Effect of injection pressure and crazing on internal stresses in injection-moulded polystyrene

G. J. Sandilands and J. R. White

Department of Metallurgy and Engineering Materials, University of Newcastle-upon-Tyne, Newcastle-upon-Tyne NE1 7RU, UK
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The influence of injection pressure on the internal stress distribution in injection-moulded polystyrene bars has been found to be rather small using the layer removal method. On the other hand, substantial differences in the stress relaxation behaviour have been discovered in specimens moulded at pressures in the range 37–143 MPa. The Kubát and Rigdahl internal stress parameter for all sets of specimens was numerically fairly small, but changed from negative to positive on increasing the injection pressure. The parameter most sensitive to variations in injection pressure appears to be the index in the power law expression used to describe the stress relaxation behaviour. Specimens were surface-crazed by bending around a cylindrical former and tested by the same techniques. A further increase in the magnitude of stress at all positions was indicated by the layer removal procedure while the gradients of the Kubát and Rigdahl plots from stress relaxation data were unchanged.

INTRODUCTION

In an earlier study[1,2] it was shown by the layer removal technique[3,4] that bars of polypropylene and of 'Sioplas' moisture crosslinked high-density polyethylene injection-moulded under fairly standard temperatures and pressures has residual tensile stresses in the interior and compressive stresses near to the surface. This is the distribution normally expected[5–7], but the difficulty sometimes experienced with ejection when using high pressures lends credence to the possibility that this distribution may sometimes be reversed. The use of very high pressures was found by Kubát and Rigdahl (KR) to reverse the sign of the internal stress parameter σ_i, derived by their analysis of stress relaxation data from injection-moulded high-density polyethylene[8]. In another paper[5] KR develop an argument based on a three-layer model in which it appears that the normal type of stress distribution in an injection-moulded bar, (tensile in the interior and compressive near to the surface), should be expected to produce a negative value of σ_i, as indeed they found in many of their studies[9]. The positive σ_i obtained with specimens moulded at high injection pressures might therefore be expected to show a substantially modified residual stress distribution. On the other hand, when stress relaxation tests and KR analyses were performed on the polyprolylene and 'Sioplas' high-density polyethylene specimens investigated in our laboratory it was found that σ_i was positive for bars in the as-moulded condition[1,2]. The purpose of the work described here was to investigate the effect of injection pressure on the internal stress as measured by both the layer removal technique and the KR stress relaxation procedure. One of the grades of material chosen for the study (KLP 35), was selected because it was the grade used by KR in their published work on polystyrene. Moulding conditions were chosen to be fairly similar to those used by them for one series of specimens, (PS–B), in order to attempt to produce a negative value of σ_i from a KR plot; in previous studies in this laboratory all σ_i measurements had been positive, in general disagreement with the KR results. In addition a study of the effect of crazing on internal stress was conducted.

EXPERIMENTAL

Specimen preparation

Specimens were moulded on a Butler–Smith 100–60 reciprocating screw injection-moulding machine using the conditions shown in *Table 1*. Specimens PS–A were moulded into the form of dumb-bell-shaped tensile test bars 190 mm long with a gauge length of 63.5 mm, measuring approximately 12.5 x 3 mm in cross-section, (BS 2782), using a polystyrene supplied by BDH. Specimens PS–B, PS–C and PS–D were moulded from BP KLP 35 polystyrene into straight bars 190 x 12.5 x 3 mm using a different cavity but the same gate and runner system on the same tool as used for the dumb-bell specimens. All specimens were end-gated from one end. Several specimens were moulded at the start

Table 1

Designation	Material	Injection pressure (MPa)	Temperatures Nozzle/Zone 2/ Zone 1* (°C)	Injection time (s)	Cooling time (s)
PS-A	BDH	56	220/230/170	15	25
PS-B	BP KLP 35	37	280/270/220	20	20
PS-C	BP KLP 35	87	230/230/170	10	30
PS-D	BP KLP 35	143	240/230/170	5	25

