The effects of heating extruded polystyrene above T_g in dry and in aqueous environments

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Sections of an extruded PS rod have been heat-treated above T_g in both dry and aqueous environments. In both cases the sections relax and shrink in the axial direction. Raised surface features reveal the presence of localized orientation due to flow past obstructions in the extruder. The heat treatment in aqueous glycerol followed by quenching results in an internal mist-like pattern which also reflects the flow pattern past the extruder breaker plate. The aqueous diffusion is rapid and apparently Fickian. About 20% of the water present in the mist pattern is in the liquid phase.

INTRODUCTION

The process of extrusion is known to impose both molecular orientation and internal stresses upon amorphous polymers. These effects can be detected by the anisotropy of the refractive index and the changes in profile which occur when the glass is heated to temperatures above T_g*. In an extruder, the flow pattern is associated with a shear gradient which is often greater near the wall than at the axis of flow. Regions of high shear gradient are associated with increased molecular orientation—detected by measuring the birefringence. Therefore it is common to find the birefringence increasing close to the wall of the extruder. This pattern of changing molecular orientation across the width of the extrudate may also be revealed by heating the glass to temperatures just above T_g. In the rubbery state the material retracts non-uniformly in an effort to reduce its free energy.

An extruded polymer glass made of transparent material (such as polystyrene (PS)) shows no sign of an extrusion fine structure either under the microscope or as a result of measuring the birefringence. Nevertheless, a fine structure is imposed upon the extrudate by the flow past the breaker plate, gauze pack, spiders (and other obstructions) used in the extruder. Such a fine structure was first revealed by etching nylon[1] and polyvinylchloride[2], and in this work a fine structure is revealed in great detail as a result of the sorption of water into transparent extruded PS.

The diffusion of water into polymers is often anomalous because the water tends to cluster in aggregates and, at higher concentrations, to cause transparent polymers to become opaque[3,4]. At temperatures near to T_g, the diffusion of water into some transparent glassy polymers has been shown to continue, apparently without reaching a sorption equilibrium[5,6]. This was associated with progressive opacity and structural damage to the material. More recently, studies of the diffusion of water from the quench bath at 101°C into crystallizing extruded polyethylene submarine cable[7,8] showed that, initially, concentrated solutions of water formed in the polymer which, on cooling, precipitated to form a very fine mist. As much as 90% of this water was found to be in the liquid phase and could be crystallized by cooling to -55°C.

The work described here makes use of these effects in order to study the fine structure imposed upon a PS glass when it flows past the breaker plate and gauze pack used in the extruder. Change in the shape of the material and its birefringence profile were observed as a result of heating the material in a dry environment to a temperature above T_g. In a second series of experiments, the material was heated above T_g in an aqueous glycerol environment, as a result of which water diffused into the polymer. When the specimen was quenched into cold water, the sorbed water precipitated as a visible pattern which revealed the flow-induced fine structure in the body of the material. Both forms of heat treatment (wet and dry) produced evidence for this flow dependent fine structure.

EXPERIMENTAL

The material was a solid extruded rod of PS of ~20 mm diameter and $T_g = (98 \pm 2)$°C as determined by differential scanning calorimetry (d.s.c.) and also by thermomechanical analysis[11]. Specimens were cut from this rod along directions normal to, and parallel to, the extrusion axis and were ground and polished until transparent. A typical specimen was ~4 mm thick.

Specimens were relaxed and allowed to shrink by being heated to ~110°C in a stirred bath of dry glycerol and then cooled slowly.

A separate treatment was to heat the specimens to ~110°C in aqueous glycerol (20% water (v/v)) and then to quench them into cold water, during which process the specimens absorbed water.

The rate of sorption of water into the specimens from aqueous glycerol was followed by interrupting the pro-

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* It must be noted that measurements neither of the birefringence nor of thermal retraction enable us to distinguish between molecular orientation and internal stress. In this article references to 'molecular orientation' may be taken to mean either molecular orientation or internal stress or both, in those cases in which the experimental methods do not distinguish between them.

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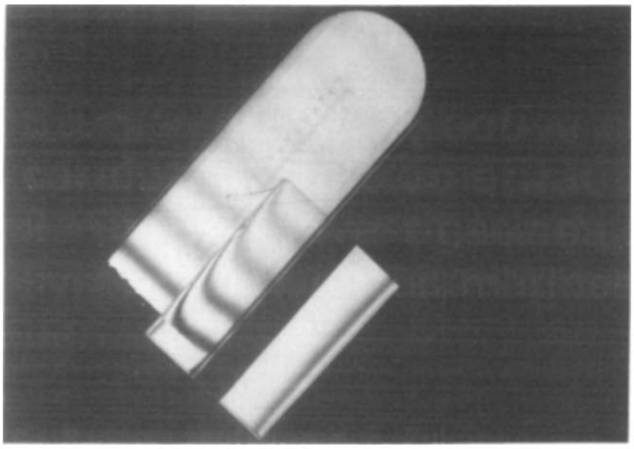

