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Chromic Acid as an Etchant for Bulk Polypropylene and its Use to Study (i) Nitric Acid Attack on Polypropylene (ii) Cracks in Polypropylene Induced by Tensile Stress

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This paper describes an etchant, chromic acid, which reveals the microstructures present in bulk samples of annealed isotactic polypropylene. It is shown how this reagent may be used first, to follow the attack of fuming nitric acid on polypropylene, and second, to identify the types of crack which occur when a bulk sample of annealed polypropylene fractures under tensile load.

1. Introduction

There have been relatively few attempts to relate the properties of crystalline plastics to their microstructures, because of the difficulties of observing the microstructures of bulk samples. Such microstructures can be revealed by (i) fracturing the material and examining the fracture surfaces [1-5]; (ii) sectioning the material and viewing the structure within the sections by transmission microscopy [6-8]; (iii) etching the material in a manner analogous to the acid etching of metals. The last method is the most desirable for it is the only method which allows microstructures to be examined during the deformation of a test specimen.

Various early attempts at solvent etching polyethylene with carbon tetrachloride, benzene and toluene have been reported [9, 10], but these were not entirely successful for the problem of polymer reprecipitating from the solution and masking the surface was never overcome. In 1964 Palmer and Cobbold [11] described the selective attack of fuming nitric acid on polyethylene. This however is not a surface etching reaction analogous to the acid etching of metals, since the microstructure of the bulk sample is not revealed when reflection optics are used to examine the treated surface. Nitric acid attacks the amorphous regions preferentially and the surface of the bulk sample quickly breaks up due to removal of the amorphous material. Hock [12] found the same effect with polypropylene.

Metallurgical etchants act by the gradual dissolution of the metal from the surface, the rate of dissolution being modified by local peculiarities of the metal. This paper describes an etchant, chromic acid, which reveals the microstructures of bulk samples of crystalline polypropylene in a manner analogous to the acid etching of metals. The amorphous regions are attacked preferentially (but very slowly) to reveal the microstructure, and the attack is then stifled so that the reaction is confined to a thin surface layer.

2. Experimental

2.1. Materials

All experiments were carried out using compression-moulded, annealed, isotactic polypropylene supplied in the form of 3.2 mm thick sheets by ICI Plastics Division, Welwyn Garden City, Herts, UK. The original properties of this material were: density 0.9135×10^3 kg m^{-3}; X-ray crystallinity 63%; weight average molecular weight 190 000.

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The chromic acid was prepared as a 6M aqueous solution by dissolving 0.600 kg of chromium trioxide flake (CrO_3) in 1 dm^3 of distilled water. No sulphuric acid was used in the preparation. The nitric acid used was 95 to 98% fuming HNO_3.

The polypropylene samples, ca. 3.2 × 5.0 × 5.0 mm, were kept under the surface of the chromic acid solutions in test tubes which were placed in an oil thermostat bath. On removal, the samples were washed thoroughly with distilled water and acetone.

2.2. Microscopy

The Reichert MeF light microscope and the Cambridge Instrument Co scanning electron microscope (the Stereoscan) were used. For the Stereoscan investigations, the samples were coated with a layer of silver to a depth of approximately 2 μm.

2.3. Density Determinations

Density measurements were made in a density gradient column made up with isopropanol and distilled water and maintained at 23° C.

2.4. Infra-red Analysis

A Grubb-Parsons spectromaster was used to perform the analyses. The samples were in the form of sections, ca. 150 μm thick originally, cut from the bulk sample with a sledge microtome.

2.5. Tensile Testing

Tensile tests were carried out on an Instron machine, Model II. In the preliminary work, strip specimens ca. 75 × 10 × 3.2 mm were used, but premature fracture inevitably occurred within the grips. Consequently, tensile specimens were prepared from the strips using a 61 mm diameter cutter to shape both edges of the strip. This gave a gauge length of ca. 30 mm and a gauge profile corresponding to the arcs of the cutting circle. The width at the centre of the gauge length was 3.2 m.

