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Measurement of internal stresses in chemically cross-linked high-density polyethylene

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Residual stresses in injection-moulded high-density polyethylene bars have been assessed by the stress-relaxation procedure of Kubát and Rigdahl, and also by the layer removal technique. Stresses were found to be tensile in the interior and compressive near to the surface. The introduction of cross-links through moisture-activated alkoxysilyl groups grafted onto the polyethylene molecules was found to increase the value of the internal stress parameter derived from the relaxation experiments and also to produce higher stress values by the layer removal analysis. Some of the relaxation curves have been analysed in addition by the technique due to Li and the significance of the internal stress parameter, σ_i, obtained by the two different relaxation analyses is discussed.

1. Introduction

The effect of radiation cross-linking on the internal stress level in both low- and high-density polyethylene has been reported by Kubát *et al.* [1]. This work formed part of a broad study of internal stresses in polymers assessed by stress-relaxation techniques [1–5], and showed that the internal stress parameter so derived increased substantially with radiation dose for doses below 40 Mrad [1]. The objectives of the work presented here were to gain further insight into the internal stress-assessment technique introduced by Kubát and Rigdahl [4], and to investigate the effect on moulding stresses of cross-linking in a high-density polyethylene containing molecules onto which are grafted alkoxysilyl groups which form cross-links on exposure to moisture. This material shows excellent resistance to environments which are normally hostile to high-density polyethylene [6], and it was because of the importance of the interaction between moulding stresses and stress corrosion agents that this study was undertaken.

2. Experimental details

2.1. Materials and specimen preparation

Sioplas E651 (Dow-Corning Corp.) is a two-component moulding material with a limited shelf-life. Following advice from the manufacturer the following procedure was employed. The two components, received in granular form, were weighed in the appropriate proportions and mixed in a ribbon blender. The mixture was fed into a 25 mm screw extruder and passed through a 3 mm circular die, then re-granulated. These screw-mixed granules were stored in air-tight bags containing silica gel in a separate compartment until moulding into tensile test-pieces using a reciprocating screw injection-moulding machine later the same day. The nozzle temperature was 150° C and the injection pressure 107 MPa. The test bars were immediately placed inside plastic bags containing silica gel and sealed for storage. All specimens were moulded during the same run, maintaining the same machine settings throughout. At least ten specimens were produced after establishing running conditions

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prior to the collection of specimens to be reserved for the internal stress assessment, since the technique employed requires many identical specimens for its execution. As an added precaution against drift in the moulding conditions, each test bar was inscribed with a serial number on removal from the moulding machine. The test bars were 190 mm long with a gauge length of approximately 63.6 mm, measuring 12.5 mm x 3 mm in cross-section, (B.S. 2782).

One set of specimens were tested in the as-moulded state, being removed from dry storage just prior to commencement of each test. Another set of specimens were immersed in de-ionized water at room temperature for 3 weeks, thought to be sufficient to complete cross-linking action in bars 3 mm thick [6].

2.2. Stress-relaxation tests

The stress-relaxation tests were conducted on specially constructed rigs based upon Pye-Ether UF2 load cells and described more fully elsewhere [7]. The temperature was controlled to $\pm 0.2^{\circ}$ C throughout the duration of each test ($\sim$3 h), but much smaller temperature variations probably attach to the first 20 min of each test during which the important point of inflection on the stress–log time curve occurs; it is the gradient at this point that is used in the derivation of the internal stress parameter.

A variation that was applied to a few tests was to re-load a specimen at the end of a test of normal duration. Relaxation was found to proceed at a very slow rate by the time 3 h had elapsed and it was at this time that the specimen was re-loaded to the initial stress of the first loading, and relaxation was allowed to continue for a further 3 h.

2.3. Layer removal

The residual stress distribution in an as-moulded bar is symmetrical [3, 7], but if a layer of material is removed the stress on the opposite side in the "balancing" layer that remains causes the bar to bend. By measuring the curvature so produced by a succession of layer removal steps, a stress distribution profile can be derived [8, 9]. The analysis presented in [8] assumes a constant value for the tensile modulus, but this is unlikely to obtain in the case of an injection-moulded polymer bar. The advantages of the method in revealing the distribution of stress and in producing estimates of the actual magnitude of stress at a particular location are retained even if the results are only approximate in the case of test-pieces with a depth-dependent modulus.

High-speed milling was used for layer removal [7], after which two small mirrors were attached to the bar 60 mm apart. The bar was mounted approximately 1 m in front of a laser which was pivoted at a point on its axis and the positions of the reflections from both mirrors were recorded [7]. It is a simple task to compute the curvature from the measurements taken.