Figure 1 A longitudinal section cut along the axis from the centre of the untreated extruded PS rod: the section is partly overlaid by a quartz wedge and viewed at 45° between crossed polarizers, (see *Figure 2*)

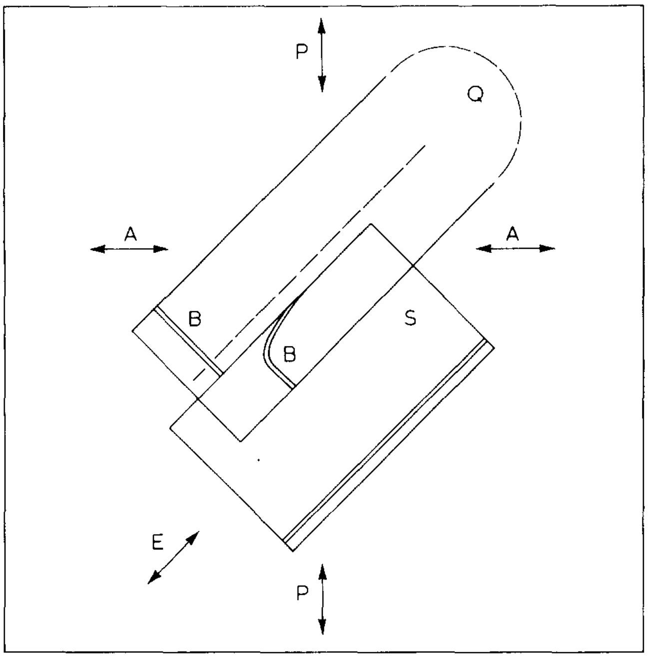

Figure 2 Schematic arrangement of *Figure 1*. (P, A, E are axes of polarizer, analyser and extrusion process, respectively. Q: quartz wedge. S: specimen. B: first order red band)

cess, quenching the specimen into ice-water, dabbing it dry on tissues and weighing it on a balance accurate to six decimal places.

The d.s.c. was carried out by using a Perkin–Elmer DSC-1B, and the microscopy using a Reichert MEF universal microscope.

RESULTS AND DISCUSSION

Thermal relaxation and shrinking

The flow velocity profile of many polymers in the extruder is one of 'plug-flow' in which there is a steep shear-rate gradient close to the extruder walls. *Figure 1* shows a longitudinal section of the virgin extruded PS rod cut along the extrusion axis (E, see *Figure 2*). It is shown partly overlaid by a quartz wedge (Q) whose slow axis is parallel to the extrusion axis of the rod. Both are viewed between crossed polarizers with their axes at 45° to the polarizer axis (P). From the shift of the first order red band (B) in the wedge we can determine the birefringence profile across a diameter of the extrudate, and the rapidly varying portion of this (i.e. the part close to the extruder wall) is shown in *Figure 3*. The maximum birefringence shown here is $|2.3 \times 10^{-4}|$ and this does not indicate a high degree of molecular orientation, values of up to two orders higher having been reported for cold drawn material[9,10]. These birefringence measurements give no indication of any fine structure in the extrudate.

From the birefringence we can predict how the polymer glass will change shape if it is heated above T_g. We can anticipate that it will shrink parallel to the extrusion direction and expand radially; further, we expect it to shrink least on the axis itself and most at the circumference where it has been subjected to the highest shear-rate gradient. This is confirmed in practice: if a transversely cut specimen is heated from ~90° to 110°C in dry glycerol over one hour and then slowly cooled, it shrinks ~5% on the extrusion axis and ~20% at the circumference and then adopts a bollard shape (*Figure 4*). At the same time the birefringence is almost lost. Unexpectedly, the faces of the specimen normal to the extrusion axis are covered with a regular concentric pattern of raised wart-like features. There are four concentric rings of these 'warts' or cells (containing 30, 24, 16 and 10 cells respectively) and an

