

Plastic fracture in poly(vinyl chloride)

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The strain fields around diamond-shaped cavities in cold-drawn rigid PVC have been determined by the application of fine grids to the specimen surface. An element of material adjacent to the diamond tip deforms predominantly in simple shear with a direction of strain parallel to the draw direction. Each element attains a maximum shear strain before the next element begins to shear. This process, possibly analogous to neck propagation in tensile tests, produces the characteristic diamond shape. Simple extension and simple shear tests on cold-drawn PVC confirm that under the stress system around a cavity, simple shear in the draw direction is a favourable mode of deformation.

1. Introduction

Recent studies [1-3] have shown that post-yield fracture in several glassy polymers is initiated by cavities which grow in the drawn material. The cavities grow from defects such as scratches or crazes on the surface of the specimens. At the surface the cavities generally have four roughly equal straight sides which form a rhombus whose long and short diagonals lie, respectively, perpendicular and parallel to the draw direction. Spurr and Niegish [4] were the first to note the "diamond-like" profile of these cavities, which subsequently have been labelled simply "diamonds". In the earlier stages of growth the interior of the diamonds has a well-defined edge which runs in a curved path from one end of the long diagonal to the other, and corresponds to the crack front in general fracture mechanics (Fig. 1a). However, in thin sheet the diamond can penetrate the thickness of the specimen and become a rhomboidal prism (Fig. 1b). In specimens with a rectangular cross-section, diamonds can grow from defects on the corners. A "corner diamond" has straight sides on adjacent faces and the crack front runs through 90° rather than 180° (Fig. 1c). Again, in thin specimens corner diamonds can penetrate the thickness and in this case they are called "edge diamonds" (Fig. 1d).

In a typical tensile test of a strain-softening glassy polymer extended at a constant rate, a neck is formed which propagates down the specimen under a constant drawing load. As the neck

propagates diamonds can be initiated in the drawn material. At low strain-rates ($<10^{-4} \text{ sec}^{-1}$) the diamonds grow in a slow, stable manner until one reaches a critical size and initiates a rapid failure, which can occur before or after the neck has propagated along the whole length of the specimen. This type of plastic fracture has been observed at room temperature in both rigid [1, 3] and plasticized [5] PVC, polycarbonate [5], cellulose acetate [5] and nylon [6]. At higher temperatures

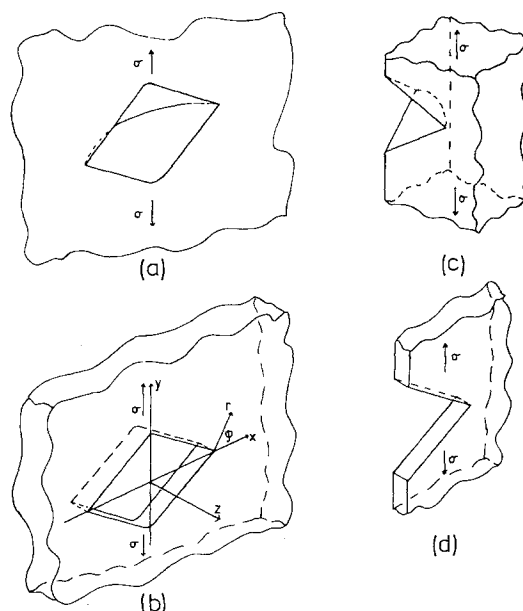


Figure 1 A schematic representation of the four types of diamond cavities.

PMMA [2], poly(ether sulphone) [2] and polystyrene [7] also fracture via diamond formation which appears to be the most common failure mode of glassy polymers at high extensions. In this study we have used rigid PVC as the material in which to study diamond formation, but it is reasonable to assume that the conclusions drawn apply to other polymers which display diamonds.

Since diamonds are embedded in a highly anisotropic medium and prior to the final failure can have dimensions comparable to the specimen width, the commonly used theoretical models can only be applied in a very general way. Consequently, any quantitative investigation must be of an empirical nature. While it is difficult to determine experimentally the stress field around a diamond, the strains can be obtained by direct observation. In this study the strain fields were derived by applying fine grids to the surface of the specimens and photographically recording the deformation as the diamonds propagated. However, the strain fields cannot be fully interpreted without a thorough knowledge of the response of the drawn material to stresses which are not in the draw direction. Since a complex stress system exists near a diamond, it would be advantageous to investigate the behaviour of the drawn PVC under at least biaxial stress. In order to obtain this information, both simple extension and simple shear experiments were performed on specimens cut from cold-drawn PVC at various angles to the draw direction.