3. Results

3.1. Stress-relaxation technique

Typical stress-relaxation curves are shown in Fig. 1. These were used to assess the internal stress by two techniques, one according to Kubát and Rigdahl (KR) [4], and the other according to Li [10]. Both are based on a power law expression for the rate of change of stress, $\dot{\sigma}$:

$$\dot{\sigma} = -EB(\sigma - \sigma_i)^n \qquad (1)$$

where E is the modulus of elasticity, σ is the

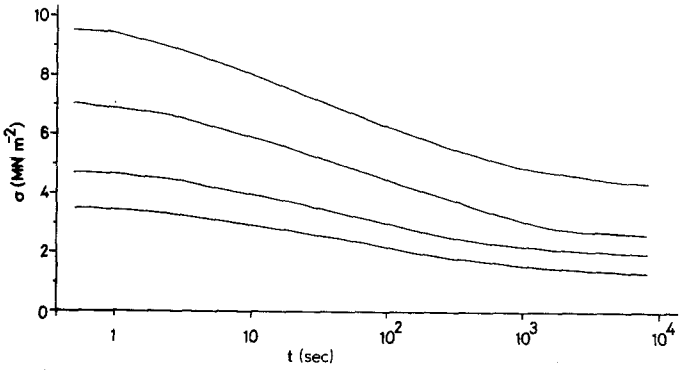

Figure 1 Stress–relaxation curves for moisture cross-linked Sioplas E651 specimens loaded to initial stresses of 3.6, 4.9, 7.2 and 9.7 MN m^{-2}, respectively.

applied stress, $(\sigma - \sigma_i)$ is the effective stress, and B and n are constants. σ_i is known as the internal stress parameter [4].

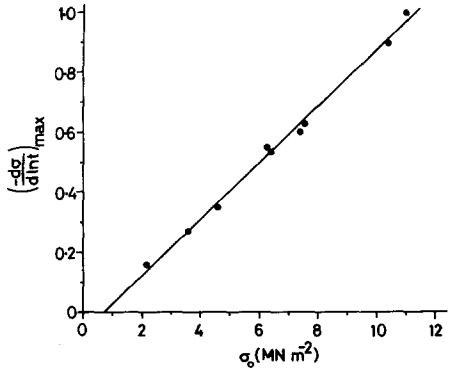

Figure 2 KR plot for injection-moulded Sioplas E651 specimens stored in a dry atmosphere.

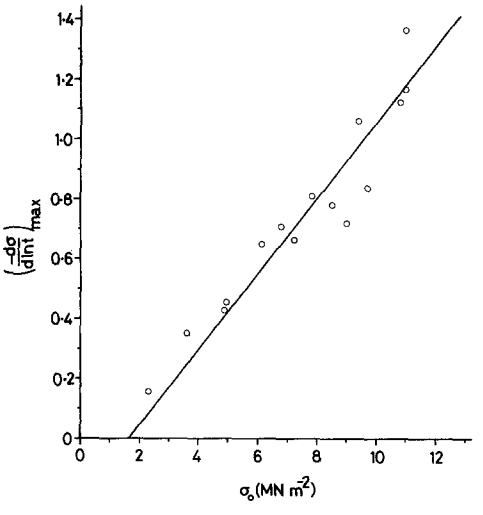

Figure 3 KR plot for injection-moulded Sioplas E651 specimens, cross-linked by submerging in water for 2 to 3 weeks.

3.1.1. KR analysis

In the KR analysis, the steepest slope of each σ versus log t curve from a series of nominally identical specimens tested at different elongations is plotted against the initial stress, σ_0. A straight line is predicted with intercept σ_i on the stress axis. Straight-line graphs were obtained for both the as-moulded and the water-treated specimens (Figs. 2 and 3). The values of n were computed from the slopes of these KR plots, $(= n^{-n/n-1})$ [4], and are shown in Table I, in which the σ_i, values are also presented.

TABLE I

	n	σ_i (MN m^{-2})
Sioplas E651, dry-stored	5.4 ± 0.8	0.7 ± 0.3
Sioplas E651, moisture cross-linked	7.8 ± 0.4	1.7 ± 0.6

3.1.2. Li analysis

In the Li analysis [10], a single relaxation curve (and hence only one specimen) is all that is required. The gradient is measured at several points on the σ versus log t curve and plotted against the corresponding value of stress, σ. A straight line is expected and the internal stress parameter is again given by the intercept on the stress axis. With this analysis a deformation-dependent term is also included in the value of σ_i obtained, so that a different result is expected for each relaxation curve [11]. The difficulty with this method is that the relaxation curves of many polymers are very flat and the changes in slope cannot be measured with sufficient accuracy. The relaxation behaviour of the material used here proved to be reasonably suited to this kind of analysis, however, and an example is shown in Fig. 4.