3. Results

3.1. Chromic Acid as an etchant for Bulk Polypropylene

Fig. 1 shows a typical view of the surface of a bulk sample of annealed polypropylene when viewed with reflected light. No microstructure can be seen in the as-moulded surface. Figs. 2 and 3 show the same surface after 96 h treatment in 6M chromic acid at 70° C. A microstructure

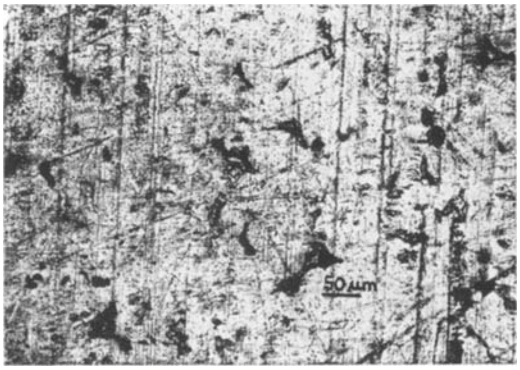

Figure 1 Typical view of the surface of an untreated bulk sample of annealed isotactic polypropylene (reflected light × 100).

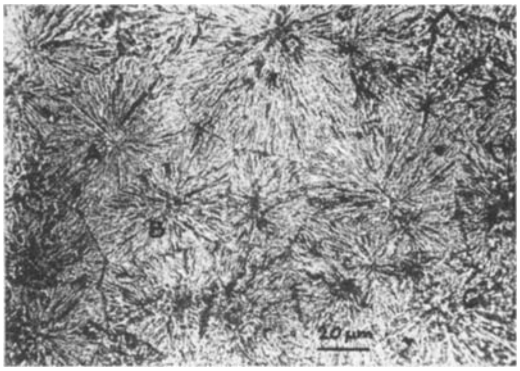

Figure 2 Surface after etching for 96 h with chromic acid (reflected light × 335).

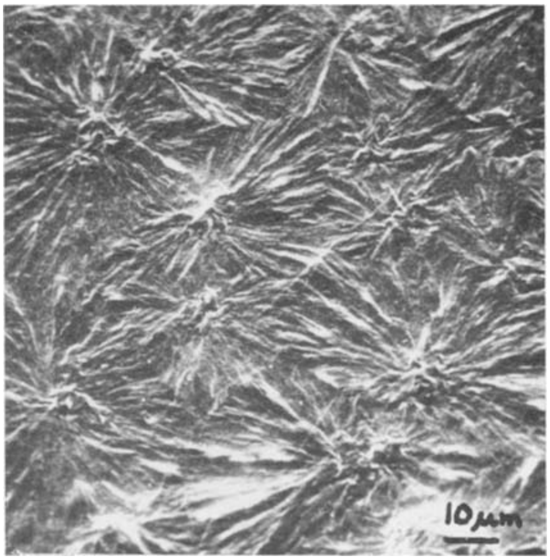

Figure 3 Etched surface viewed with the Stereoscan (× 820).

consisting of large spherulites (ca. 30 to 70 μm diameter range) with radiating fibrillar habits is clearly revealed.

It is necessary to show that the microstructure revealed by the chromic acid is representative of the texture of bulk polypropylene and is not due to some surface deposition by the acid itself, or to some degradation product resulting from the attack. A visual examination of the sample before and after treatment showed that the original glossy surface had been replaced by a matt surface. No charring or discoloration had occurred. The spherulites revealed by the acid and viewed with reflected light fall in the same size range as those observed when a section of the bulk material is viewed using standard transmission optical techniques. Furthermore, the size, shape and general appearance of spherulites revealed by etching an internal surface (i.e. one revealed by cutting away with a microtome about 1 mm of original surface material) were the same as those revealed in the original surface [13]. Examination of the sections showed that there were no spherulitic structures peculiar to the surface layers.

The spherulites themselves have various polyhedral shapes. The regions where they adjoin are sometimes clearly delineated, but usually a continuous, interwoven, fibrillar structure extends across the boundaries, Various structural features are observed within the spherulites. In some, the structure consists of well-defined fibrils radiating from the centre to the periphery. The spherulite indicated A in fig. 2 is an example of this type. Other spherulites, generally smaller and more irregularly shaped, display a radiating fibrillar habit nearer the peripheries, but have a granular structure in the central regions (fig. 2, spherulite B). Finally there are small, polyhedrally-shaped spherulites which display only the granular type of structure. Examples of this type are shown in fig. 2 (spherulite C) and fig. 13.