2. Experimental details

PVC sheet was formed from a commercial mass polymer, trade name Breon, supplied by B.P. Chemicals. The polymer was obtained as a fine powder with an average particle size around $100\ \mu\text{m}$. The weight and number average molecular weights were determined by G.P.C. to be 80 500 and 30 000, respectively. To reduce degradation, the PVC powder was mixed with 3% by weight of an organo-tin stabilizer, trade name Irgastab, in a Papenmaier high-speed mixer. Sheet material was then formed in a conventional heated press using a temperature of 200°C and a pressure of 9 MPa for 90 sec. After that period the press was cooled rapidly using circulating water. The former employed produced sheets $150\text{mm} \times 150\text{mm} \sim 1.1\text{mm}$ thick. It is known from recent studies [8] that sheet formed in this manner has very little molecular orientation and the small amount of crystallinity usually found in commercial PVC has

been removed. Also, the structure of the resin particles which can persist in PVC fabrications has been removed with the crystallinity. The PVC sheet so formed is, therefore, effectively amorphous, isotropic, and apart from the stabilizer, free from additives. Conventional dumb-bell specimens complying with the former British Standard test BS2782 method 301E [9] were cut from the sheet. These specimens had a narrow section 51.0mm long and 12.7mm wide. Each specimen was polished with alumina papers and diamond paste to produce a surface finish comparable with that of commercial sheet.

In order to observe the strain fields around the growing diamond, a fine copper mesh was placed on the surface of each specimen and 80–20 Gold–Palladium alloy was evaporated on to the assembly. A rectangular area ($\sim 40\text{mm} \times 12.5\text{mm}$) of the surface was thereby covered by squares of deposited metal. This method has been successfully employed in fracture studies of rubbers and uniformly extending polymers by Andrews and Fukahori [10]. The size of the squares was equivalent to the apertures in 400 mesh electron microscope grids ($\sim 64\ \mu\text{m} \times 64\ \mu\text{m}$). Initially, diamonds were examined as they arose by chance in the area covered by the grid, but later it was found prudent to initiate diamonds in the centre of the specimen by touching the surface with a scalpel point which usually produced a sharp defect covering two or three horizontal grid squares. The specimens were then extended on an Instron testing machine at 23°C and 50% r.h. It was found that at cross-head speeds greater than 0.2cm min^{-1} any diamond which formed grew rapidly and initiated a fast fracture. A possible explanation is that the temperature rise in the propagating neck is significant ($>10^\circ\text{C}$) and thermal softening enhances diamond growth. At lower cross-head speeds, the diamonds grew in a slow, stable fashion and could be observed more easily. Generally, the tests were performed with cross-head speeds in the range 0.01 to 0.1cm min^{-1} . During each test the propagation of the diamonds was recorded photographically by means of a travelling microscope fitted with a 35 mm camera.

The characterization of the mechanical properties of the drawn PVC required large plastically deformed areas from which to take specimens. Consequently, the width of the tensile specimens was extended to 60 mm. These specimens were then extended at a slow strain-rate

($\sim 10^{-5} \text{ sec}^{-1}$) until the neck had travelled the whole length of the narrow section or diamond fracture occurred. Away from the propagating neck the thickness of the drawn area was fairly uniform and generally in the range 0.65 to 0.75 mm. The draw ratio of the two types of specimens described above did not differ significantly and was close to 2.4 in all experiments. Tensile specimens were cut from the drawn material at various angles to the draw direction. These were conventional dumb-bell specimens (narrow section 25 mm \times 4 mm) whose dimensions conformed to the former British Standard test BS2782 method 301K [9], although the gripping area was reduced in some instances in order to conserve material.

The simple shear experiments were performed by use of the testing rig shown in Fig. 2. This rig was built to the basic design given by Coker and Filon [11] but with certain modifications. A sheet of the material under test is clamped in the three grips and then the central grip is drawn through the base of the rig and extends the specimen in the simple shear mode. The separation of the grips was adjustable but was maintained at 5 mm during these experiments. The guide plates at the extremity of the central grip are to prevent any movement out of the plane of the rig. For convenience and to conserve material, simple shear specimens were cut from the drawn PVC in two sections and spacers of the same width were placed in the outermost halves of the stationary grips. A simple shear rig of this type has the disadvantage that the free edges cannot support a normal stress component and, therefore, the adjacent material cannot be deformed in simple shear. However, the length of the specimens was generally around 50 mm and the high length/width ratio reduces the errors produced by this edge effect. This configuration also ensures that the material remains in simple shear at high extensions provided the

specimen remains planar. The effect of orientation on the simple shear properties was also investigated. Here we define the angle of orientation to be between the direction of shear stress and the draw direction.

At low extension rates diamonds grow in a slow, stable manner, and yet since the matrix is already plastically deformed, the tip cannot be "blunted" by the creation of a plastic zone or a craze. It is obviously important to understand how the material separates to form new surfaces. The resolution provided by scanning electron microscopy is not adequate to produce any significant evidence other than the absence of large scale cavitation [3]. Consequently, to obtain more information on the propagation mechanism, single stage carbon-platinum replicas were taken from the fracture surfaces of diamonds and examined in the transmission electron microscope.