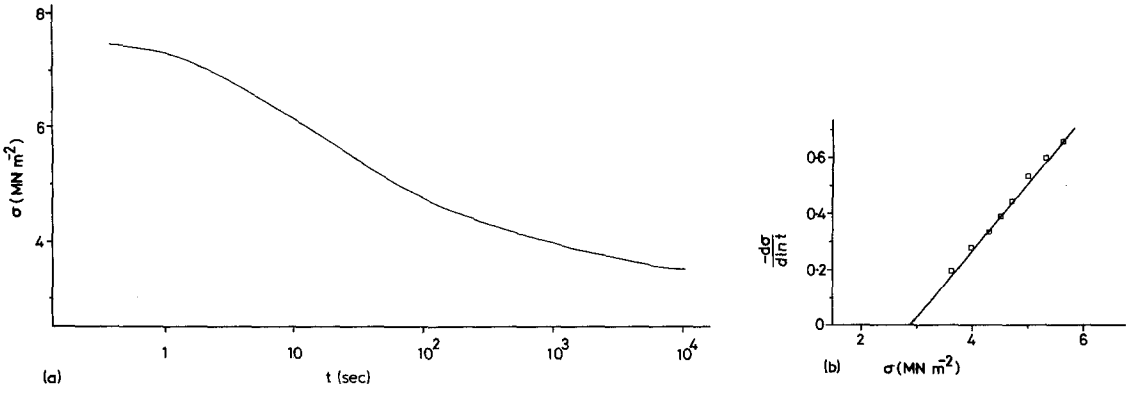

Figure 4 (a) Stress-relaxation curve for a Sioplas E651 specimen stored in a dry atmosphere and tested with an initial stress of 7.5 MN m^{-2}. (b) Li plot derived from this curve.

Since the internal stress parameter derived from a Li analysis is deformation-dependent, the σ_i measurements obtained from a series of tests were plotted against the corresponding initial stress values, σ_0 (Fig. 5). Although the relationship is unlikely to be linear the results fall sufficiently close to a straight line to give a rough extrapolation to $\sigma_0 = 0$. The intercept with the σ_i axis at this point is taken to be equal to the residual stress contribution to σ_i (see later).

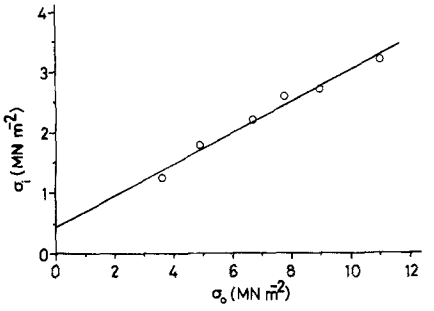

Figure 5 Plot of σ_i values obtained from Li analyses on several moisture cross-linked Sioplas E651 specimens for a series of initial stresses, σ_0.

TABLE II Li analysis internal stress parameter measurements for moisture cross-linked Sioplas E651 for a series of initial stresses, σ_0. $\sigma_{i,1}$ is the result for the first loading experiment and $\sigma_{i,2}$ that obtained after re-loading to σ_0

σ_0 (MN m^{-2})	$\sigma_{i,1}$ (MN m^{-2})	$\sigma_{i,2}$ (MN m^{-2})	$2\sigma_{i,1} - \sigma_{i,2}$ (MN m^{-2})
6.7	2.2	2.9	1.4
7.8	2.6	3.8	1.4
8.5	2.7	3.3$_5$	2.0
11.0	3.2	4.0	2.4

Fig. 6 shows the results of Li analyses on re-loaded specimens. Note that the internal stress parameter is larger for the second loading in each case. Results from these experiments have been collected together in Table II in which the internal stress parameter from the first test has been recorded as $\sigma_{i,1}$ and that from the reloading

