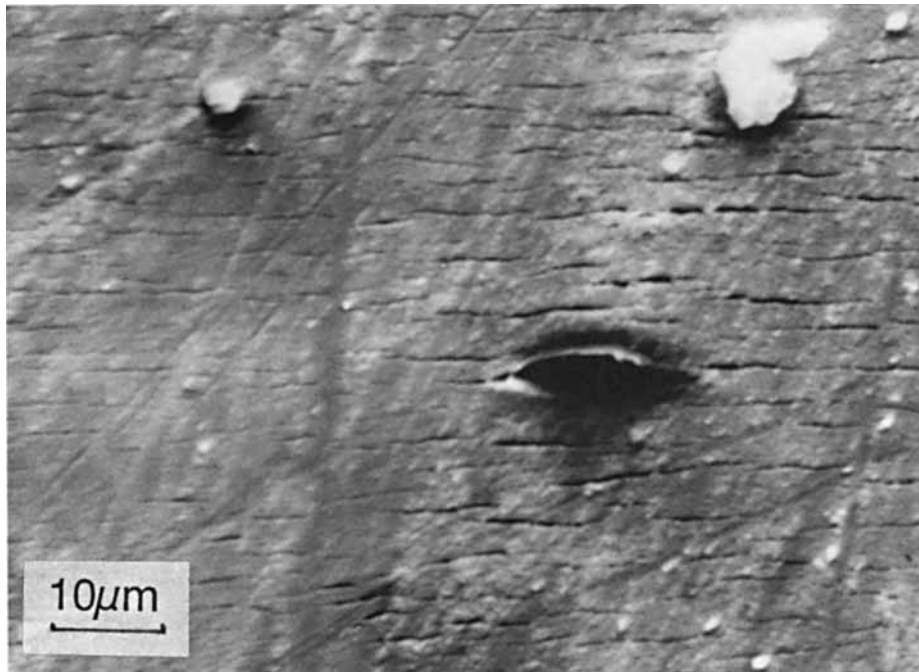
(a)

(b)

(c)

Figure 20   (a,b) Two low magnification SEIs of the fracture surface of a bar tested in uniaxial tension after conditioning in water at 60°C for 90 days; (c) sketch of the cross section of the bar showing the approximate locations of the areas photographed in (a) and (b).

(a)

(b)

Figure 21   SEIs of the molded surface of a bar tested in uniaxial tension after conditioning in water at 80°C for 14 days: (a) pattern of surface cracks; (b) diamondlike flaw.

to a desorption effect. Clearly there must be factors operating additional to those attributable to the residual stresses to cause the stresses to reverse sense.

Bars conditioned in a temperature gradient showed progressive development of the reversal of the sense of the residual stress distribution, with tensile stresses forming at the surface and replacing the compressive stresses normally found there. The mechanism most likely to account for this observation is the one described previously to explain the same phenomenon in polystyrene, polypropylene, and glass-fiber-filled polypropylene.[16] Briefly, this
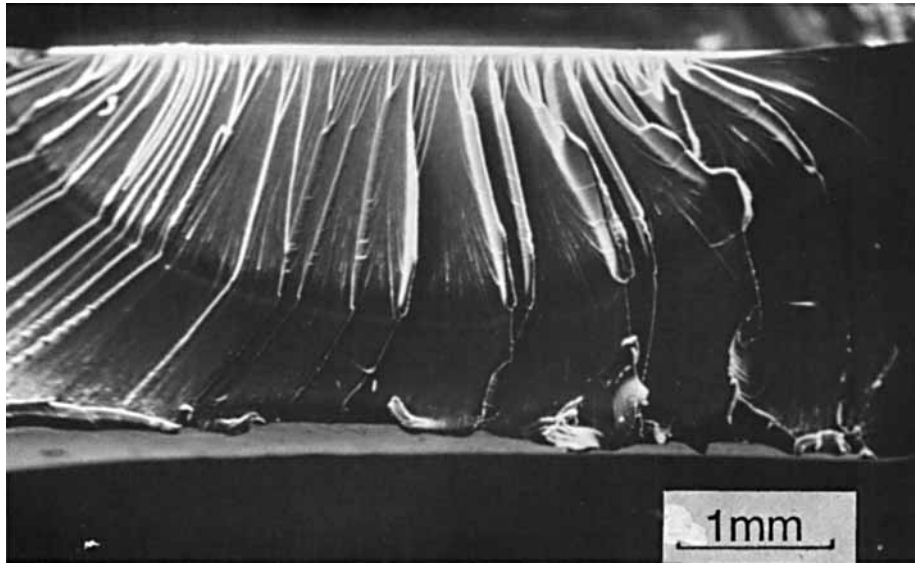
Figure 22   Fracture surface of a bar conditioned for 1 h in a temperature gradient with hot/cold surfaces at 80/25°C.