Experiments were also made to investigate whether there was a minimum defect size required to initiate a diamond. Specimens were stamped with metallographic polishing papers to produce a series of discrete defects. Each specimen was extended until fracture occurred and then the defects were examined in the scanning electron microscope.

3. Results

When extended each specimen exhibited the normal behaviour associated with the tensile yielding of PVC. At yield, a fall in the load was accompanied by the formation of a shear band which developed into a neck and travelled along the specimen at constant load. As an induced defect was engulfed by the neck it dilated markedly, and although the diamond shape was not immediately apparent a "crack front" was formed inside the defect. Every defect formed by stamping with metallographic papers underwent the same deformation. Fig. 3 shows a typical

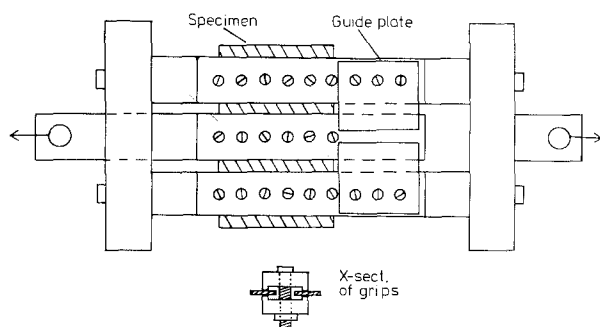


Figure 2 The simple shear rig used in this work.

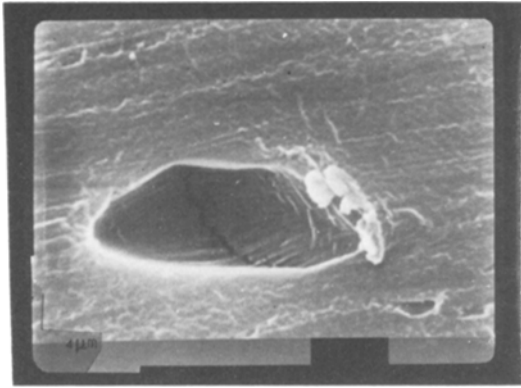


Figure 3 A typical defect in cold-drawn PVC, $\times 2500$.

defect which has developed an internal crack front perpendicular to the tensile direction which lies horizontally in the micrograph. The characteristic straight faces have also begun to grow on each side of the defect. Diamonds were found to grow from defects $2\ \mu\text{m}$ diameter, which was the smallest size examined here. The minimum defect size required for diamond initiation is, therefore, quite small, and on any normal laboratory specimens such defects would not be uncommon.

The examination of the strain fields was confined to specimens where the diamond had completely penetrated the specimen thickness and become prismatic, so that the analysis was essentially two-dimensional. Fig. 4 shows a diamond at two stages in its growth. The diamond appears to maintain its shape as it grows and merely becomes magnified with time. In both micrographs the angle subtended by the faces at the tip is close to 80° . When the diamond propagates rapidly and becomes comparable in size to the specimen width, then this angle diminishes markedly. During the cold-drawing, the $64\ \mu\text{m}$ squares are elongated into

rectangles around $150\ \mu\text{m} \times 40\ \mu\text{m}$ and the thickness is reduced by approximately one-third. The rectangles are deformed further under the stress system around the diamond. Using the co-ordinate system shown in Fig. 1b, it can be seen that along the x -axis ahead of the diamond tip, the elements are elongated further, and along the y -axis the rectangles appear to have contracted and widened considerably. However, the most striking feature of the distorted grid is the large number of elements which have deformed in the simple shear mode with a direction of strain parallel to the y -axis. The greatest shear strain appears along the edges of the diamond, but the sheared region extends for some distance into the matrix. From the magnitude of the shear strains and the fact that the diamond retains its shape on unloading, it is evident that this shear deformation is mainly plastic.

Using the method outlined by Nadai [12] the magnitudes and directions of the principal elongations of each element were estimated. Fig. 5 shows the contours of equal maximum principal elongation in a quadrant of Fig. 4b. There are two areas where the maximum principal elongation differs markedly from that produced by the necking process. As would be expected, there is a large increase near the diamond tip where a significant amount of elastic deformation occurs. Also there is a region directly above the centre of the diamond where the maximum principal elongation decreases considerably. This decrease cannot be accounted for by elastic strains, and since the elements in this region remain rectilinear then considerable plastic flow perpendicular to the draw direction must have taken place. Along the diamond face there is little change from the elongation produced by the necking process. When