These observations of the internal structure are consistent with the observations one would expect to make if a random cross-section were taken through a block of spherulitic material and the cross-sectional appearance of the spherulites revealed. Assuming the bulk spherulites to have an approximately spheroidal shape and a radiating fibrillar structure, the cross-sectional outline of any particular spherulite could range from a circle to some kind of polyhedral shape. The actual appearance of the spherulites would depend upon the orientation of the fibrils at the plane where the spherulite was sectioned. A radiating fibrillar structure would be seen when the section coincided with the growth centre of the spherulite. A granular structure would be seen in a periphery section of the spherulite in which the fibrils were oriented perpendicularly or at some oblique angle to the section. The appearance of the etched surfaces is consistent with these models and it is therefore concluded that the chromic acid is revealing the *in situ* structure and deposition of the spherulites. Such internal structural variations could not be explained by surface deposition.

The nature of the attack will now be considered.

3.1.1. Weight Change

Fig. 4 is a graph showing the change in weight of a bulk sample for treatment times up to 1500 h. The rate of weight loss is linear and is ca. 8×10^{-6} g/h.

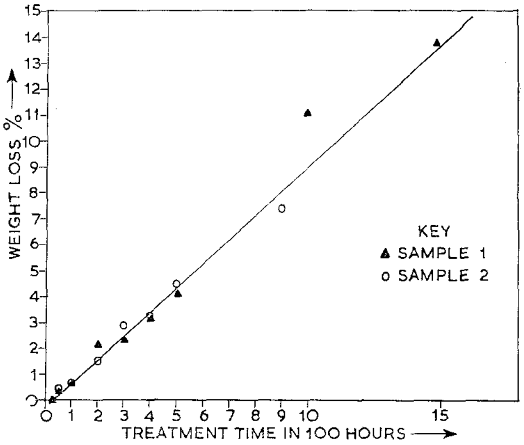

Figure 4 Weight change graph.

3.1.2. Thickness Change

Measurements of the thickness of bulk samples and of sections (ca. 150 μm thick originally) were made before and after treatment for various times. The rate of thinning was found to be linear and equal to ca. 0.10 μm/h.

3.1.3. Density

The densities of the bulk samples showed no change from the original value of 0.9135×10^3 kg m^{-3} for treatment times up to 1000 h.

3.1.4. *Infra-red Analysis*

It was reported [13] from the preliminary investigations that no changes occurred in the infra-red spectra of sections of polypropylene during treatment. However, as a result of more detailed work it was found that a small peak in the spectrum did emerge during treatment. Fig. 5 shows a series of three spectra obtained from a section before treatment, after treating for 115 h, and finally after 327 h treatment. The small change occurs at about 5.8 μm indicating the presence of some carbonyl bonds.

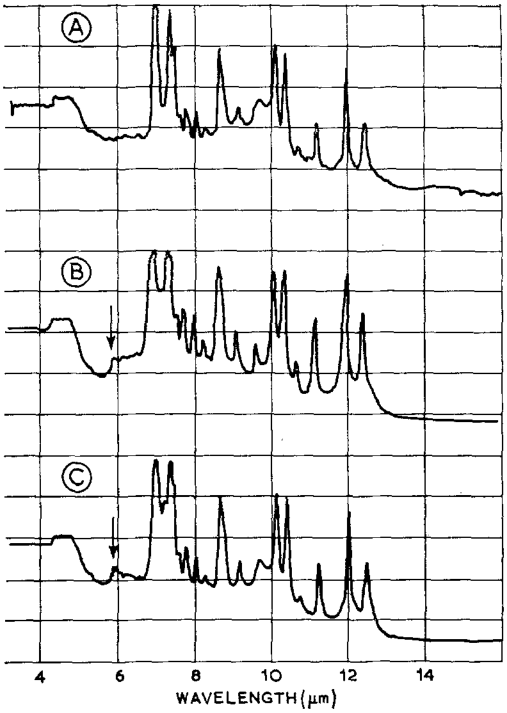

Figure 5 Infra-red spectra obtained from sections of annealed polypropylene: (A) untreated section; (B) section treated for 115 h in 6M chromic acid at 70° C; (C) section treated for 327 h in 6M chromic acid at 70° C. The small changes in spectra B and C at approximately 5.8 μm indicate the presence of some carbonyl bonds.

The previous conclusion [13] drawn from these results was that chromic acid attacks the ordered and disordered, and high and low molecular weight material at approximately the same rate, thereby removing layers of polypropylene uniformly. The density value does not change during treatment indicating that there is no overall preferential removal of the less dense, disordered material or of the low molecular weight material such as occurs with fuming nitric acid. However the fact that the microstructure is revealed at all shows that some preferential attack and removal of material must occur. Fig. 6 shows a typical Stereoscan micrograph of the centre of a spherulite revealed by chromic acid. The topography indicates that interfibrillar material has been removed preferentially to reveal the fibrils emerging from the centre and growing radially towards the periphery. This is also shown in fig. 12.