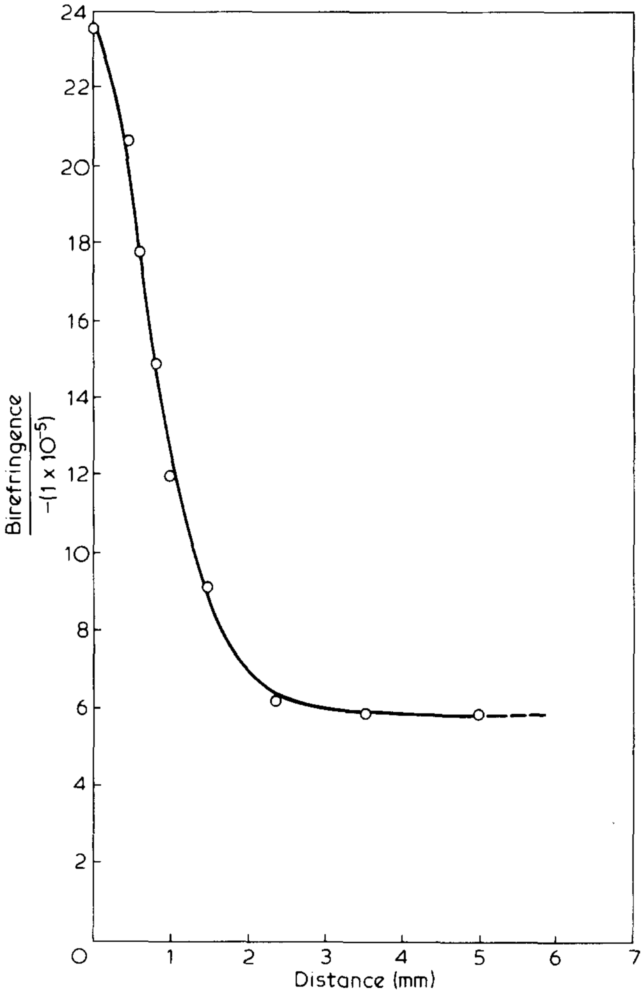

Figure 3 Birefringence profile of extruded PS rod, determined from *Figure 1*. (n.b. the profile of only the outer 5 mm of the radius is shown)

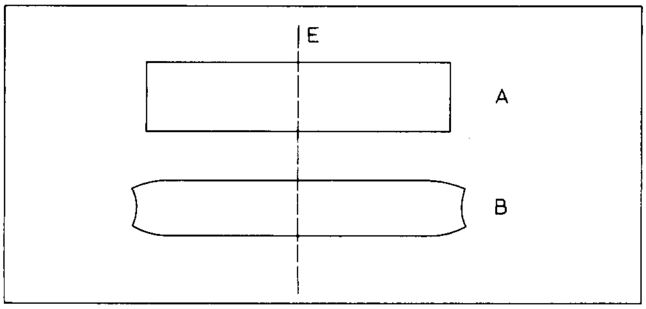

Figure 4 Schematic: shape of transversely cut specimen of extruded PS (A) before, (B) after heating above T_g the profile is now bollard shaped. (E: extrusion axis)

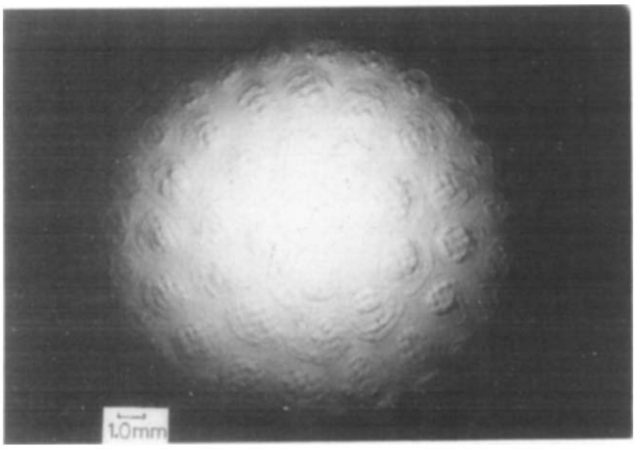

Figure 5 The polished transverse face of a specimen which has been heated above T_g. (Surface aluminized to reflect incident light: the outer ring of cells cannot be seen due to the curvature of the surface)

inner zone of four cells. By silvering the surface, a low magnification reflected light photograph of the pattern may be obtained (see *Figure 5*: the outer ring of cells has not been fully recorded here owing to the curvature of the surface). Each cell is roughly 2 mm across. Within each cell a pattern of between 25 and 30 similar, roughly four-sided subcells can be seen $\sim(0.4 \times 0.4)$ mm in size. Across the whole section these subcells roughly line up as a rectangular grid. Each cell corresponds to a hole in the breaker plate and each subcell to a hole in the gauze filter pack. More detail may be seen in *Figure 6*.

These raised surface cells result from elements of the polymer shrinking axially more than others when the specimen is heated above T_g. Downstream of an obstruction in a polymer flow is a zone of stretching-flow[12]. Polymer elements which are lying in the flow-shadow of the breaker plate and gauze pack ribs during extrusion will be more completely aligned along the flow direction, as a result of this stretching-flow, than those in neighbouring regions to either side. When the hot extrudate is chilled some elements acquire more molecular orientation than others. Later, when the specimen is heated to $\sim(T_g+10)$°C, segmental chain mobility permits the aligned molecules to approach their equilibrium configurations more closely, with the result that the most highly stretched zones also shrink most. Each cell is therefore separated from its neighbours by sunken cell walls which have shrunk more than their surroundings as a result of having been more fully stretched by the extrusion process than in the centre of the cell. The geometry of the breaker plate and gauze pack can be deduced from these observations, and in this case the thermal shrinkage reveals a flow structure in the extrudate not detected by measuring the birefringence alone.

