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The effect of spherulite size on the fracture morphology of polypropylene

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Tensile tests show that for isotactic polypropylene the graph of yield stress versus spherulite size goes through a maximum at a critical spherulite size. Scanning electron and transmission optical microscopy indicate that this represents a change-over from spherulite yield to boundary yield, caused by an increased segregation of impurities at the boundaries coupled with voidage owing to contraction of the spherulites on cooling.

1. Introduction

The effect of spherulite size on the mechanical properties of crystalline thermoplastics is not well understood. In 1959, Starkweather and Brooks [1] showed that as the spherulite diameter increased for various samples of Nylon 6.6 the yield point stress decreased linearly. Today most plastics' moulders avoid slow cooling rates (and, therefore, large spherulite sizes) because these usually result in the materials having low impact-strength, elongation at break and yield point stress. Yet Haward and Mann [2] showed that for a number of Ziegler polyethylenes, the tensile yield stress increased linearly with increasing crystallinity, and in the absence of nucleating agents an increase in crystallinity is often accompanied by an increased spherulite size. (Any annealing process may of course increase the crystallinity by refining the existing spherulitic structure or by causing further crystallization of crystallizable material within and between spherulites.)

One solution to the apparent contradiction is the following. When the spherulite diameter is small (say less than 1 μm), the yield stress is likely to increase with increasing spherulite diameter. It has long been known [3] that it is the crystalline rather than the amorphous regions which are strong and less easily deformed. However, when the spherulite diameter is relatively large (greater than 10 μm), it is to be expected that the existence of voids at spherulite boundaries, owing to the greater contraction of the crystalline regions on cooling, and the segregation of impurities at these boundaries could play a dominant part such that boundary-weakening effects override all others. Thus the yield stress will not continue to increase with spherulite diameter and may indeed be expected to go through a maximum.

It is important to appreciate and understand these problems for two reasons: first, in order to obtain the optimum mechanical properties when the materials are moulded and secondly, to achieve a successful joint when crystalline thermoplastics are welded. In this paper we describe the effect of average spherulite radius on some mechanical properties and on the fracture behaviour of isotactic polypropylene.

2. Tensile testing

Compression moulded samples of isotactic polypropylene with different spherulite sizes (the average spherulite radius, R, varied between 0.04 and 0.16 mm) were made in a press designed in this laboratory by a previous worker [4]. The polypropylene was ICI "Propathene", grade HWM-25, kindly supplied in the form of granules by ICI Plastics Division, Welwyn Garden City, Herts, UK. The polypropylene granules were placed evenly on the top of a piston (120 mm in diameter), inside a cylinder into the bottom of which oil was fed from a pressure system. A head was bolted down on top of the cylinder to form the top surface of the mould. There were facilities for evacuating the mould cavity and for controlling the heating and cooling of the press. The granules in the mould were first evacuated and then heated up at a rate of 2.8°C min^{-1} to a temperature of 250 ± 5°C. A pressure of 1.7 × 10^{6} N m^{-2} was maintained at this temperature. Cooling was then begun and the pressure increased in stages until ambient temperature had been reached when the pressure was at least 1.4×10^7 N m^{-2}. Varying the cooling rate resulted in a variation in average spherulite radius. The average spherulite radius was calculated from an intercept count on microtomed sections viewed in transmitted, polarized light.

Simple tensile tests on dumbbell specimens cut from these samples were then carried out using an Instron tensile testing machine. The strain-rates used varied from 3.28×10^{-2} to 3.28×10^{-3} sec^{-1}. The gauge length of the specimens was 25.4 mm with a nominal cross-sectional area of 5 mm $\times$ 6 mm and all tests were carried out at ambient temperature (*c.* 18°C). Fig. 1 shows the effect of spherulite radius on the stress-strain curves.