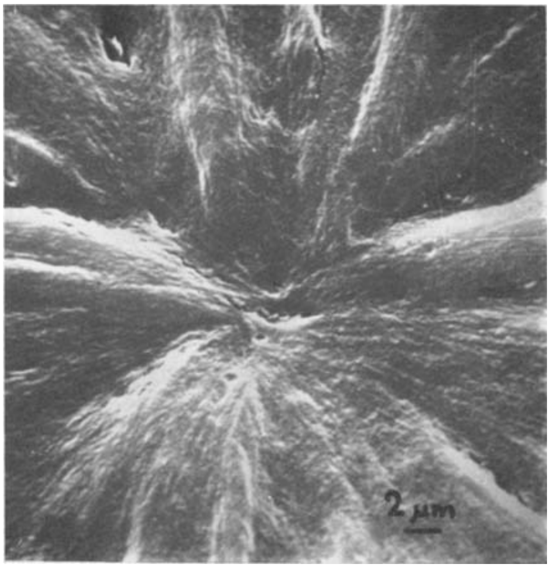

Figure 6 Stereoscan micrograph showing the central region of a spherulite revealed by chromic acid etching (× 2520).

The chemical mechanism of attack is expected to be oxidative and will result in the addition of some carbonyl bonds on to the polymer chain. A possible reaction scheme is shown in fig. 7. We favour sequence (b). It can be shown [14] that carbon dioxide is evolved during the attack, the volume of gas being directly proportional to the treatment time. The infra-red spectra indicate that there is only a small percentage of carbonyl bonds present, suggesting that the reaction is confined to a thin surface layer. A similar mechanism of attack for ozone on polyethylene has been reported by Cooper and Prober [15].

Thus the microstructure of a bulk sample of annealed polypropylene can be revealed by the mildly oxidative attack of chromic acid. Initial preferential removal of interfibrillar material

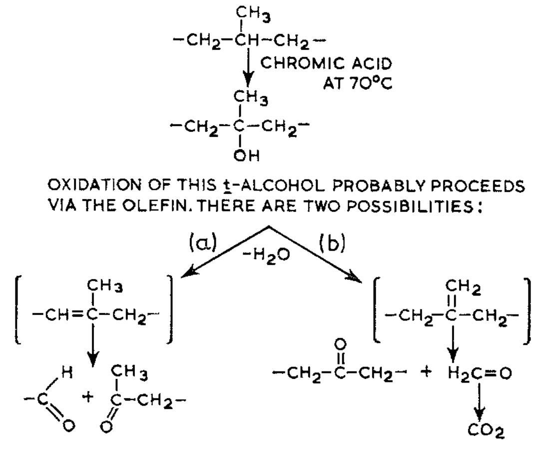

Figure 7 Reaction scheme.

reveals the microstructure, but the attack must then be stifled by some mechanism since diffusion into the polymer bulk with subsequent internal attack does not occur. The sample is progressively thinned by the slow removal of material from the exposed surfaces. A mechanism of attack will now be proposed to explain the observations.

It is probable that the interfibrillar material is removed preferentially. This material is expected to be rich in atactic and low molecular weight material, and perhaps some disordered isotactic material which has been rejected into the interfibrillar regions during crystallization. Keith and Padden [16] have shown that the fibrillar growth of spherulites can be attributed to such an impurity segregation mechanism. It is possible that when the removal of the interfibrillar material has been completed, the acid attack is partially stifled and is prevented from penetrating into the bulk, partly by the highly crystalline fibrillar array, and partly by the presence of highly crystalline interfibrillar links. As these links are gradually severed, the crystalline material may be removed with more ease and the attack may continue with the removal of further interfibrillar material. Therefore the attack is limited by the slow rate at which the acid can diffuse into the polymer. Consequently the overall rate of attack probably represents the rate of removal of highly crystalline material from the surface.

To summarise, the acid attack is limited to surface layers only, is self-stifling and non-penetrative, and relatively slow. Chromic acid reveals the microstructure of polypropylene in a manner analogous to the acid etching of metals.