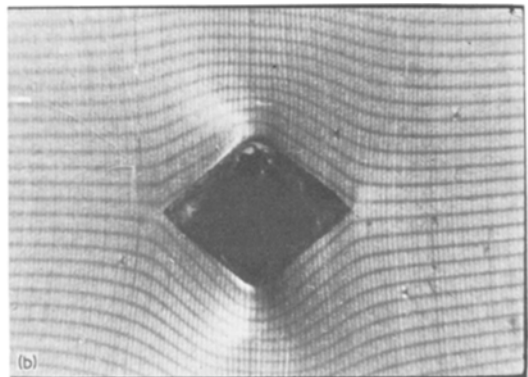
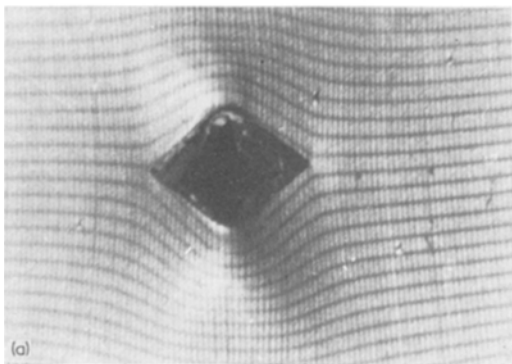


Figure 4 A diamond at two stages in its growth.

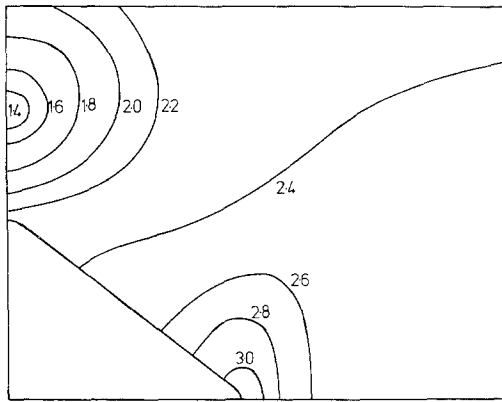


Figure 5 The contours of equal maximum principal elongations in a quadrant around the diamond shown in Fig. 4b.

the directions of the principal elongations are examined it is found that the maximum principal elongation remains within 5° to the draw direction over the entire quadrant. Presumably this is because the elongation caused by the necking process is much larger than that caused by the simple shear. It is, therefore, evident that the molecular orientation is not altered appreciably by the simple shear deformation. Edge diamonds do not show a similar contraction of the elements above the diamond because of the presence of the free surface. Fig. 6 is a micrograph of a large edge diamond which clearly shows that the deformation is almost exclusively in the simple shear mode. All the vertical lines remain in their original orientation while the horizontal lines change direction as they approach the diamond. There is no significant change in the spacings of either set of lines and the horizontal lines remain parallel in the sheared region.

Since diamonds are not found in isotropic materials, their formation is a direct consequence of the anisotropy of the matrix. The mechanical tests on the cold-drawn PVC show clearly the effect of the anisotropy on the yield point and the post-yield behaviour of the matrix. Fig. 7 shows the engineering stress versus elongation curves for a typical series of tensile tests on cold-drawn PVC. When the PVC is extended further in the draw direction, there is no clearly identifiable yield point and the material strain hardens. At 15° to the draw direction there is a small 'kink' followed by strain-hardening, but at the higher angles a well-defined yield drop occurs followed by cold-drawing. The 0° and 15° specimens extended

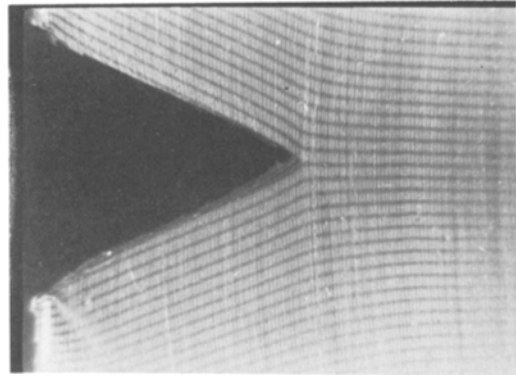


Figure 6 An edge diamond.

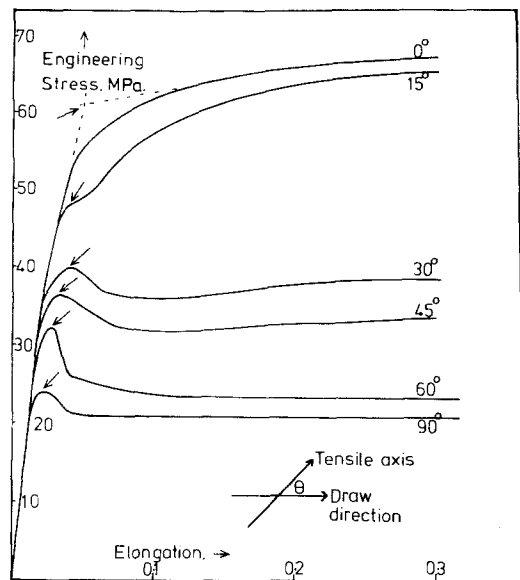


Figure 7 Engineering stress-strain curves for tensile specimens cut at various angles to the draw direction.

uniformly while the higher angles produced necks. The arrows in the figure indicate where the yield stress was calculated in each case. Obviously the yield stress falls markedly as the angle to the draw direction increases, and this can be seen more clearly in Fig. 8. The variation of tensile yield stress agrees generally with that found by Rider and Hargreaves [13] who used PVC that had been hot-drawn to a draw ratio of 3.3.