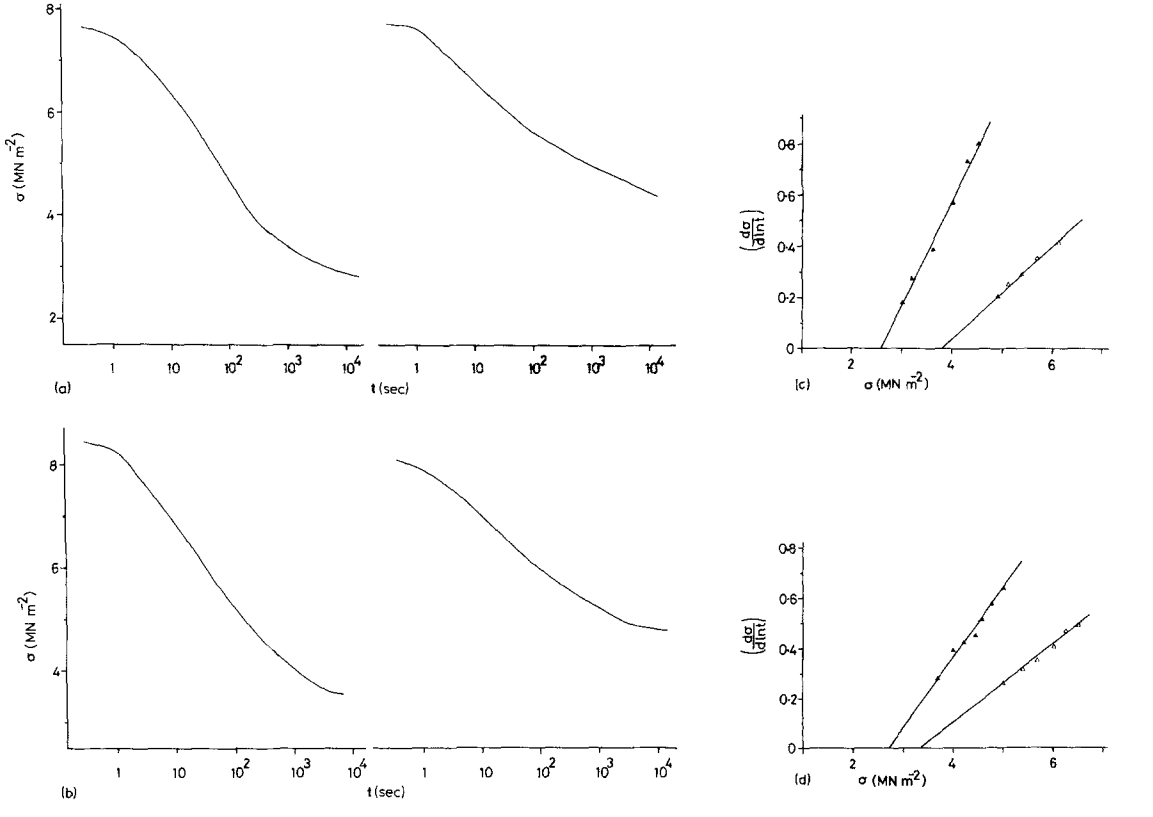

Figure 6 (a) Stress–relaxation curves for a moisture cross-linked specimen loaded initially to a stress of 8.5 MN m^{-2}, and re-loaded to 8.3 MN m^{-2} after approximately 3 h. The time in the second graph is measured from the time of re-loading. (b) Stress–relaxation curves for a moisture cross-linked specimen loaded initially to a stress of 7.8 MN m^{-2}, and re-loaded to 7.8 MN m^{-2} after approximately 3 h. (c) Li plots for the curves shown in (a): closed symbols, first loading; open symbols, second loading. (d) Li plots for the curves shown in (b): closed symbols, first loading; open symbols, second loading.

experiment as $\sigma_{i,2}$. If the residual internal stress is written as $\sigma_{i,r}$ and the contribution from the deformation term is $\sigma_{i,d}$ then the internal stress measured by the Li analysis is [11]

$$\sigma_i = \sigma_{i,r} + \sigma_{i,d}.$$

For a first loading experiment this becomes

$$\sigma_{i,1} = \sigma_{i,r} + \sigma_{i,d,1}.$$

$\sigma_{i,r}$ is deformation-independent and should be the same for all specimens in a batch of idential specimens. If we now make the assumption that a second loading adds a further increment to $\sigma_{i,d}$ equal to that of the first, (clearly a crude approximation, the accuracy of which is not known), then for the second loading:

$$\sigma_{i,2} = \sigma_{i,r} + \sigma_{i,d,2} = \sigma_{i,r} + 2\sigma_{i,d,1}$$

$$\therefore 2\sigma_{i,1} - \sigma_{i,2} = \sigma_{i,r}.$$

Values of $(2\sigma_{i,1} - \sigma_{i,2})$ have been computed and are shown in Table II. These values should be compared with the result of $1.7\,MN\,m^{-2}$ obtained by the KR analysis.