3.2. Fuming Nitric Acid Attack on Polypropylene

The use of fuming nitric acid to break down bulk samples of polyethylene [11] and polypropylene [12] for microscopy investigations has been reported. Part of our study on the mode of attack of this acid on bulk samples of polypropylene was to determine what routes the cracks, induced by a 4 h treatment at 70° C, took through the spherulitic microstructure. The samples were etched in chromic acid to reveal the spherulitic structure and then treated in fuming nitric acid at 70° C.

The initial stage of attack was the formation of blisters on the surface (fig. 8). These were the result of small areas of the surface being loosened by the highly penetrative acid attack and subsequently raised by a build-up of oxidation products and the acid itself within small internal cracks. The blisters burst during further treatment and after 3 to 4 h the surface was covered in a crazy-paving network of cracks. Fig. 9 shows the general appearance of a cracked surface when viewed with the Stereoscan. The central spherulite is shown at a higher magnification in fig. 10.

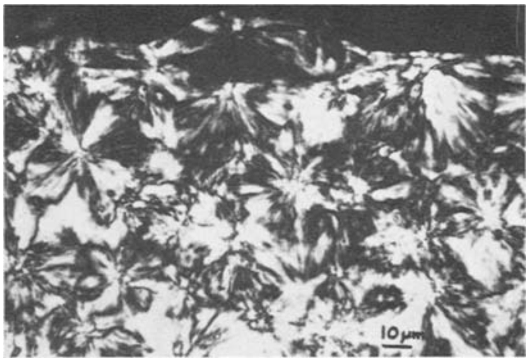

Figure 8 Microtome section from a bulk sample of annealed polypropylene which has been treated for 1/2 h in fuming nitric aid at 70° C. A small blister is seen at the surface. Transmitted light and crossed polars (× 335).

Micrographs of the cracked surface taken in the reflected light microscope were not of the highest quality since it was difficult to focus over large areas of material that was cracked and eroded and consequently in a very uneven condition. However, using reference marks inscribed on the surface, particular groups of the

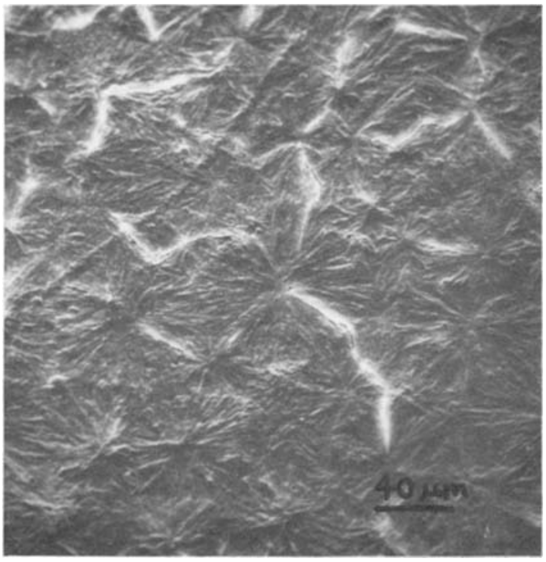

Figure 9 Crazy-paving network of cracks produced in the surface of a bulk sample of annealed polypropylene by treatment in fuming nitric acid at 70° C for 4 h (Stereoscan micrograph × 385).

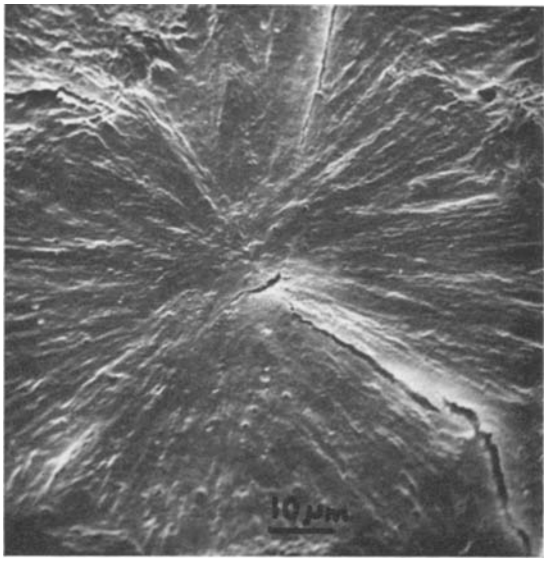

Figure 10 Stereoscan micrograph showing the spherulite in the centre of fig. 9 at a higher magnification (× 900). Radial cracks can be seen.

spherulites were examined in the etched, blistered and cracked conditions. The microscope plates of the surfaces in the etched and the cracked conditions were then carefully compared and crack paths related to the spherulitic structure.