Treatment in aqueous glycerol

The dry heat treatment, described in the previous section, has the effect of raising the surface of the specimen in response to its changes of internal structure. The flow fine structure may also be revealed within the body of the material by causing water to diffuse into the structure at $\sim(T_g+10)$°C and then precipitating the water by quenching. Because T_g for this PS is ~ 100°C it is necessary to raise the boiling point of the water, and so a 20% (v/v) aqueous glycerol mixture was used which boils at ~ 115°C. Specimens were put into a stirred bath of aqueous glycerol at ~ 90°C, and the temperature was raised to 110°C over a period of ~ 1 h. They were then quenched into water at 20°C. The specimens remained transparent whilst hot, but became opaque on cooling. Similar results were found by Pogany[6] when heating compression-moulded PS in boiling water at 100°C. At first the opaque haze is dense (*Figure 7a*) but on storage in laboratory air for 3 days it clears a little to reveal a regular pattern which again shows the influence of the breaker plate and gauze pack (*Figure 7b*). These specimens were cut transversely—*Figure 8* shows a transmitted light macrograph of the pattern. Again a pattern of concentric cells due to the breaker plate appears and the number of these is the same as those revealed on the surface due to thermal shrinkage (*Figure 5*). Within each cell one can also see the subcells due to the gauze filter pack. A view through a longitudinal section (*Figure 7c*) shows a collection of thin streaky zones parallel to the extrusion direction. Using thinner specimens, cut transverse to the axis, it is possible to observe the cells in the microscope. *Figures 9a* and *9b* show four such cell walls. Within each cell the subcell pattern can be seen. A single cell is seen at higher magnification in *Figure 10*, and in *Figures 11* and *12* the individual components of the pattern can be seen; shaped like a leaf ~ 40 μm long and (10–20) μm wide, having one difficult-growth and two easy-growth directions.

Figure 6 The cell/subcell structure of *Figure 5* at higher magnification

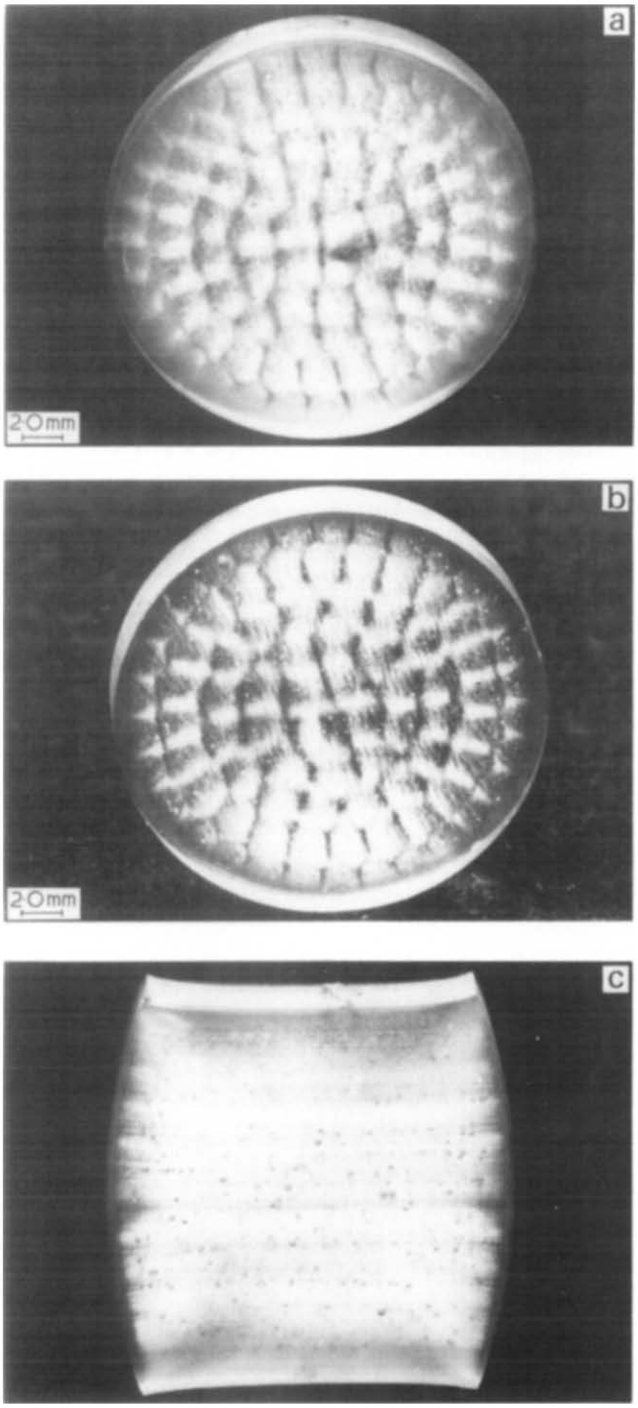

Figure 7 Specimens of extruded PS which have been slowly heated to 110°C in 20% (v/v) aqueous glycerol and quenched into cold water. (a) Transverse cut specimen (2 h after treatment). (b) Transverse cut specimen (3 days after treatment). (c) Longitudinally cut specimen

This process of permitting water to diffuse into the polymer in the rubbery state followed by quenching to a glass, provides an easy technique for probing the flow-induced fine structure at some depth in the material and shows that the patterns formed on the surface due to retraction are due to structural features which run the whole length of the extrudate in the extrusion direction. The dry thermal retraction technique is like a conventional surface etching, whereas the aqueous thermal treatment etches to some depth within the body of the structure.