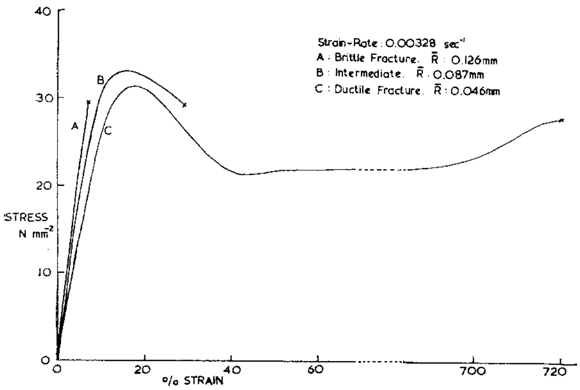

Figure 1 Graph showing the effect of spherulite radius on the nature of the stress-strain curve.

The yield stress quoted in this paper is defined as the maximum stress reached in a nominal stress/strain curve. When the spherulite size is large and fracture is totally brittle, the "yield" stress will, in fact, be the fracture stress. This definition is used because the recorded load/extension plot has no linear elastic portion. For a similar reason a stiffness parameter has been defined in terms of the σ_Y/ϵ_Y ratio: that is, the yield stress divided by the yield strain. It should be appreciated that this parameter will not be applicable for normal service loads when only small strains are encountered. For service conditions, stiffness is better defined using the tangent modulus at the origin of the stress/strain curve. However, the σ_Y/ϵ_Y ratio is more informative for studying yield deformation, rather than elastic behaviour.

Figs. 2 and 3 are graphs of yield stress and σ_Y/ϵ_Y ratio against spherulite radius for strain-rates of 3.28×10^{-2} and 3.28×10^{-3} sec^{-1}. Other strain-rates gave similarly-shaped plots showing maxima, with the higher strain-rates giving higher values for the yield stress and σ_Y/ϵ_Y ratio for a given spherulite radius. It is noteworthy that there is a maximum in the yield stress curve at a spherulite radius which corresponds to the break in the σ_Y/ϵ_Y ratio plot. Plots of elastic and plastic strain versus spherulite

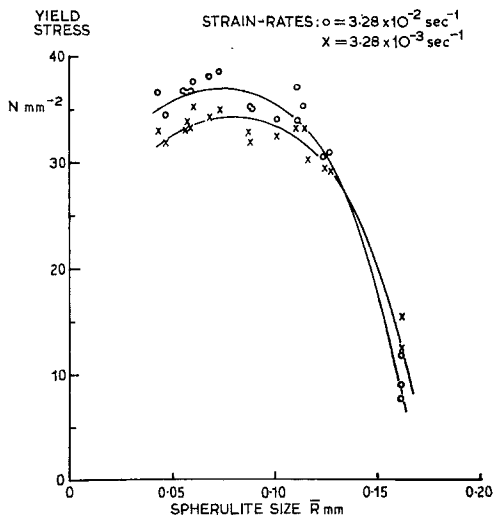

Figure 2 Graph of yield stress versus spherulite radius at two different strain-rates.

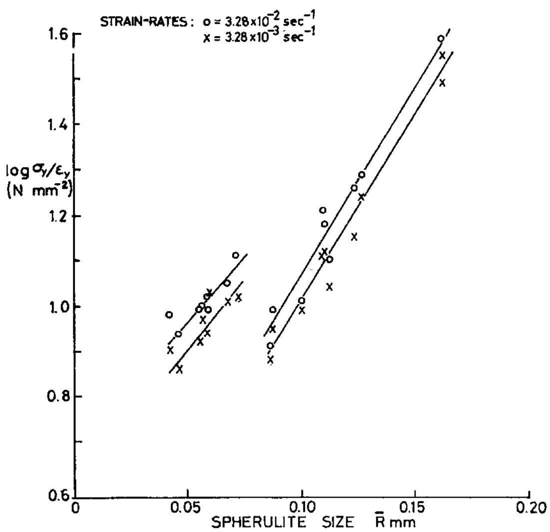

Figure 3 Graph of yield stress divided by yield strain (i.e. σ_Y/ϵ_Y) versus spherulite radius at two different strain-rates.

radius also show a large change in value at this point, going from large strain at small spherulite radii to small strains at large spherulite radii.