The cracks were then classified into three categories: (i) Radial cracks: one radial crack was considered to be a crack running from the centre to the periphery of a spherulite in a direct radial route; (ii) boundary cracks: one boundary crack was considered to be a crack which followed the boundary between two spherulites; (iii) any others. In all, 160 cracks were examined and classified in this manner: 81% were radial cracks, 8% were boundary cracks and 11% could not be placed definitely in either category.

The radial or trans-spherulitic nature of the acid-induced cracks indicates that the spherulites in bulk samples of annealed polypropylene are prone to failure, due to chemical oxidative attack, predominantly along radial paths. The boundaries between spherulites appear to be relatively resistant. These results are at variance with those reported by Hock [12] who suggested that the margins where the spherulites adjoin are locations of preferred attack. However he presented no micrographs in support of this statement.

3.3. Tensile Cracking Studies

Investigations were carried out on tensile specimens that had usually been etched before testing. It was shown, by comparing the tests on etched and unetched specimens, that the etching treatment had no significant effect on the load-extension curve of annealed polypropylene. Two types of test procedure were adopted: (i) the test was stopped during yielding, before fracture occurred; the centre portion of the gauge length in which the cracks were forming was then cut out and the etched surface examined in the Stereoscan; (ii) the specimen was pulled to fracture and the etched side surface examined in the Stereoscan. All the tests reported here were carried out using a constant strain rate of 0.5 mm/min.

Figs. 11, 12 and 13 are micrographs taken of a specimen on which the test was stopped during yielding. In fig. 11 several cracks are seen running from centre to centre of neighbouring spherulites. Occasionally a crack is seen to run along a boundary. Fig. 12 is a view at higher magnification of the central spherulite in fig. 11. The surface topography has been revealed clearly by the chromic acid etchant and the crack paths can be related to the microstructure. Fig. 13 shows a spherulite which is split across by a crack which closely follows the radiating fibrillar structure. The triangular region top of centre is

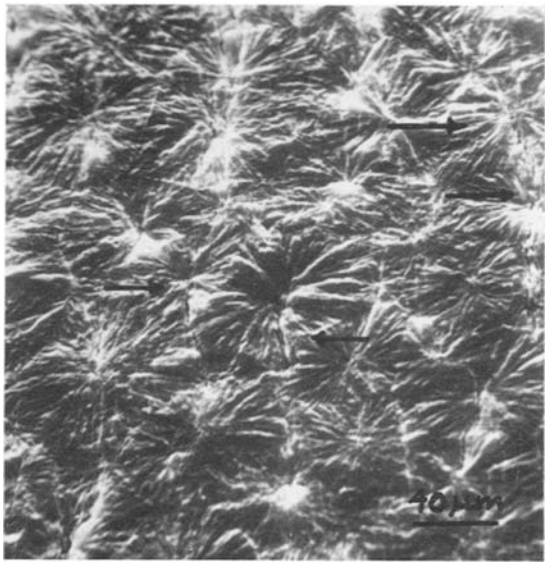

Figure 11 Side surface of an etched tensile specimen of annealed polypropylene. The tensile test was stopped whilst the specimen was yielding. Cracks are indicated on the figure by arrows. The direction of the applied stress is horizontal (Stereoscan micrograph × 385).

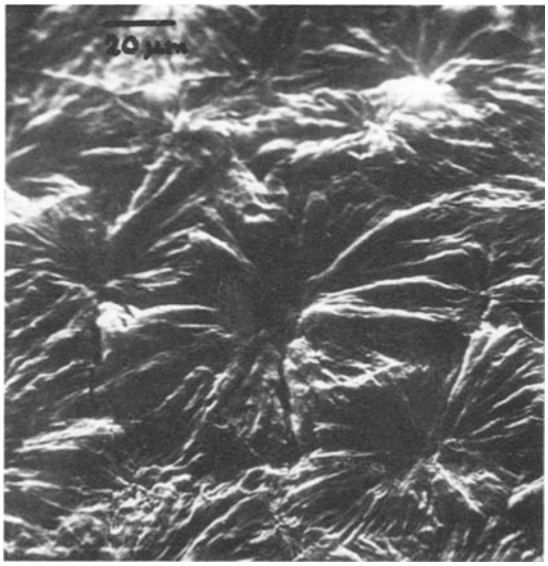

Figure 12 The central spherulite of fig. 11 (Stereoscan micrograph × 870).

an example of the type C spherulites considered earlier.