A different variation is found when the drawn material is deformed in simple shear. Here the angle of orientation, θ , is measured clockwise from the original draw direction to the direction of shear stress. Two distinct types of behaviour are found when θ lies in either the range $0 \leq \theta \leq 90^\circ$

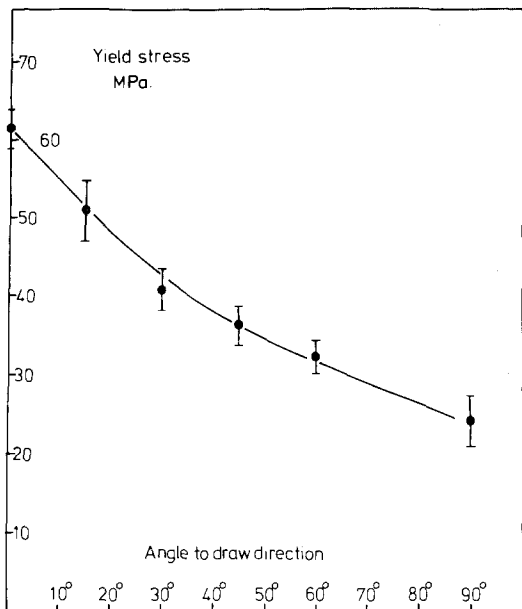


Figure 8 The variation of the tensile yield stress in cold-drawn PVC cut at various angles to the draw direction.

or $90 < \theta < 180^\circ$. Fig. 9 shows the stress-strain curves of typical experiments performed in the lower range of θ . In these tests, the deformation is homogeneous and we are justified in using true stresses and strains. All the curves have a well-defined change of slope which corresponds to the yield point except at $\theta = 45^\circ$, when the slope changes continuously and the yield point is difficult to determine. Only the $\theta = 0^\circ$ curve displays a yield drop, while the remainder strain-harden immediately after the yield point. The

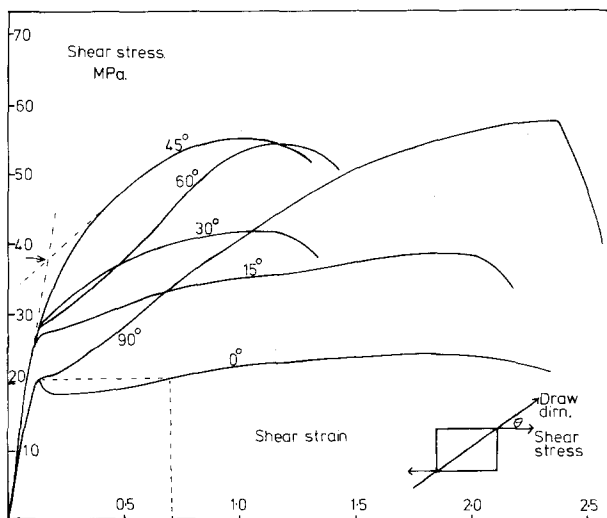


Figure 9 Stress-strain curves of simple shear specimens cut from cold-drawn PVC in the range $0^\circ \leq \theta \leq 90^\circ$.

decreasing slope at high strains is caused by the specimens folding in order to accommodate the imposed displacement, and obviously in these regions the specimens are not deformed in true simple shear conditions. Above $\theta = 90^\circ$ (Fig. 10) it can be seen that a yield drop generally occurs followed by a certain amount of cold-drawing. Although specimens with $\theta = 90^\circ$ and 180° deformed homogeneously, the intermediate values produced many shear bands. When such a specimen is positioned between circular polarizers and illuminated with sodium light, the shear bands can easily be seen (Fig. 11a). A simple shear specimen with $\theta = 0^\circ$ is shown in Fig. 11b and even at large strains the deformation is quite uniform apart from the areas near the free edges. The dark fringes in the interior of the specimen were present in the drawn material prior to the experiment. Fig. 12 shows the variation of the measured yield stresses with the angle of orientation. Each point is the average of four experiments, and while there is some scatter in the measured values of yield stress at any one angle, it can be seen that apart from a slight increase at $\theta = 135^\circ$ the yield stresses above $\theta = 90^\circ$ do not differ greatly. The general form of the tensile and simple shear stress-strain curves agrees with that found by Brown *et al.* [14] who performed similar experiments on orientated polyethylene terephthalate.