The visible characteristics of fracture also change with spherulite radius. Tensile specimens with small spherulites deform by necking and cold drawing followed finally by fibrillar fracture, while at large spherulite radii the fracture is brittle. At intermediate spherulite radii there is a different mode of failure as follows. There may be some initial stress whitening up to the yield stress, but as soon as this is reached a number of opaque planes lying perpendicular to the stress direction appear in the gauge length. These increase in number and extent, with an associated drop in the measured load, until there is final brittle fracture initiated at one of the larger planes. These opaque planes, or initiation regions, can cover about 25 % of the cross-section before fracture. They also appear to originate at faces or corners, highlighting the importance of surface finish when preparing the specimens. The tensile specimens were shaped using a high speed air-driven router and the cut faces polished with fine emery.

3. Electron microscopy

The fracture surfaces were studied in a Cambridge Stereoscan. After mounting the fractured ends on stubs, the fracture surfaces were coated with silver to a thickness of approximately 20 mm in a vacuum evaporator.

The specimens with the small spherulites fractured in a fibrillar fashion and it was found that in the magnification range usable (up to $\times$ 1000) no other structure was visible apart from fibrils of all sizes. The problem associated with this kind of surface is its susceptibility to melting in the electron beam, especially as the magnification increases. Lower accelerating voltages helped but only at the expense of the resolution. It has been suggested [5] that the ultimate units composing microfibrils are single lamellar blocks perhaps 10 to 20 nm thick and if so they would be unresolvable under these conditions.

The intermediate-spherulite-sized specimens, where deformation resulted in the occurrence of opaque planes, showed two distinct surfaces corresponding to an initiation region and the final, brittle, fracture region. The former was ductile and extensively drawn (Fig. 4), while the latter was typically brittle and with a seemingly random crack path. The drawn region was found to have an underlying spherulitic structure with the crack, or craze, running through spherulites and drawing occurring at the centres and at the edges (Fig. 5). This figure also shows the sharp change from the ductile region to the brittle region which is at the top of the picture.

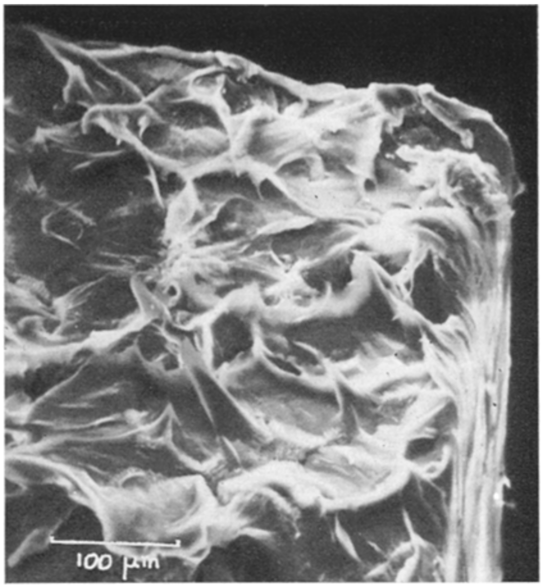

Figure 4 Initiation area; fracture surface of intermediate-spherulite-radius specimen. Stereoscan micrograph.

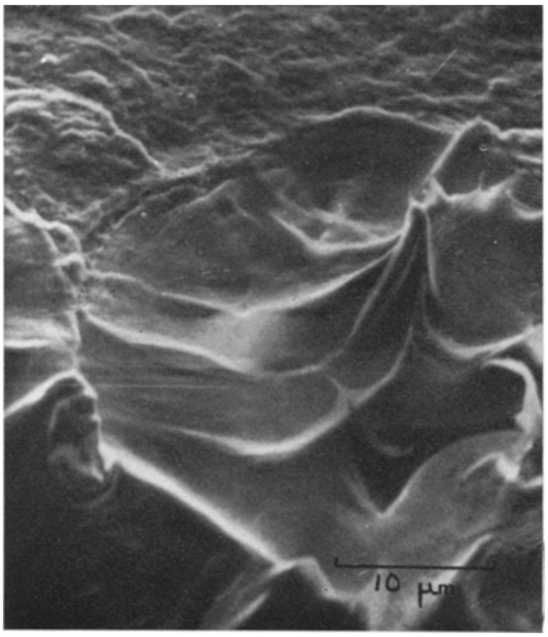

Figure 5 Boundary between ductile initiation area and the brittle region at the top of the picture. Stereoscan micrograph.