The nature of the water etching process

When considering the absorption of water by polymers at or near T_g, previous authors have used the following model[5–8]. The water diffuses into the structure from the surface down a concentration gradient; diffusion is relatively rapid in the rubbery phase and is assisted by the active chain segments. At first the water is widely dispersed so that the material is transparent. The equilib-

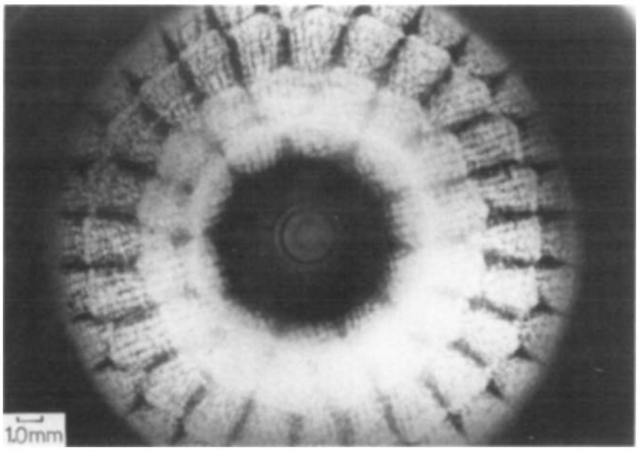

Figure 8 Transmitted light macrograph of specimen shown in *Figures 7a* and *b*. (The darker centre region is due to a patch stop used to increase the contrast in the outer regions)

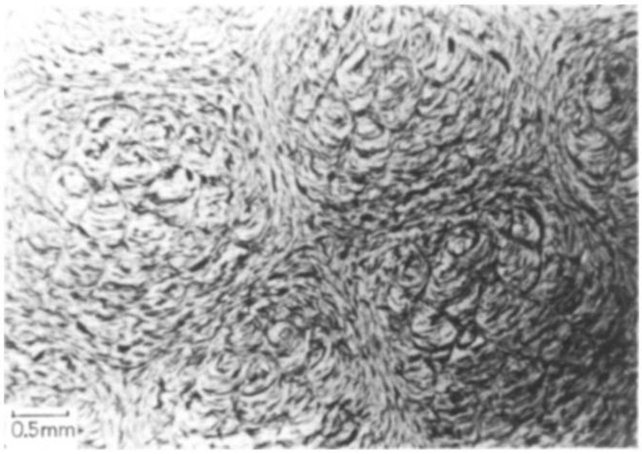

Figure 9a As *Figure 7b* (transmitted light)

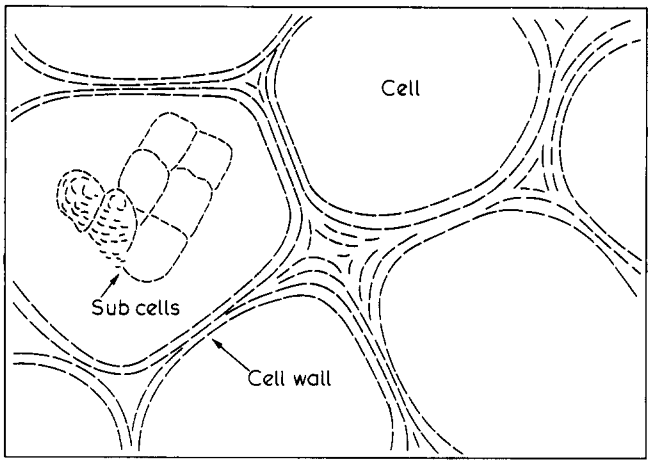

Figure 9b Schematic: identity of components of *Figure 9a*

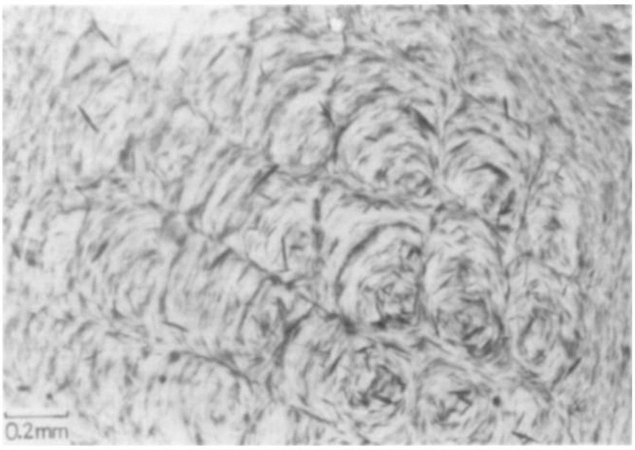

Figure 10 As *Figure 7b* (transmitted light)