The large amount of elastic energy absorbed by the simple shear yielding must reduce the energy available for producing new surfaces at the diamond tip. The diamond can, therefore, be regarded as being 'blunted' by the shearing process. Since little

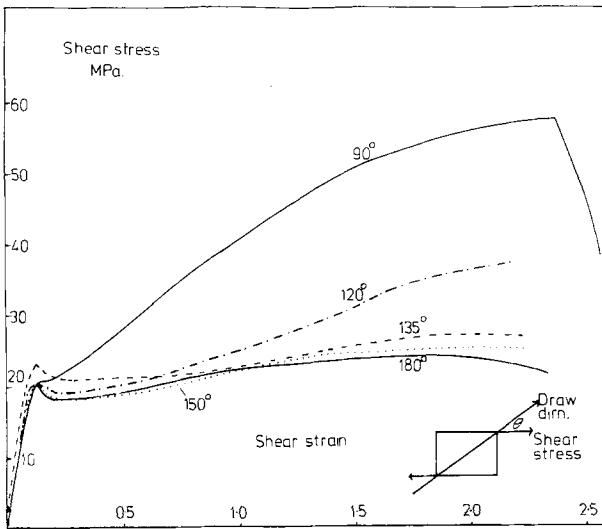


Figure 10 Stress-strain curves of simple shear specimens cut from cold-drawn PVC in the range $90^\circ \leq \theta \leq 180^\circ$.

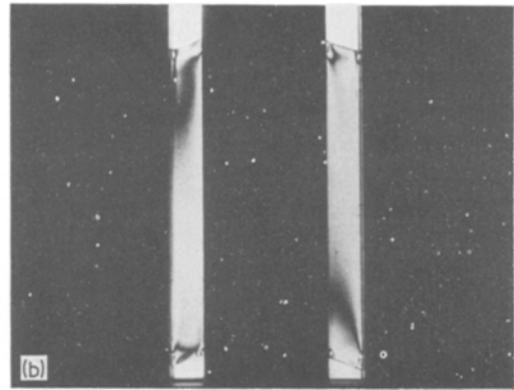
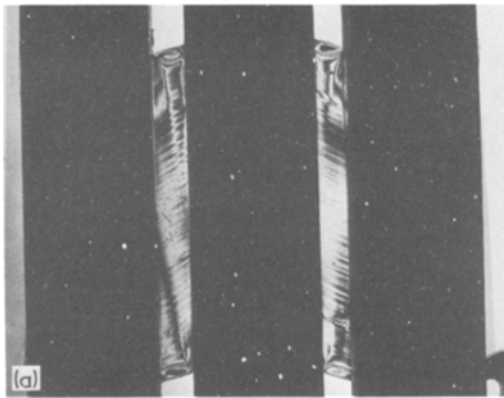


Figure 11 Simple shear specimens of cold-drawn PVC cut at (a) 135° , and (b) 0° to the original draw direction. (Illuminated with sodium light and between circular polarizers.)

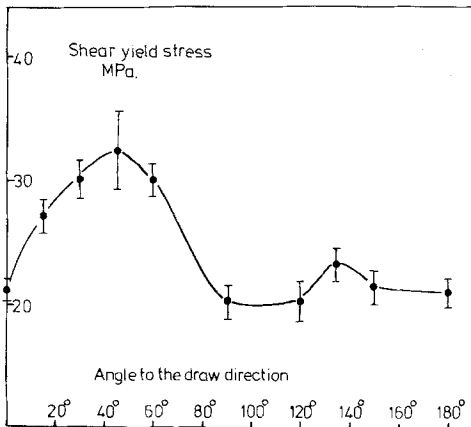


Figure 12 The variation of the yield stress in simple shear of cold-drawn PVC cut at various angles to the draw direction.

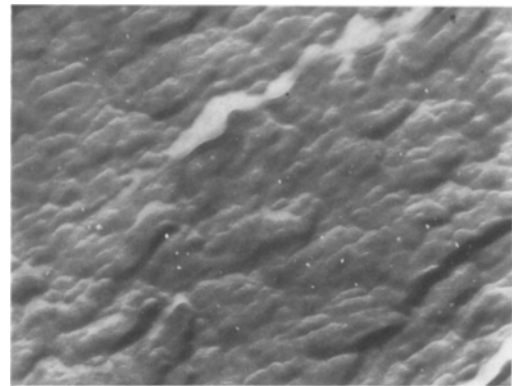


Figure 13 The replicated fracture surface of a diamond cavity grown in PVC, X 45 750.

is known of the mechanism by which the diamond grows, it was hoped to gain some relevant information from the fracture surfaces. However, as Fig. 13 reveals, the replicated fracture surfaces were merely covered by a rough granulation and no other significant features were visible. A very similar morphology was found on the fracture surfaces of diamonds grown in polycarbonate, and it appears, therefore, that the growth mechanism cannot be deduced in this manner.