* Zone 2 of the barrel is the one located next to the nozzle

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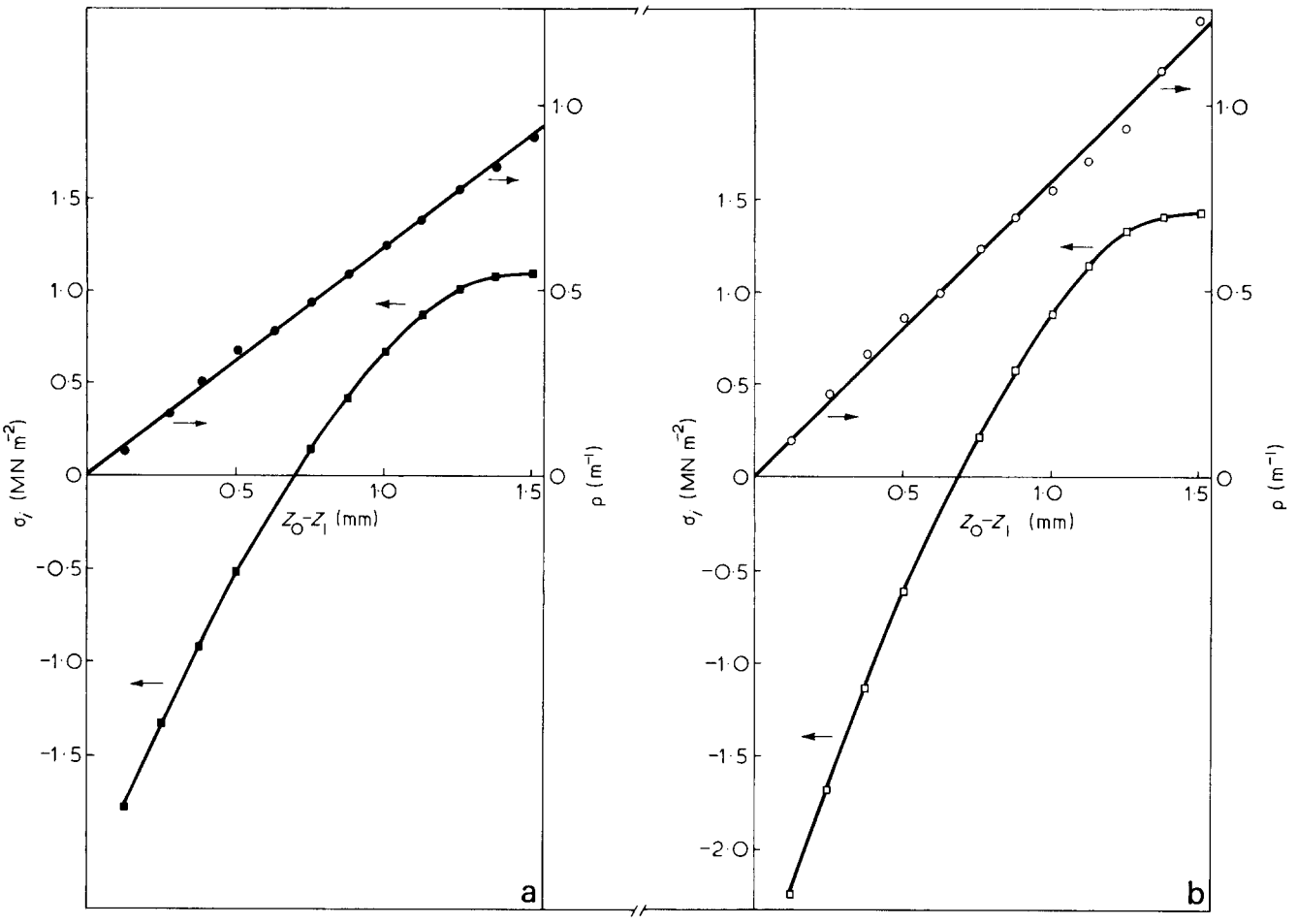

Figure 1 Curvature measurements as a function of material removed and the computed residual stress distribution in one half of bars moulded with an injection pressure of 37 MPa: (a) uncrazed; (b) crazed. The surface of the bar coincides with $z_0 - z_1 = 0$ and the centre coincides with the right hand side of the graphs

of each production run before collecting those to be used for subsequent studies. Each specimen was given a serial number before storing in order that any drift in moulding conditions occurring during the run but escaping the monitoring devices could subsequently be detected. Specimens designated PS–B were produced in two separate runs on different days to check whether any batch-to-batch variation could be detected when using nominally identical conditions.