A similar argument is used in interpreting Fig. 5; for a σ_0 value of zero the $\sigma_{i,d}$ contribution must disappear and the extrapolation to $\sigma_0 = 0$ should, therefore, produce a value of $\sigma_i = \sigma_{i,r}$.

3.2. Layer removal technique

In Fig. 7 are shown curvature measurements as a function of z_1, the distance from the centre of the bar (thickness $2z_0$), to the surface after removal of material (the amount removed being of thickness $z_0 - z_1$). These graphs have been used to derive the values for terms found in the formula presented by Treuting and Read, suitably modified for the case of bending about one axis only [8], and hence to compute the internal stress profiles shown in Fig. 8.

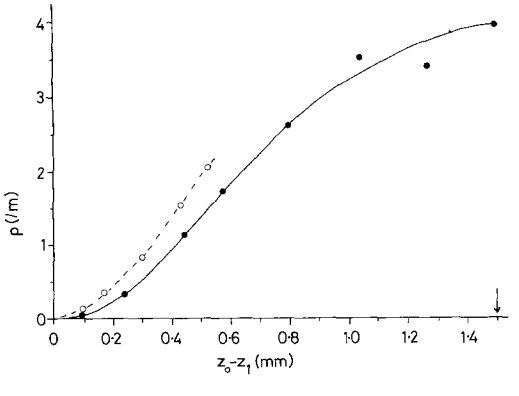

Figure 7 Measurements of curvature, ρ, of specimens from which layers were removed to depths z_1, measured from the centre of the bar. The position of the as-moulded boundary is indicated by the arrow. Solid line, as-moulded, dry-stored specimen; broken line, moisture cross-linked specimen.

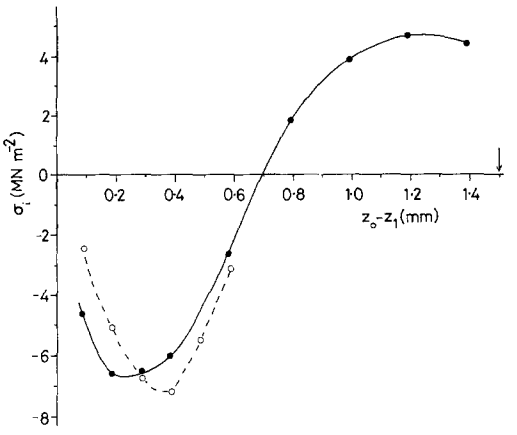

Figure 8 Internal stress values computed from Fig. 7. Solid line, as-moulded, dry-stored specimen; broken line, moisture cross-linked specimen. Tensile stresses are plotted as positive values.

4. Discussion

The internal stress parameter derived from the KR plot for the as-moulded bars is clearly positive. That a non-zero value can be obtained at all might at first sight seem surprising, but this can be explained by assuming that there are two or more regions within the specimen that have different relaxation behaviour characterized by different values of n [3]. Kubát and Rigdahl took the view that in an injection-moulded bar with the familiar three-layer morphology [12-16] the values of n in the oriented layer beneath the surface should be greater than that attaching to the slowly cooled core that is structurally much more nearly isotropic. Most of their experiments on injection-moulded bars produced negative values for the internal stress parameter [4] and according to their three-layer computations this corresponds to tensile stress in the interior of the specimen, opposed by compressive stresses near to the surface [3]. Such a stress system is easily accounted for. When the polymer enters the cold-mould cavity the material adjacent to the cavity wall cools rapidly and sets. The molecules in this region may be frozen into conformations determined

partly by the elongation and shear flow characteristics of the material during the mould-filling operation. The material in the interior of the moulding will cool much more slowly because of the poor thermal conductivity of the polymer both in the molten and in the solid state. Thermal shrinkage of the interior then takes place and if no more material can enter the mould to counteract this effect a state of hydrostatic tensile stress will be generated. This is restrained by the skin which must now go into compression. In addition, there will be a tendency for molecules which were oriented parallel to the flow direction during mould-filling to relax back to more coiled conformations on slow cooling, and in the absence of the restraining influence of the skin this would result in macroscopic shape changes analogous to the well-known die-swell effect in extrusion. In a bar-shaped moulding this will generate an axial tensile stress in the interior.