Fig. 14 is a general view of the side surface, containing cracks, in a specimen pulled to fracture. Fig. 15 is a view at higher magnification of the same surface after etching, and in fig. 16 the central spherulite of fig. 15 is shown with a crack following the radiating fibrillar structure through the centre.

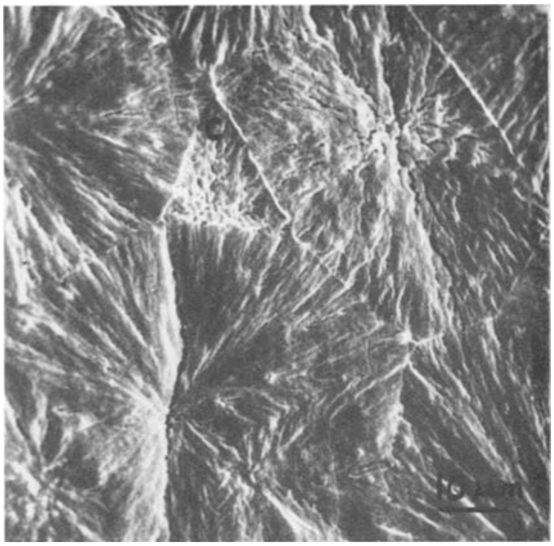

Figure 13. As fig. 11. The largest spherulite is split across the centre by a radial crack (Stereoscan micrograph × 870).

These observations show that the cracks produced by yielding and subsequent fracture can be related to the structure of the spherulites.

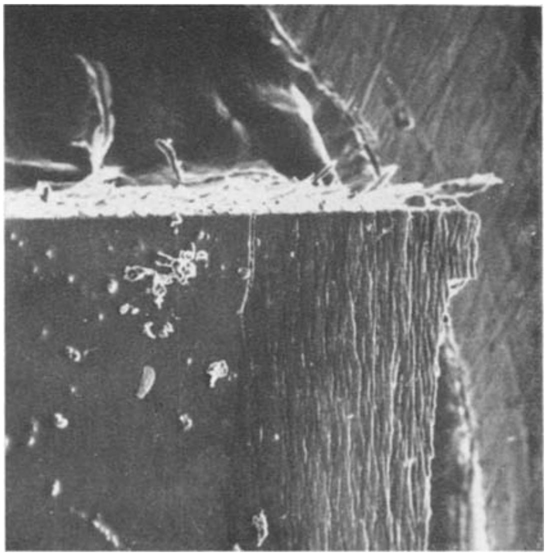

Figure 14 Unetched side surface of a fractured tensile specimen of annealed polypropylene. The direction of the applied stress is horizontal. The cracks run perpendicular to this direction (Stereoscan micrograph × 23).

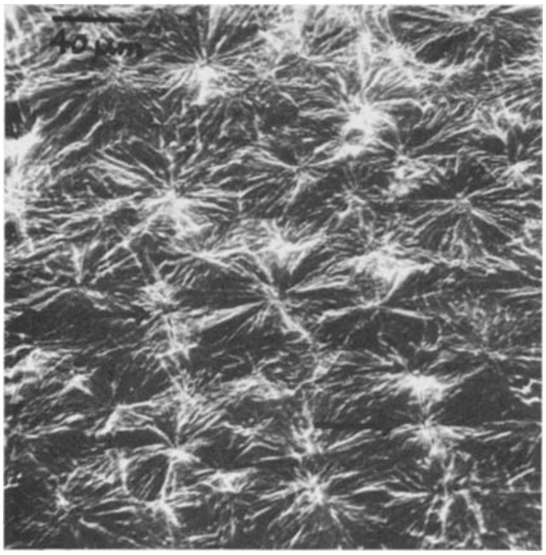

Figure 15 Side surface of an etched and fractured tensile specimen of annealed polypropylene. Cracks are indicated on the figure by arrows. The direction of the applied stress is again horizontal.