Crazing

Some specimens were surface-crazed immediately prior to a layer-removal or stress-relaxation experiment by bending around a cylindrical former 135 mm in diameter. It was found that if a specimen was bent in one sense for 15 s and then turned over and bent in the opposite sense for 5 s it later returned to its original shape. The craze distributions on both surfaces were visually identical and this procedure was adopted as standard. Specimens PS–D moulded at the highest pressure used in this study were found always to fracture on applying this deformation, while no specimen from any of the other batches failed.

Layer removal procedure

If a bar which is initially straight has an internal stress distribution, the removal of a thin surface layer creates an imbalance in the forces, and the bar bends to restore equilibrium. If the surface layer was in compression prior to the removal, then the bar will bend such that this surface becomes concave. The relationship between the curvature and the internal stress has been derived by Treuting and Read[3] and used for polymers by So and Broutman[4].

Layers of approximately 0.15 mm were removed from the polystyrene bars using a high-speed milling machine, taking care over the alignment procedure each time[10]. After each removal the curvature was measured using the deflection of a laser beam reflected from mirrors attached to the as-moulded surface in the manner described previously[2,10]. Scanning electron microscope inspection of the milled surfaces showed no evidence of melting or of other damage resulting from this procedure.

Stress relaxation testing

Stress relaxation tests were conducted on rigs described previously[1,2,10] for which specimen enclosures were constructed to provide a constant temperature environment by means of open circuit air heating provided by a fan heater governed by a thyristor-based temperature controller. Preliminary tests established that 40°C gave stress relaxation data with the required characteristics[9] and this temperature was used for all tests reported here.

RESULTS

Layer removal tests

The results are shown in *Figure 1*. *Figure 1a* shows curvature measurements taken on an uncrazed specimen of PS–B. The data points fall very close to a straight line through the

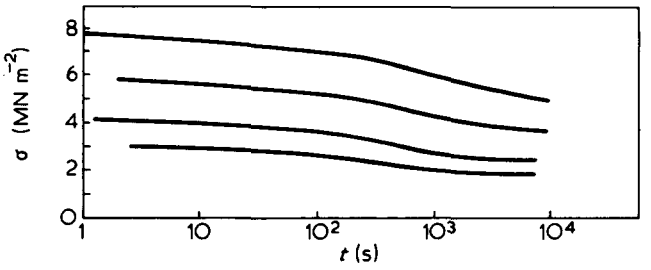

Figure 2 Stress relaxation curves for specimens moulded at 37 MPa

Table 2

Designation	State*	σ_i (MN m^{-2})	n
PS-A	UC	0.7 ± 0.4	10.8 ± 0.6
PS-A	C	−1.3 ± 0.9	10.6 ± 0.4
PS-B	UC	−0.8 ± 0.6	13.8 ± 1.4
PS-B	C	−0.3 ± 0.4	14.1 ± 0.9
PS-C	UC	0.1 ± 0.5	9.6 ± 1.2
PS-C	C	−0.1 ± 0.4	9.5 ± 0.9
PS-D	UC	1.5 ± 0.1	8.2 ± 0.1

* C = crazed, UC = uncrazed

origin, and once having selected this as the best description of the data the residual stress distribution derived from the Treuting and Read formula is necessarily parabolic in shape; this can easily be confirmed by substituting $\rho = a(z_0 - z_1)$ into the relevant formula, where ρ is the curvature, $(z_0 - z_1)$ is the depth of material removed and a is a constant. It is thus confirmed that, for the conditions used to produce these specimens, the residual stress distribution is closely parabolic, subject only to departure attaching to any innaccuracies associated with the straight-line approximation mentioned above, and also with the assumption that the tensile modulus of the bar is the same throughout the thickness; some variation might be expected as a consequence of the variation in molecular orientation through the bar.