proposes that during the conditioning treatment relaxation occurs preferentially close to the hotter surface; the bar is prevented from bending to partially relieve the imbalance of forces that set up in the bar as a result. On cooling the bar down to room temperature, the region near the surface that was formerly at the higher temperature will attempt to shrink more than those parts which do not experience such a large fall in temperature and which therefore restrain the shrinkage near the surface,

causing tensile stresses to form. The presence of tensile residual stresses at the surface is generally acknowledged to be detrimental to mechanical properties and this is most likely a contributing factor in the reduction in ductility observed. This is supported by the SEM observations in which it is found that fracture initiated at the surface that had been adjacent to the hot surface during conditioning. It must be recognized that the elevated temperature at the hot side may cause additional changes in the
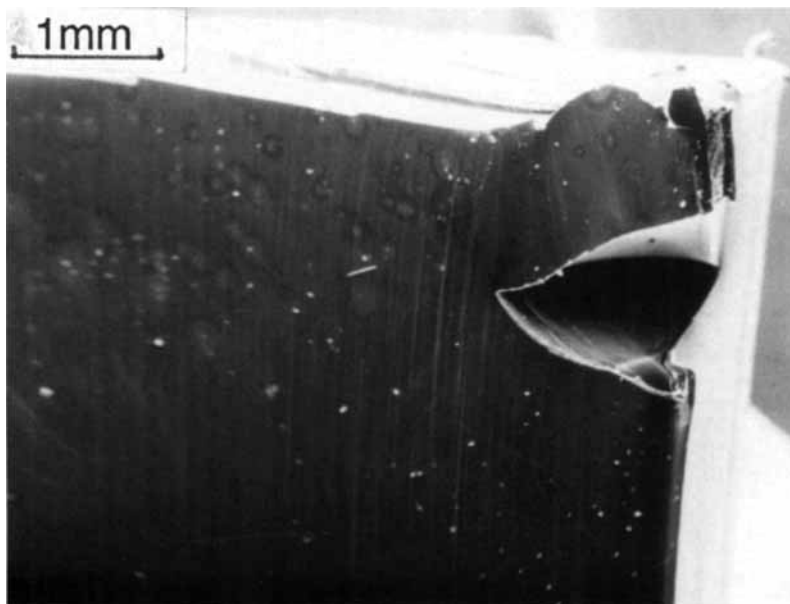

Figure 23   Diamondlike cavity at the corner of a bar conditioned in a temperature gradient with hot/cold surface temperatures of 120/35°C.

material there ("physical aging"[42]). These changes are generally detrimental.

The relationship between these results and the behavior of polycarbonate in service can now be considered. It is evident that serious deterioration occurs if polycarbonate is in contact with hot aqueous solutions. There will be a particularly hazardous condition if the polycarbonate is used as the material for a containment vessel (for example, a pipe) if hot fluid is inside and the outer surface is cold, leading to the formation of residual tensile stresses at the inner surface when the vessel is allowed to cool down.

Even if the service conditions are confined to natural effects, these may still imitate the less extreme of the laboratory conditions used here. Temperatures in excess of 60°C are possible at the surface in direct sunlight in very hot regions even if the polymer does not contain a strong ultraviolet radiation absorber such as carbon black. This can lead to a temperature gradient, though it is unlikely to be as steep as those used here. On the other hand, rainfall may produce sudden cooling at one surface that may give rise to a large temperature gradient for a short period of time. Rainfall can clearly be the source of water which absorbs to produce the effects investigated here.

CONCLUSIONS

Water absorption and temperature-gradient conditioning have both been found to cause serious deterioration in mechanical properties in polycarbonate. Water absorption caused a reduction in the level of residual stresses. A reduction in compressive stress was observed at the surface of moldings and, although this will inevitably reduce the resistance to cracking, this effect is not enough to explain the levels of degradation observed. Instead the explanation lies in the formation of flaws—probably water clusters—within the moldings. This has been observed before by others, but a new observation is that when the moldings are allowed to dry out and desorption occurs, these clusters disappear in the regions near the surface, that is, the parts that were formerly in compression.

Temperature-gradient annealing caused tensile residual stresses to form at the surface held at the hot temperature during conditioning and these were considered large enough to have an influence on failure, though it is likely that there will be other changes in the material that may also contribute to the deterioration. The changes in residual stresses cause a strong asymmetry to develop and distortion occurs.

The measurement of molecular weights by gel permeation chromatography was conducted at RAPRA by S. R. Holding.

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