4. Discussion

4.1. The effect of the molecular anisotropy on the mechanical properties of cold-drawn PVC

The results of the mechanical tests can be more easily understood by considering the orientation of the principal stress axes to the original draw direction. In the simple shear experiments the principal stresses are equal and opposite in sign and aligned at 45° to the applied shear stress. Fig. 14 shows four experimental configurations. When these configurations are compared with the variation of yield stresses shown in Fig. 12, it is evident that the yield stress is reduced when a compressive stress component acts along the aligned chains. In other words, cold-drawn PVC shows the Bauschinger effect which implies that the material will have a reduced yield stress in a certain direction if it had previously been plastically

deformed in the opposite direction. Brown *et al.* [14] have shown that drawn polyethylene terephthalate also shows a marked Bauschinger effect in simple shear. When $\theta = 0^\circ$ and $\theta = 90^\circ$, there is no net tensile or compressive stress along the direction of orientation at zero strain and similar yield points are obtained. The Bauschinger effect is not seen in the tensile experiments because there is always a tensile component acting along the aligned chains.

The post-yield behaviour is also greatly influenced by the molecular anisotropy. For example, the simple shear tests at $\theta = 0^\circ$ and $\theta = 90^\circ$ produce similar yield points but their post-yield behaviour is very different. At finite strains the aligned chains in the $\theta = 90^\circ$ specimen rotate towards the tensile principal stress, and the specimen strain-hardens. At $\theta = 0^\circ$ the angle between the initial draw direction and the principal axes does not change. As yet it is not fully understood why this particular configuration produces true strain-softening. For $0^\circ < \theta < 90^\circ$, there is always a tensile stress component along the aligned chains which tends to increase the degree of orientation and the material strain-hardens.

The tensile specimens also produce tensile stress components along the direction of orientation, and yet for $\theta \geq 30^\circ$ the specimens appear to strain-soften and cold-draw. However, because of the Poisson's ratio effect, at high θ there is a lateral strain which acts in the opposite direction to the original draw direction and may produce strain-softening. Also, when necking occurs, the 'deformation' of the specimen becomes three-dimensional since the shear plane of the material entering the neck is perpendicular to the plane of the specimen. It is, therefore, difficult to ascertain the motion of the aligned chains under these circumstances.

The simple shear experiments with $90 < \theta < 180$ also showed inhomogeneous deformation. However, in these experiments orthogonal sets of shear bands were observed. It is most probable that the constraints imposed by the simple shear apparatus help to maintain an approximately biaxial strain field. Although the compressive component along the aligned chains in these experiments reduces the molecular anisotropy, again it is difficult to predict the motion of the molecules. The configuration in Fig. 14 is, therefore, an over-simplification. However, it is evident that the material strain-softens initially and at

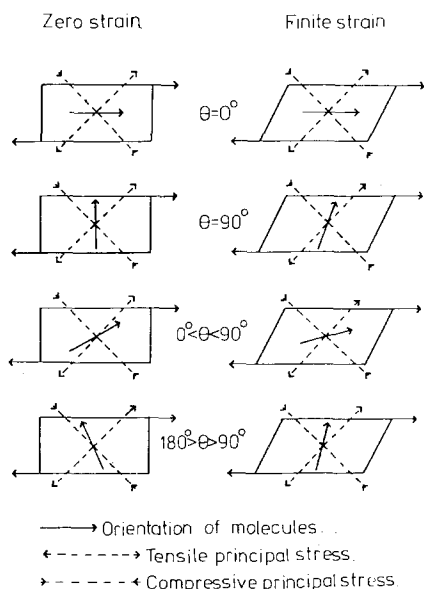


Figure 14 The relative orientation of the principal stresses and the initial draw direction in four simple shear experiments.

sufficiently high strains strain-hardening may take place.

4.2. Diamond formation

From the above considerations, it is evident that the shear yield stress of cold-drawn PVC is greatly reduced and strain-softening occurs when a compressive stress component acts along the aligned chains. Here it is assumed that large-scale plastic deformation will only be seen when the yield stress is exceeded in one of the strain-softening orientations. However, while all the strain-softening orientations have similar yield points, only one is observed in the vicinity of the diamond (i.e. when $\theta = 0^\circ$). In order to understand why this occurs, we require some knowledge of the stress distribution around the diamond. Although the linear elastic model of a line crack derived by Irwin [15] is well removed from the physical reality of diamond formation, it is possible to use it as a first order approximation to estimate the relative magnitudes and directions of the stresses around the diamond. For simplicity it is assumed that yielding will occur at a particular point when the maximum in-plane shear stress, τ_{\max} , reaches a critical value which depends on the molecular orientation. Although the principal stresses around a crack are always tensile, by using a critical value of τ_{\max} we are considering only the deviator stress tensor which does not have compressive components. Since hydrostatic pressure has little effect on the yield behaviour of polymers, most commonly applied yielding criteria (e.g. Tresca or Von Mises) are also derived from the deviator tensor. Using the polar co-ordinates (r, ϕ) as shown in Fig. 1b, the linear elastic model predicts that close to the crack tip τ_{\max} varies as $\sin \phi$ and its direction bears an angle of $3\phi/4$ to the x -axis. If τ_{\max} around a diamond varied in this way, then a compressive strain would only occur along the original draw direction when $\phi \geq 2\pi/3$. Since the magnitude of τ_{\max} is decaying with ϕ in this region, large-scale plastic deformation will first occur at that transition. At that point, the direction of τ_{\max} is parallel to the draw direction. Obviously these results cannot be applied directly to the diamond cavity, but it is reasonable to assume that there will be a transition from strain-hardening to strain-softening orientation of τ_{\max} in the second quadrant of ϕ . Gross shear deformation first takes place at that transition and in a direction parallel to the original draw direction.