The curvature *versus* removal depth data for specimens moulded at the highest pressure, (PS–D), almost superimposed on that shown in *Figure 1a* and the corresponding residual stress distribution was therefore almost indistinguishable also. The maximum tensile stress for the PS–B specimen was approximately 1.09 compared with 1.05 MN m^{-2} for PS–D.

The presence of crazing caused a substantial increase in the magnitude of stress at all positions, as shown in *Figure 1b*. A linear approximation for the curvature *versus* removal depth was again used, although it is to be noted that the departure of data points from the line follows the same pattern as with the uncrazed specimens, lying above the line at points corresponding to small distances from the surface and falling below the line at points near to the centre of the bar. It is possible that it would have been more accurate to have constructed a curved line following more closely the curvature data points, but the consequent modification to the residual stress profile is unlikely to have been very drastic. The maximum tensile stress for the crazed PS–B specimen was 1.43 MN m^{-2}.

Stress relaxation tests

Stress relaxation data from each test were plotted in the form of σ *versus* ln$t$ curves (*Figure 2*), and the gradient at the steepest point measured, $[=(-d\sigma/d\ln t)_{max} = F)$. KR plots, ($F$ *versus* σ_0, the initial stress), were then generated. These plots normally produce a straight line and the extrapolated intersection with the $F = 0$ axis is taken to be σ_i, the internal stress parameter[9]. The slope of the KR plot is equal to $n^{-n/(n-1)}$ where n is the index in the Power Law description of stress relaxation upon which the KR analysis is based[9]:

$$\dot{\sigma} = -EB(\sigma - \sigma_i)^n$$

where $\dot{\sigma}$ is the rate of change of stress, σ is the applied stress, E is the tensile modulus and B and n are material parameters. The values of σ_i and n presented in *Table 2* were estimated from the KR plots, using a linear regression analysis to assess accuracy.

PS–B, uncrazed. The KR plot for this set of specimens is shown in *Figure 3a*. Points obtained from the two different batches of specimens are distinguished and there is no interbatch variation detectable in the presence of considerable scatter. In addition to testing interbatch variation some aging experiments are contained in this Figure, with specimens stored for periods ranging from 1 day to 50 days without noticeable differences appearing. The negative intercept on the σ_0 axis gives a value for σ_i that is numerically much smaller than that obtained by KR using the same grade of material and fairly similar moulding conditions.

PS–B, crazed. Again results from the two batches of specimens show no serious departure from each other (*Figure 3b*), and aging variations were likewise undetected. The intercept with $F = 0$ is very close to $\sigma_0 = 0$. The gradient of the F *versus* σ_0 line is very similar to that obtained with uncrazed specimens, and the n value is consequently very similar also.