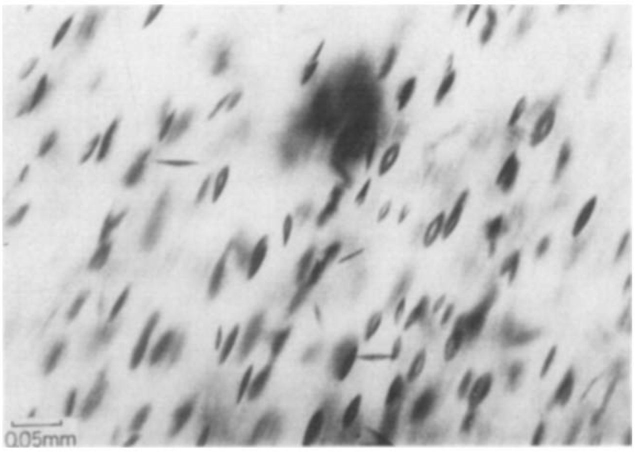

Figure 11 As *Figure 7c*: longitudinal cut specimen: components of pattern

rium solubility of the water in the rubbery phase exceeds that of the glass. When it is quenched, the polymer attempts to discard the excess water, but at these lower temperatures desorption is slow therefore that which does not reach the surface precipitates as a second (liquid) phase. At this stage the body becomes opaque if the globules are large enough to interact with light. Nucleation occurs at sites of least resistance and the nuclei grow to become visible features having shapes which minimize their free energy (usually spherical)[6,7]. The holes created in the glassy structure survive drying and remain while the material is in the glassy state.

In many ways the water etching process follows this model. For example, the etch pattern survives storage in laboratory air for 18 months and also survives complete drying at 20°C in a vacuum. If it is removed by heating to 110°C in air or dry glycerol, when cooled, no trace of the pattern remains. However, a further treatment in aqueous glycerol produces the pattern again. Parallels can be seen with the way in which crazes respond to heating and re-stressing[13]. Time and temperature are also important variables in the etching process, therefore to produce the pattern it is not enough just to heat the specimen to temperature in aqueous glycerol and to quench at once into cold water. Instead, sufficient soaking time at the high temperature must be allowed before quenching, and the duration of this soaking time depends upon the soaking temperature and the prior thermal history of the specimen. For example, a fully annealed specimen requires soaking for ~2 h at 110°C before quenching, whereas, at 95°C (just below T_g) a 15 h soak would be necessary. Considering the effect of the state of order of the glass, if a fully annealed specimen requires a 2 h soak at 110°C, a virgin specimen of extrudate (which is in a lower state of internal order) requires only 30 min. So, in various ways the pattern behaves as if controlled by the segmental chain mobility responsible for the glass transition and ageing in polymers[14]. It is possible, however, to show that whilst the molecular motions responsible for thermal retraction of the extrudate operate at the same time and temperature as those responsible for water etching, the two do not depend upon each other. Thus, when virgin extrudate is water etched it shrinks and suffers the etch process; on the other hand, a virgin specimen may initially be allowed to retract under dry conditions and then, in a second and separate process, the shrunken specimen may be etched in aqueous glycerol. Hence, the driving force for shrinking must be decoupled from that for etching.

The question of whether or not the components of the etch pattern actually contained liquid water was tackled by d.s.c. Daane *et al.*[7] showed that water droplets dispersed in polyethylene could be frozen at -55°C and detected by a melting endotherm at 0°C. A specimen was cut from the centre of the etched PS rod and cooled in the calorimeter to -100°C, then scanned through the temperature range up to $+40$°C. In *Figure 13* curve (A) shows the result of a typical scan and the presence of a small endotherm at about 0°C. The mean of four determinations gave the transition temperature as ~ -3.5°C. The specimen was heated to $+120$°C and the scan from -100°C to $+40$°C was repeated. Curve (B) shows that the endotherm at ~0°C has disappeared, presumably as a result of drying the specimen at 120°C. The endotherm peak height is small (in fact only about two and a half times the instrumental noise—*Figure 13* curve C) but it is consistent, and from its area we can determine approximately the mass of water in the sample. The mean of three measurements gave the fractional mass of crystallizable water in the specimen as 0.02%. Other experiments showed that the equilibrium solubility of water in the specimen was ~0.1%, so these experiments indicate that about one fifth of the total sorbed water in the specimen was in a form that could be crystallized to ice.