As the spherulite radius increased, the initiation region decreased in size and more initiation sites appeared in different parts of the same fracture plane. Also the drawing was of a somewhat different form, being of a "coronet" type as shown in Fig. 6. At the same time, recognizable features appeared in the brittle region. One was evidence of fracture across spherulite diameters, leaving a coarse, radiating, plate-like structure; the other resulted from interspherulitic fracture, leaving polyhedrons. Both features can be seen in Fig. 7. It was noticed that there were often lines of holes along the boundaries between the polyhedrons and the rest of the surface.

As the spherulite radius increased further, the initiation regions became very difficult to define and the polyhedrons more common until, finally, fracture was almost totally interspherulitic (Fig. 8).

4. Optical microscopy

The deformation was also followed by microtoming sections perpendicular to the fracture surface and viewing these sections in transmission between crossed polars. The deformation characteristics of the small-spherulite specimens have been dealt with in a previous paper [6]. The development of the planes in the intermediate-spherulite-radius specimens is by a crazing process. Optical micrographs show that multiple fine crazes are usually initiated at a surface defect and grow into the specimen in a band perpendicular to the stress. Although most of the initiation regions start at a surface, there

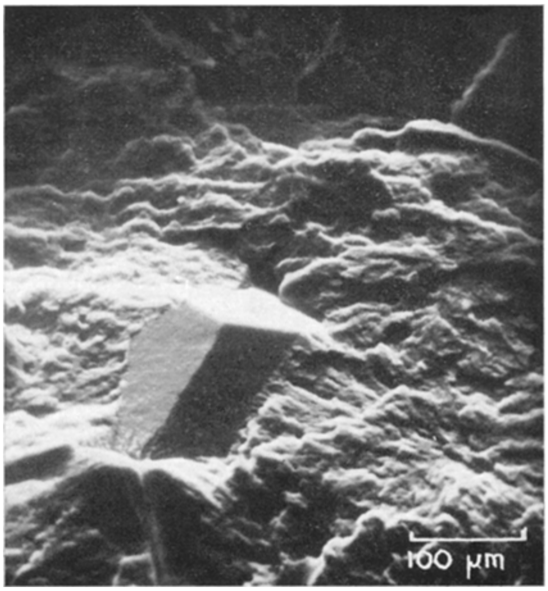

Figure 7 Interspherulitic fracture in brittle region for intermediate-spherulite-radius specimen. Stereoscan micrograph.

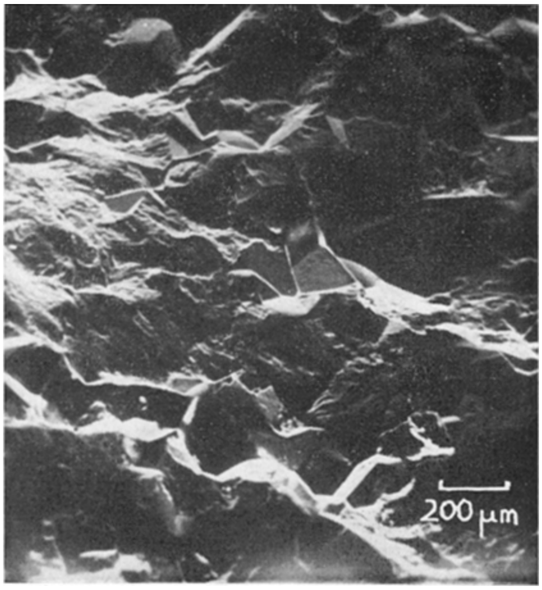

Figure 8 Highly-faceted surface produced by the fracture of specimens with large spherulites. Stereoscan micrograph.