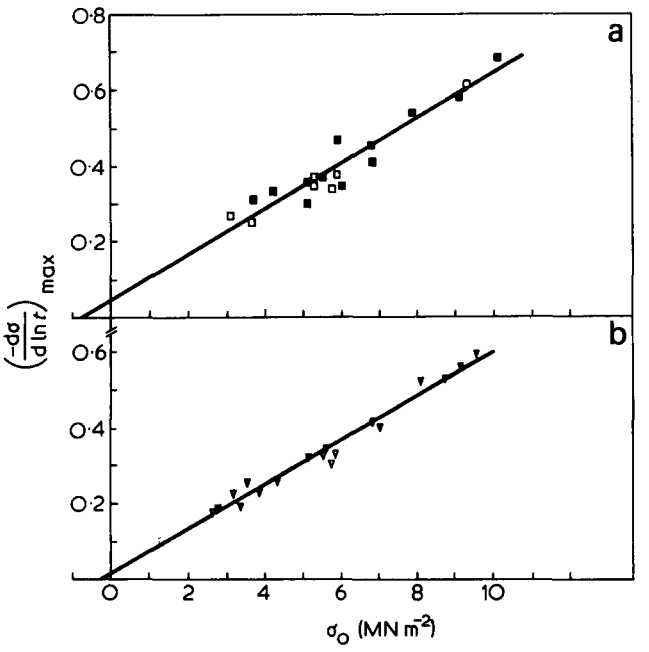

Figure 3 KR plots for polystyrene specimens moulded at 37 MPa. Different symbols signfiy specimens taken from different batches moulded on different days but using identical machine settings: (a) uncrazed; (b) crazed

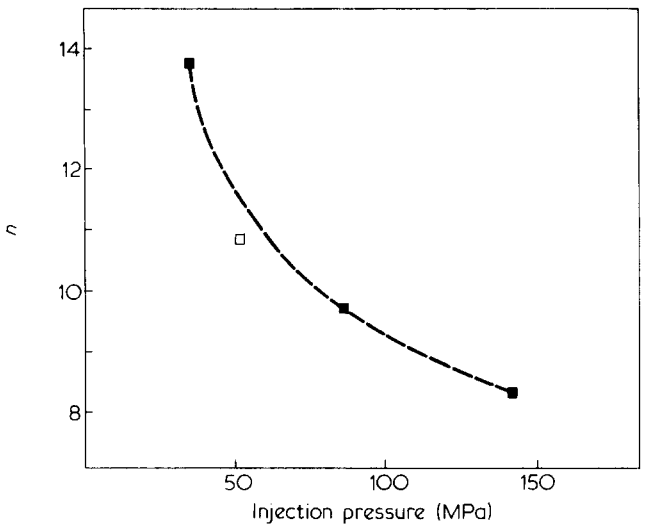

Figure 4 Plot of n as a function of injection pressure. ■, KLP 35; □, BDH

PS–C. Crazed and uncrazed specimens moulded at 87 MPa showed a small and possibly insignificant difference in σ_i, but the shift in the σ_i value compared with that obtained at the lower moulding pressure (PS–B) does seem to be significant and is in the positive sense. The value of n is much lower than that produced by the PS–B specimens, and again it seems unaffected by the introduction of crazing.

PS–D. These specimens fractured on applying the surface crazing procedure. For the uncrazed specimens the positive shift in σ_i is maintained, as is the downward shift in n.

PS–A. These specimens were produced from a different grade of material and using pressure and temperature settings within the range used with KLP 35 (*Table 1*). The value of n again appears to be unchanged by crazing, and it is interesting to note the monotonic dependence of n on moulding pressure, (*Figure 4* and *Table 2*).

Craze formation in uniaxial tension. A limited investigation into craze formation in uniaxial tension was conducted using a tensile testing machine operated under constant crosshead speed conditions. Specimens were strained to failure, which occurred at a stress close to 40 MN m^{-2} for all samples moulded from KLP 35. The appearance of the crazes, formed using a deformation rate of 50 mm min^{-1}, was quite different for each of the three batches (*Figure 5*). In none of the specimens did the crazes reach the surface: this is consistent with the observation that the tensile residual stresses are located in the interior of the bar and that the surface is in compression.

The results are similar to those reported previously by White *et al.*[11]. The PS–B sample (*Figure 5a*) contained smaller crazes and a far smaller craze density than the PS–D sample (*Figure 5c*), with PS–C intermediate in both respects. At a much smaller deformation rate only the specimen moulded at the highest pressure (PS–D) produced any crazing prior to fracture, and then only to a much lesser extent. With a deformation rate of 80 mm min^{-1} the specimen produced at the intermediate moulding pressure of 87 MPa showed crazing similar to that in *Figure 5c* which shows the 143 MPa specimen crazed at 50 mm min^{-1}.