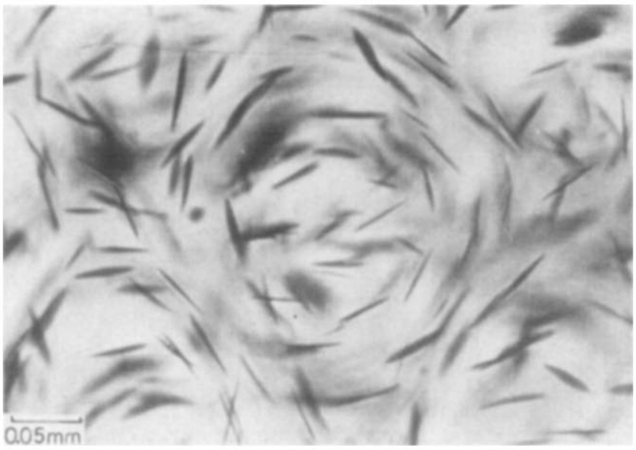

Figure 12 As *Figure 7b*: transversely cut specimen: components of pattern

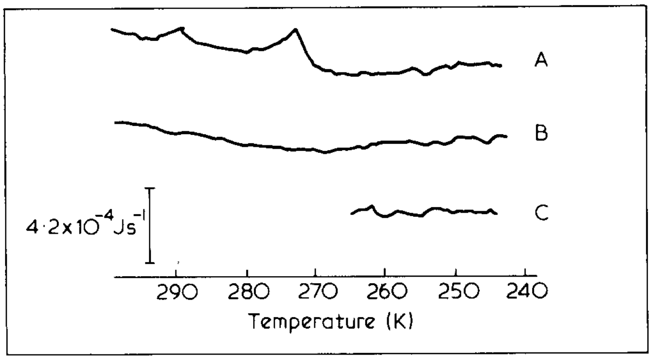

Figure 13 D.s.c. results on a specimen cut from the centre of extruded PS rod. (A) After water etching: (B) as Curve (A) but after drying in the calorimeter: (C) instrumental noise

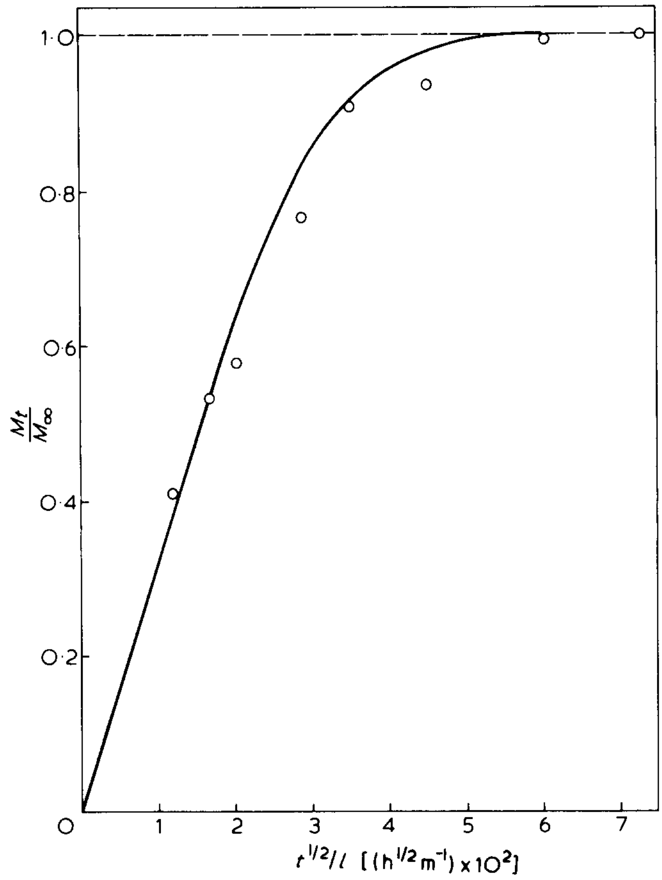

Figure 14 The fractional uptake of water into fully shrunk and dried PS extrudate from 20% (v/v) aqueous glycerol at (101 ± 1)°C. (l = 3.50 mm). (○: experimental data. ——: solution of equations (1) and (2) with $D = 5.3 \times 10^{-6}$ cm^2 s^{-1})

Another interesting feature of the water etching process was the apparent speed with which it occurred. Superficially it seemed as if the water could penetrate to a depth of ~2 mm (i.e. half the thickness of a specimen) in about an hour at 110°C, a fairly rapid process when compared with many other diffusion-based processes. Pogany[6] studied the sorption kinetics of liquid water into compression moulded PS at temperatures up to 80°C. He found that so long as the temperature did not exceed 80°C, the diffusion process remained Fickian and the specimens did not become opaque on cooling. In this regime, both the diffusivity (D) and the equilibrium sorption of water increased with increasing temperature following an Arrhenius-type relationship. In this study the diffusion of water, from 20% (v/v) aqueous glycerol into fully shrunk and dried extruded PS, was studied at 93° and 101°C. *Figure 14* shows the results at 101°C.

For diffusion into an infinite parallel sided slab, Stephan[15] showed that at small values of the fractional change in mass the solution of Fick's Law approximates to the following form:

$$M_t/M_\infty = 4(Dt/\pi l^2)^{\frac{1}{2}} \qquad (1)$$

where M_t is the mass of water sorbed after time t and M_∞ is the mass sorbed at equilibrium, in a slab of thickness l, made of material of diffusivity D. Andrews and Johnstone[16] showed that when $M_t/M_\infty > 0.36$ the following approximation holds:

$$\ln(1 - M_t/M_\infty) = \ln(8/\pi^2) - (D\pi^2 t/l^2) \qquad (2)$$

Equations (1) and (2) have been used to construct the solid line in *Figure 14*. The equilibrium sorbtion M_∞ was found to be 0.11% in this case, and from the gradient at the origin and equation (1) the diffusivity was found to be $D = 5.3 \times 10^{-6}$ cm^2 s^{-1}(1 cm^2 s^{-1} = 1×10^{-4}m^2 s^{-1}). The results are summarized in *Table 1*.