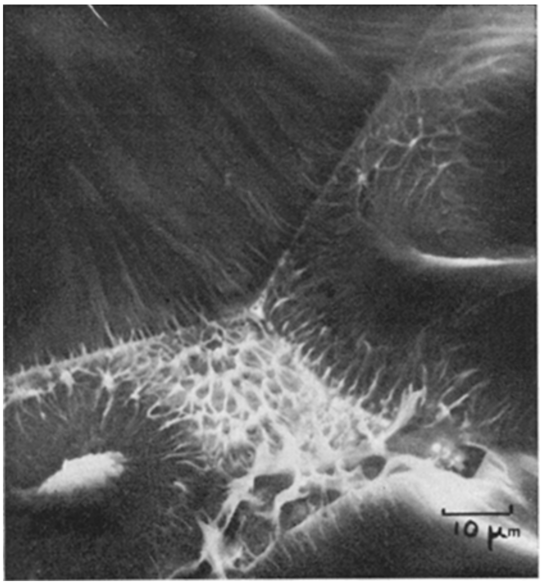

Figure 6 "Coronet" type of initiation showing interspherulitic links and voids at boundaries. Stereoscan micrograph.

is also some evidence that primary initiation can occur at spherulite boundaries lying perpendicular to the stress. Once a crack has started, deformation appears to be restricted to the width of one spherulite along the stress direction, although the spherulite crazes severely before drawing. This kind of crack growth, whereby crack formation is slow and narrowly confined to a plane perpendicular to the stress and little affected by spherulite orientation, suggests that the whole structure is uniformly strong and that a substantial stress concentration is required for deformation to occur. This state corresponds to the maximum in the yield stress versus spherulite radius plot.

The deformed spherulites when viewed in polarized light were seen to have their fibrils re-orientated to lie along the drawn peaks of the fracture surface, in addition to the more common mode of deformation by crazing within the spherulite. This re-orientation of the fibrils shows the probable continuity of the fibrils under slow strain conditions.

Fig. 6 shows links bridging spherulite boundaries and voids between these links. It was not possible to see any voids in an optical study on thin, undeformed sections of the intermediate-spherulite-radius specimens. This was to be expected since the resolution obtainable using polarized light optical microscopy is not sufficient to show the existence of voids of this size. At the larger spherulite radii, definite cracks were found between the spherulites in undeformed specimens. By extrapolation this suggests the existence of some voids at the intermediate spherulite radii.

Microtomed sections of fractured, larger-spherulite specimens showed that fracture was indeed interspherulitic (Fig. 9), with the only plastic deformation being a highly-drawn (white) region immediately adjacent to the fracture surface. This would account for the dimpled surfaces seen on the polyhedrons in the Stereoscan. The dimples are presumed to be due to the drawing and fracture of the interspherulitic links.

5. Discussion

The changes in the deformation characteristics of the specimens as the spherulite radius increases can be explained in terms of differences in impurity segregation, contraction on crystallization and crystal growth arising from the different cooling rates during moulding.

At the faster cooling rates, there is not enough time for significant segregation of low molecular weight species or uncrystallizable impurities, and, consequently, these are spread throughout the microstructure. Contraction during and after solidification is similarly accommodated. For these specimens, therefore, deformation is mainly dependent on lamellar size and configuration [6]. As the cooling rate decreases, the crystallinity increases. The crystallinity was determined using a density gradient column and assuming a linear relationship between density and crystallinity. Fig. 10 shows the relationship between spherulite radius and, hence, cooling rate and crystallinity. The increased crystallinity should lead to greater stiffness and strength as found in

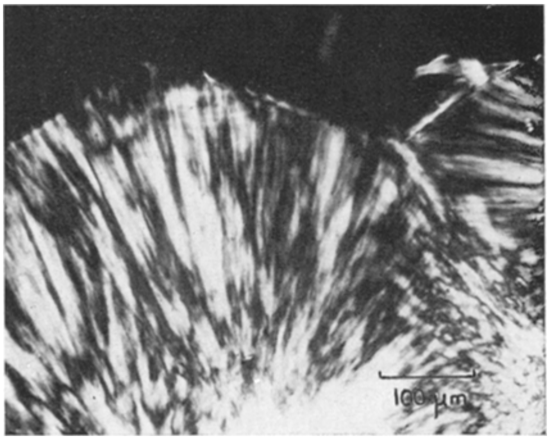

Figure 9 Microtome section through interspherulitic fracture surface showing a thin, highly-drawn surface layer. Transmission optical micrograph with polarized light.