DISCUSSION

The mechanical properties of injection-mouldings are often quite sensitive to moulding pressure. This is illustrated by the refusal of those specimens moulded at the highest pressure to craze when applying the standard conditions under which consistent crazing was obtained with all specimens moulded at lower pressures. Such effects are sometimes attributed to pressure-related differences in internal stress, and the first result, namely that the residual stress is not very sensitive to changes in moulding pressure is therefore unexpected. Kubát and Rigdahl, however, observed that the solidification temperature of a polymer increases with increase in pressure[8], this effect being 32°C/100 MPa with polystyrene[8,12]. We were unable to monitor mould cavity pressure and temperature during production runs, but it seems possible that conditions may have been generated in which the solidification position–time characteristic for the whole bar remained almost unaltered, so creating thermal stresses of similar magnitude and distribution each time.

The results of the analyses of the stress relaxation data show that the power law index, n, is highly sensitive to moulding pressure, and it is quite possible that a correlation with other mechanical properties may be found. A slight tendency for σ_i, as assessed by the KR procedure, to increase with injection pressure, passing from negative to positive, was observed, in agreement with KR results using semicrystalline polymers[8]. The flow properties of the materials in the solidified state may differ either as a consequence of batch-to-batch differences in orientation or in density or in the distribution of these two properties. It is

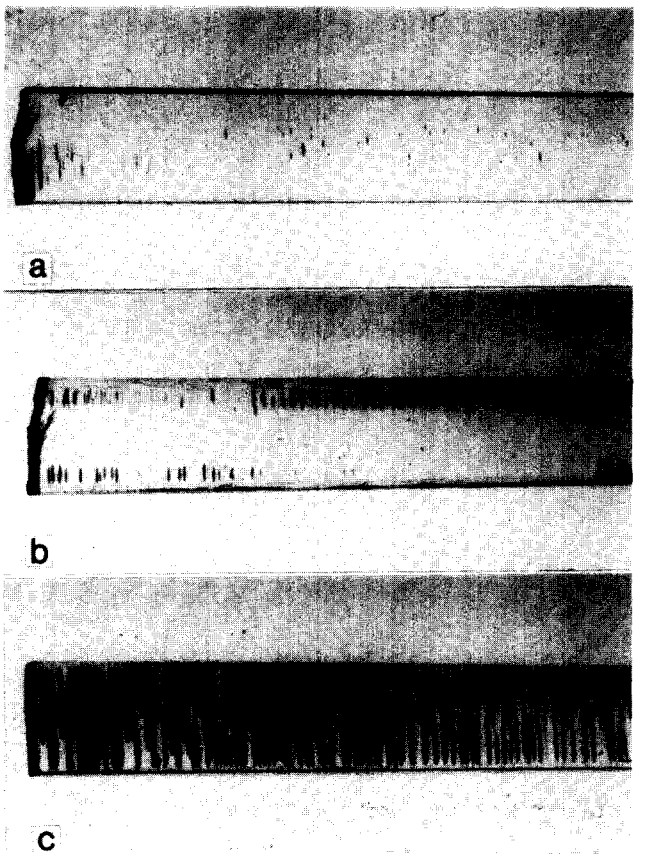

Figure 5 Specimens crazed in uniaxial tension using a deformation rate of 50 mm min^{-1}: (a) PS–B; (b) PS–C; (c) PS–D. The 12.5 mm wide face is shown in each case

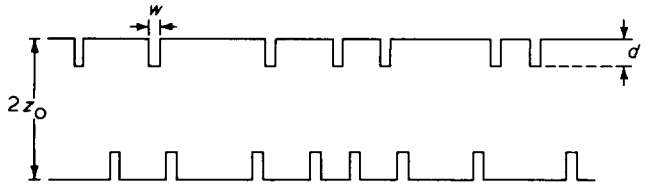

Figure 6 Model of craze shape and distribution used in the estimation of their contribution to the residual stress level

quite clear that an assessment of internal stress cannot be based upon stress relaxation data alone and equally clear that a knowledge of the internal stress distribution (from the layer removal method) does not adequately characterize an injection-moulded bar.