Figure 14 shows that even at these temperatures, so close to T_g, the process is still approximately Fickian, only small quantities of water being sorbed and at rather high rates, confirming the earlier qualitative expectations. The inference is that a normal diffusion process is in control, conforming with the main features of the model previously outlined[5-8].

There are, however, features which are unique to the etching process and require special consideration. Firstly the necessity for a definite soaking time; secondly the shape of the individual components of the pattern; and finally the arrangement of the pattern which reflects the fine structure imposed upon the polymer when it flows past obstacles in its path.

To produce the etch pattern the polymer must be in contact with water at a temperature above T_g for a sufficient duration, and then be quenched. We may enquire what part segmental chain motion can play in such a process. The diffusion studies, for example, showed that diffusion was Fickian and proceeded more rapidly at higher temperatures. The segmental mobility of the polymer must be important during diffusion since it must control the rate at which the water molecules make their diffusion jumps. It was also found that the duration of soaking is decreased at increased temperatures. In the normal process of water etching (when virgin extrudate is treated) two features are observed simultaneously; shrinkage and etching. Both these processes require a temperature above T_g and must involve segmental motion, so it is interesting to consider how they interact. Only shrinking occurs under dry conditions, and in this case the

Table 1 Water in extruded polystyrene

Temperature (°C)	Equilibrium sorption (% w/w)	Diffusivity (cm^2 s^{-1})*
93 ± 1	0.09	4.8×10^{-6}
101 ± 1	0.11	5.3×10^{-6}

* (1 cm^2 s^{-1} ≡ 1×10^{-4} m^2 s^{-1})

segmental motions are not completely random but are biased by the entropic shrinking force. We have also shown that the pre-shrunk and annealed polymer can later be etched so that although both processes depend upon sufficient segmental motion, each can occur in isolation. We observed that the isothermal soaking time for etching was longer for annealed polymer and shorter for the virgin extrudate (which both shrinks and is etched at the same time). From this we can infer that the biased segmental motions which cause shrinking must assist the diffusion process, although they are not vital to it. It is reasonable to suggest, therefore, that the need for a definite soaking time is to build up a sufficient concentration of water in the structure, so that quenching can form the etch pattern. Hence, soaking is a diffusion process which is accelerated by concurrent shrinking, but can occur without it.

The organization of the etch pattern is controlled by the prior flow of the polymer melt past various obstacles in its path. What we observe is an uneven distribution of the individual leaf shaped units which have their long axes organized into a special pattern (*Figures 9, 10* and *12*). The pattern disappears when the polymer is heated under dry conditions to (T_g+10)°C and cooled slowly, but the pattern returns if the specimen is water etched once again. Each element of the pattern is quite large therefore considerable molecular motion is required to open and fill such a cavity. Apart from this, however, ideas about segmental mobility do not help us to understand why the components are leaf-shaped and why they are organized into such a particular pattern. Instead, the behaviour suggests that the components are forming upon nuclei whose position is a function of the melt flow pattern. These nuclei are most likely to be found at defect sites in the structure—places where it is easier for the matrix of chains to open and permit the water molecules to precipitate. The defect sites are most dense in the flow shadow of obstacles such as the ribs of the breaker plate and gauze pack. If we consider how the melt must first part in order to pass such obstacles and then fuse together on the downstream side, we can see that if the fusion is imperfect it might be a source of defect nuclei. In this way we can attribute the defect site density to imperfect fusion of the flowing elements of the melt. The density of nuclei is thus responsible for the process of imaging the shapes of the obstructions in the flow path. When the etch pattern is viewed down the flow axis (*Figures 9, 10* and *12*) we see that the axes of the leaf-shaped units are aligned roughly parallel to each other in the flow shadow of the obstructions. On the other hand where the melt has flowed through the gaps in the obstacle, the units adopt a roughly concentric pattern. It is possible that the leaf shape of the components and the orientation of their axes may also be a result of the melt flow behaviour. We have seen that the leaf shape suggests that the nucleus can grow easily in two roughly orthogonal directions but with difficulty normal to that plane. Such a shape suggests that the water precipitates in cavities which open up between layers of polymer, so that growth is easier between the layers than across them. The polymer melt flows through each gap in the obstruction more slowly near the walls than at the centre. The symmetry of flow through each gap may produce a system of flowing concentric layers with the outer layers moving more slowly than the inner ones. Between these moving layers defect nuclei exist, and when these grow the final elements are leaf shaped with their long axes following the layer direction. In this way it is suggested that the details of the etch pattern give us an insight into how the flow behaviour of the polymer melt controls both the density of defect nuclei and also the shape and orientation of the individual components of the pattern which grows from them.

CONCLUSION

A defect fine structure is imposed upon PS which has been extruded through a breaker plate and gauze pack. The fine structure is associated with stretching flow in the wake of obstructions and can be revealed at the transverse surface of specimens by thermally relaxing them above T_g. The defect sites themselves can be revealed within the body of the material by immersing the extrudate in aqueous glycerol above T_g and then quenching into cold water, when about 20% of the sorbed water is in the liquid phase.

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