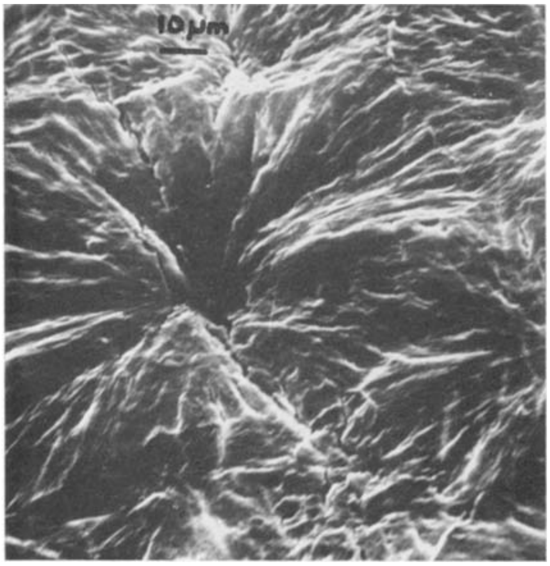

Figure 16 The centre spherulite of fig. 15 (Stereoscan micrograph × 1500).

The cracks form in a direction normal to the applied load between those radiating fibrils which are suitably oriented in this direction: few cracks follow the boundaries. Therefore the brittle failure of our polypropylene is due to the susceptibility of the spherulites to crack formation between the radiating fibrils.

No reports have been found in the literature on the tensile cracking of spherulites in bulk material, probably because of the difficulties associated with the *in situ* examination of bulk polymer samples. However there have been investigations on thin films and it is instructive to review this work.

Cracks in thin films may appear during the crystallisation process [17], or be caused by oxidatively ageing [18] or heat ageing [19] the specimens. Both types of crack (i.e. radial and boundary) usually occur, with the boundary cracks predominating at the higher crystallisation or ageing temperatures. Harris and Magill [20], and Barish [21], protected thin films from oxidative ageing and showed that fracture induced by tensile stress always occurred along spherulite boundaries. Barish postulated that this cracking was due to the considerable retraction that is present in the formation of spherulites: the spherulites "dome-up" and the central regions thicken at the expense of the boundary regions. The boundary cracks developing during crystallisation or ageing could be explained using this boundary thinning concept. Indeed, boundary thinning is likely to be a general phenomenon which should occur in all thin films and always lead to some boundary cracking. There is no similar explanation for radial cracking. Radial cracks probably represent genuine lines of weakness. There is evidence that radial as well as boundary cracking occurs when highly spherulitic polypropylene is fractured, but the papers by Maxwell [22] and Oppenlander [23] do not give details of the type of specimen or the test procedure.

4. Discussion

It has been shown that 6M chromic acid at 70° C can be used to etch crystalline polypropylene. The nature of the etching process has been discussed.

Studies have been made of the nature of the attack of fuming nitric acid on polypropylene and of the types of crack that form in the microstructure when a bulk specimen of annealed polypropylene fractures under a tensile load. It has been shown that cracks induced by fuming nitric acid, and tensile cracks both favour radial routes through bulk spherulites. Thus cracks produced by chemical oxidative attack and by a tensile stress are found to follow the same paths through the structure. This indicates that the spherulites in our material are inherently weak along radial paths and relatively strong along their boundaries.

These observations can be explained if one considers a spherulite model in which the fibrils are mainly isotactic material of high molecular weight in a highly ordered state (these fibrils may extend across spherulite boundaries), whilst the interfibrillar regions are rich in atactic material of lower molecular weight. The boundaries will probably be rich in isotactic material of high molecular weight in a disordered state. Boundaries between adjacent spherulites will be interconnected to an extent which will depend upon the cooling treatment from the melt. If the material is annealed commercially, there is still a considerable degree of interspherulitic linking. Hence a crack would find it easier to travel between fibrils, through the lower molecular weight and atactic material where there are relatively few interfibrillar links to break, rather than along the boundaries. However Maxwell [22] has made the point that, with slow cooling, large spherulites grow, which in the process of growth pull in chains from the surrounding melt. There will then be fewer inter-spherulitic fibrillar links and boundary cracking would be expected to occur.

In conclusion, it appears to us that bulk polypropylene produced normally in such a way that there is a reasonable degree of fibrillar linking across the spherulite boundaries will generally fail along radial paths through the spherulites. On the other hand, if polypropylene is annealed to such an extent that large spherulites form with few inter-spherulitic links, then boundary cracking will also occur. A further point [23] is that if crystallisation is carried out very slowly, voids can form between spherulites and, acting as fracture sites, these voids cause fracture to occur preferentially in the boundary regions. We are at present investigating the effects of thermal historys on spherulite size and cracking behaviour.

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