The effect of crazes on the internal stress distribution can fairly easily be accounted for assuming that the elastic stresses arise from the volumetric change that occurs on crazing. Crazes are less dense than the unchanged material, having a void content of typically 50%[13] so that in the unstressed state a crazed layer would expand in the direction perpendicular to the crazes. In the case of a bar containing crazes near to the surfaces but not in the interior, this expansion will be resisted by the uncrazed central region which will therefore go into a state of tension, this force being opposed by compressive stresses in the crazed layer. This is similar in sense, and additional to the pre-existing moulding residual stress distribution in the specimens studied in the present work.

A simple model can be used to estimate the magnitude of this effect. Suppose that the crazes are all of the same depth, d, and width, w, and for simplicity that they are flat-bottomed instead of wedge-shaped, as they have been shown to be in reality[13–15] (*Figure 6*). Consider a portion of bar, l_0 in length, in the uncrazed condition, This length increases to l on crazing. Hence the tensile stress in the interior becomes:

$$\sigma_c = \left(\frac{l - l_0}{l_0}\right) E_c$$

and E_c is the tensile modulus of the material in this region. If there are N crazes/unit length there are Nl_0 altogether and the amount of material accommodated by elastic strain must be:

$$(l - l_0) - \mathrm{N}l_0 w\not{f}$$

where $\not{f}$ is the fraction of craze material that is void. Hence the (compressive) elastic strain in the crazed depth is:

$$\frac{l - l_0 - Nl_0 w\not{f}}{l_0}$$

Therefore, the stress near the surface (tensile modulus E_s) produced by the crazing is:

$$|\sigma_s| = E_s \left(\frac{l - l_0 - Nl_0 w\not{f}}{l_0}\right)$$

If A_c and A_s are the cross-sectional areas of the interior (uncrazed) and the surface (crazed) regions, respectively, then:

$$|\sigma_s| A_s = \sigma_c A_c$$

and on rearranging it is found that:

$$\sigma_s = \frac{E_s E_c A_c N w\not{f}}{A_s E_s - A_c E_c}$$

In a typical example $E_s \sim E_c$ and this becomes:

$$\sigma_s = \frac{E A_c N w\not{f}}{A_s - A_c}$$

In the case examined here $E \sim 2 \times 10^9$ N m^{-2}, $N \sim 40 \times 10^3$ m^{-1}, and $A_c \sim 2A_s$ (i.e. $A_s/A_c \sim d/(z_0 - d)$ where z_0 is half the thickness of the bar). Thus:

$$\sigma_s = -160 \times 10^{12} w\not{f} \quad \mathrm{N\,m^{-2}}$$

We have no direct measurements of w or $\not{f}$ as yet. Both values will be sensitive to stress and the value of w cannot measured by any technique involving sectioning as this would relieve the stress and so change the value. An attempt was made to decorate the crazes by evaporating gold onto them prior to coating with carbon and inspection in the scanning electron microscope, but positive identification was not achieved.

Although the width of crazes is likely to vary from one grade of material to another and be dependent also upon the conditions under which they form, it is instructive to examine the consequence of choosing an average value of $w = 0.2$ μm for dry, unstressed crazes in polystyrene[16]. Taking $\not{f} = 0.5$ the product $w\not{f}$ for such a craze therefore becomes 10^{-7} m. On applying a compressive stress it appears that crazes collapse at least partly, however, and their visibility reduces dramatically. This is to be expected from a consideration of their structure, and it is anticipated that considerable densification may be possible with quite moderate compressive stresses. Indeed marked healing (densification) of crazes has been observed in polycarbonate merely on aging in the absence of stress[17]. In the case of the surface-crazed injection-moulded bars under scrutiny here, there is a pre-existing compressive stress near to the surface quite apart from the additional contribution that attaches to craze formation and the restraint applied by the uncrazed interior. This causes partial healing of the crazes and their visibility was markedly reduced once the bar was straightened and free from external load. Visibility increased as soon as a tensile load was applied during the subsequent stress–relaxation test.