Along the x - and y -axes there are no shear stresses in the vicinity of the diamond, and here we see purely uniaxial deformation. The high stress at the diamond tip produces considerable extension in the draw direction even though the material strain-hardens rapidly in that direction. On the other hand, because of the adjacent free surface, along the y -axis the major stress component near the diamond is perpendicular to the remotely applied stress and the deformation should be comparable to that of the $\theta = 90^\circ$ tensile test. However, no inhomogeneous deformation analogous to neck formation is observed. It appears that the material constraints around the diamond only allow in-plane shear deformation to take place. The post-yield deformation in the tensile tests performed with $\theta \geq 30^\circ$ is, therefore, probably not relevant to the strain field around a diamond.

At this point it is possible to outline a simple explanation for the formation of diamonds. In a normal test, the cold-drawn polymer ideally only supports a uniaxial tension. However, any defect present will act as a stress concentrator and produce a biaxial stress field. Because of the Bauschinger effect, in some orientations the yield stress will be exceeded and further plastic deformation occurs. If we consider the defect as a crack, the accompanying stress field determines that the most favourable deformation mode is that of shear in the draw direction. As the defect grows into a diamond, this shearing takes place above or behind the diamond tip. However, after initially strain-softening, the sheared material gradually strain-hardens and eventually reaches the upper yield point again. It is then energetically more favourable for the next element to yield rather than the same element to be strained further. The manner in which the plastically sheared area extends is, therefore, somewhat analogous to the progress of a neck in a tensile specimen. As each element is sheared to a maximum strain, each diamond face is constrained to be linear and the characteristic shape is produced. From the simple shear experiments with $\theta = 0^\circ$ (Fig. 9) the maximum strain in the vicinity of the diamond is estimated to be near 0.7. The angle between the diamond faces at the tip is then predicted to be around 70° . The discrepancy between this value and the measured angle of 80° may be caused by the different elastic strain fields and material constraints in the two experiments.

5. Conclusions

The characteristic shape of diamond cavities is produced by material adjacent to the diamond tip deforming plastically in a simple shear mode parallel to the draw direction. Since there is a maximum shear strain attainable, the faces of the diamond remain linear and at a constant angle to each other. Simple shear experiments on cold-drawn PVC confirm that the most favourable orientated yielding mode accompanied by strain-softening is that of simple shear parallel to the draw direction.

References

1. P. L. CORNES and R. N. HAWARD, *Polymer* **15** (1974) 144.
2. P. L. CORNES, K. SMITH and R. N. HAWARD, *J. Polymer Sci. Polymer Phys. Ed.* **4** (1976) 349.
3. K. SMITH, M. G. HALL and J. N. HAY, *Polymer Letters* **14** (1976) 751.
4. O. K. SPURR, W. D. NIEGISH, *J. Appl. Polymer Sci.* **6** (1962) 585.
5. N. WALKER, to be published.
6. J. W. S. HEARLE and S-C. SIMMENS, *Polymer* **14** (1973) 273.
7. K. SMITH and R. N. HAWARD, *ibid* **18** (1977) 745.
8. N. WALKER, Ph.D. Thesis, Birmingham University (1976).
9. British Standards Institution, Publication BS2782, "Methods of Testing Plastics" (1970).
10. E. H. ANDREWS and Y. FUKAHORI, *J. Mater. Sci.* **12** (1977) 1307.
11. E. G. COKER and L. N. G. FILON, "A Treatise on Photoelasticity" (Cambridge University Press, 1970).
12. A. NADAI, "Theory of Flow and Fracture of Solids", Vol. 2 (McGraw-Hill, New York, 1963) p. 89.
13. J. G. RIDER and E. HARGREAVES, *J. Polymer Sci. A-2* **7** (1969) 829.
14. N. BROWN, R. A. DUCKETT and I. M. WARD, *Phil. Mag.* **18** (1968) 483.
15. G. R. IRWIN, *J. Appl. Mech.* **24** (1957) 361.

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