In another paper [5], Kubát and Rigdahl have presented a study of the influence of injection-moulding pressure on internal stress. They used a specially modified injection-moulding machine and showed that positive values for σ_i were obtained when using pressures substantially higher than those available with conventional machines. In the current work the pressure used was well within the capability of standard injection-moulding equipment, but higher than that used by Kubát and Rigdahl in their preliminary studies [4]. It is however, well known that the use of pressures at the higher end of the range available on standard machines can often cause difficulties with ejection of mouldings and this is attributed to over-packing of the mould. This would seem to suggest an internal compressive hydrostatic pressure, and corroborative evidence for the existence of such a stress distribution has been presented by Koda [17]. An important factor in determining whether this situation can arise is the time during the moulding cycle at which the gate freezes. If the gate is small and tends to freeze-off early-on then it is impossible to make up for any subsequent shrinkage in the material in the moulding by adding more material so that only the elastic compression of the melt at the time of freeze-off will remain to counteract the thermal shrinkage and a state of hydrostatic tension is soon established.

On the other hand, if the gate is of generous dimensions and admits a path to the molten polymer in the centre of the moulding until an advanced stage in the solidification process during which the most important contribution to shrinkage will take place in most crystallizing polymers, then material will continue to be packed into the mould. The mould used in the work described here had a cavity gated at one end through a large gate. Polypropylene specimens produced with the same tool and using normal pressures were also found to be characterized by a positive σ_i value [7].

The results of the layer removal experiments show quite clearly that the interior of the moulded bars were in tension and that compressive stresses resided near to the surface of the specimens. This appears to contradict the interpretation deduced by Kubát and Rigdahl for the meaning of a positive σ_i value for injection-mouldings [3]. Similar results have been obtained with injection-moulded polypropylene in which the question of cross-linking does not arise [7], and an investigation into the significance of these observations is currently in progress. It must again be emphasized that the layer removal stress calculations are only approximate, based as they are on the assumption that the tensile modulus remains unchanged throughout the test-piece. It is most unlikely to do so in an injection-moulding with a skin-core morphology, and the fact that the areas on the stress–position graphs attaching to the tensile and the compressive portions respectively are not equal as they should be for a self-stressed body probably derives from this.

A significantly higher (positive) value for σ_i was obtained with the moisture cross-linked material. This is consistent with the results obtained by Kubát *et al.* [1], although there are several differences between the work they described and that presented here. They employed compression-moulded specimens and, in addition, examined cold-drawn samples, while the specimens used in the present work were injection-moulded. The methods of cross-linking were different; Kubát *et al.* used irradiation, while cross-linking of the Sioplas material used here is a chemical process. Finally, Kubát *et al.* used the Li technique to assess internal stress and so may include a deformation-related term, while the work described here includes an analysis by their own method which should produce a value related only to the residual stress level. Since the magnitude of the internal stress parameter deduced from a KR plot is dependent upon the depth-dependence of the flow properties of the material (as represented by the

index n), the increase in σ_i cannot automatically be taken to signify higher stress levels within the moulding. The same effect could be produced by widening the gap in n values displayed by the different morphological constituents while retaining the same stress distribution. Therefore, the exact effect of the cross-linking remains to be established.

The layer removal experiments reproduced the sense of the stress distribution obtained by the same technique with as-moulded specimens, showing once again that the interior of the moulding was in tension and that the compressive stresses were located near to the surface. The cross-linked specimen displayed much more marked curvature than the as-moulded bar and the stress levels derived from these measurements are consequently greater in magnitude for the cross-linked bar. This seems to indicate that the change in σ_i value on cross-linking is indeed caused by an increase in the stress levels rather than a change in the flow properties of the constituents, though provides no clarification of its exact significance. The load–deformation curves for as-moulded and for cross-linked specimens, respectively are sufficiently similar to indicate that changes in modulus, unless very localized, are unlikely to be sufficient to account for the differences in the stress distributions as determined by the layer removal method.

The results of the Li analyses are consistent with the above observations. Both the extrapolation procedure and the double loading experiments provided evidence in support of the fact that this method produces values for σ_i that are the sum of a contribution due to residual ("moulding") stresses plus a deformation-related term. The magnitude of $\sigma_{i,r}$ obtained by extrapolation was significantly lower than that produced by the KR analysis, however, and further study of the exact meaning of these parameters is still required.

The increase in internal stress promoted by cross-linking might be expected to improve the resistance to environmental failure since the stress is compressive near to the surface, and may supply an important contribution to the good environmental crack resistance property of Sioplas polyethylene.

Acknowledgements

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