When a compressive load is applied to a craze both w and $\not{f}$ diminish. If the void content $\not{f}$ is 0.5 when unstressed as assumed above then the limit to which a craze of unstressed width, w_0, can reduce is 0.5 w_0, at which point $\not{f}$ becomes zero. It is therefore clear that the change in visibility of the crazes is associated mainly with a change in the density of the crazed material rather that in a change in craze thickness. To explain a change of stress of the order of 0.4 MN m^{-2}, as observed, the product $w\not{f}$ is required to be approximately 2.5×10^{-9} m. Hence, if w reduces to $\sim 10^{-7}$ m in the straightened bar, free from external loading, it is required that $\not{f}$ is of the order of 0.025, a value that does not appear unreasonable. We have attempted to measure the value of $\not{f}$ using the total internal reflection method of Kambour[13,17,18] but have been unable to obtain reliable data probably because the crazes are too tightly

packed and/or because they do not span the whole thickness of the specimens. A value for f of 0.025 would not be inconsistent with our observations.

That the introduction of crazes left the value of the index, n, unchanged indicates either that their relaxation behaviour exactly matches that of the uncrazed material or, as would seem more likely, that their effect is swamped by that of the uncrazed material. It should be remembered that the interior remains unchanged and it is this material that is under the greatest tensile stress during a stress relaxation test. The applied deformation is usually sufficient to reverse the sign of the stress in the surface of the specimen, and its first effect will be to re-extend the collapsed crazes. The stress in the surface will remain much smaller than that in the interior, the relaxation behaviour of which will therefore dominate the total net relaxation behaviour of the bar. Furthermore, it is likely that there will be less opportunities for molecular relaxation parallel to the tensile axis in the stretched craze than in the uncrazed material so that relaxation in the uncrazed material, which probably accounts for more than 99% of the total, will be favoured.

Finally, we have noted that the crazing behaviour of polystyrene bars tested in uniaxial tension is dependent upon moulding conditions. This has been reported by White, Murphy and Haward[11] and Hoare and Hull[19]. In the previous studies[11,19] the specimens were characterized by birefringence measurements and the results taken to be indicative of the state of orientation. Although stress will also cause birefringence we agree with the previous authors that the major contribution to birefringence in specimens of this kind is produced by orientation; we intend to report some of our own birefringence measurements at a later date[20]. The discovery that the magnitude and distribution of residual stress was closely similar in specimens moulded under different conditions and which gave different crazing behaviour shows that some factor other than stress must be responsible. The significant feature may well be orientation, though it is important to realize that, in specimens with different thermomechanical histories, the free volume may be different, causing differences in deformation behaviour as has been found in the comprehensive studies by Struik[21,22]. The deformation-rate dependence of craze morphology noted above might be explained on this basis, though it is clear that much more detailed experimentation is required to identify positively the crucial parameters.

It is also worth noting that in our studies as in those of Hoare and Hull[19] the properties of the injection mouldings were much more sensitive to processing conditions than to the grade of material employed.

CONCLUSIONS

(i) The residual stress distribution in injection-moulded polystyrene bars was found by the layer removal technique to be fairly closely parabolic with tensile stresses in the interior and compressive stresses near to the surface.

(ii) The magnitude of the residual stresses was not very sensitive to changes in injection pressure in the range 37–143 MPa, though barrel temperatures were adjusted to maintain the production of visually satisfactory mouldings and may have provided a compensating effect on the residual stress level.

(iii) The internal stress parameter, σ_i, obtained using the Kubát and Rigdahl procedure has been found to change from negative at the lower end of the injection pressure range to positive at the higher end; the total change was fairly modest.

(iv) A correlation between the power law index, n, and injection pressure was noted, with n falling markedly as injection pressure increased.

(v) The introduction of surface crazes caused a further increment in the tensile residual stress level in the interior of the bar, with a compensating increase in the compressive stress level at the surface. A simple explanation based on the accommodation of the void content of the crazes accounts for the magnitude of the stress increment observed.

(vi) The value of n remained unchanged in the presence of crazes and it seems that the relaxation behaviour of the bars is not much modified by their introduction.

ACKNOWLEDGEMENTS

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