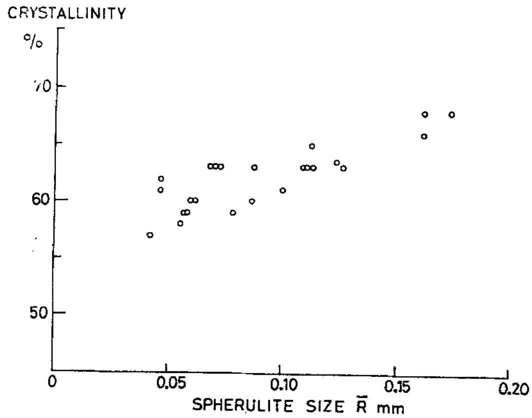

Figure 10 Plot of crystallinity (determined using a density gradient column) against spherulite radius.

rubbers [3]. However, the slow cooling results in more time for segregation effects and presumably this leads to spherulite boundaries with a higher concentration of low molecular weight polypropylene and any other impurities. Also, there may be as much as 10% contraction on crystallization to be accounted for [7].The overall effect is that the boundaries are weakened by the presence of ductile material and voids. The voids are considered to be the major factor in the interspherulitic fracture of the large-spherulite specimens. The amorphous nature of the boundaries is shown by the localized drawing seen in parts of the initiation region and in the interspherulitic fracture surfaces.

At intermediate spherulite radii, the formation of initiation regions is considered to be partly due to the defects in the surface and partly due to the occurrence of the occasional boundary which is weaker than the general spherulitic structure, hence acting effectively as a defect. As the spherulite radius increases, the boundaries become weaker and less and less of the strain is accommodated by spherulite deformation but rather by boundary yielding and cracking. This accounts for the rapid drop in the yield stress.

The σ_Y/ϵ_Y ratio drops significantly at the intermediate spherulite radii because the formation of the ductile opaque planes results in large localized yield and an overall drop in the ratio.

By analogy to Lüders bands it may be expected that localized plastic deformation only occurs after the yield point has been reached, in other words the σ_Y/ϵ_Y ratio would not be affected. However, the σ_Y/ϵ_Y ratio does drop considerably over a particular spherulite radius range and it is the same range over which the ductile opaque planes were observed to appear in the gauge length as the yield point was passed. Since the yield stress varies in a continuous manner, a decrease in σ_Y/ϵ_Y to the extent shown in Fig. 3 means that the yield strain increases substantially (roughly 60%). As the spherulite radius increases, the only obvious change in deformation characteristics is the change from homogeneous yielding and drawing to very localized deformation along particular planes, and it is felt that it is this which is contributing to the greatly increased yield strain. Although these planes were only noted at the yield stress, it is very probable that they were initiated considerably before this but only grew slowly and on a small scale, so were not visible. It is possible that the energy required to deform the spherulites and to form these localized yield regions is similar and so the two processes go side by side. However, it results in greater strain than if the spherulites deformed on their own. As the yield strain is reached, decohesion occurs in the planes and much larger voids are found, making the regions visible, and the plane becomes unstable and grows rapidly in length and width with an associated drop in the load. This change in form between small regions of oriented material to a voided, craze-like structure is probably related to an energy balance. There are two problems associated with this kind of explanation, both related to the range of structures liable to be found in any polymers. Firstly, why are the opaque planes only seen at the yield stress? Variation in the structural integrity of the moulding might be expected to result in the formation of one or more of these planes before the yield stress is reached. Secondly, why is there apparently such a sharp change in the σ_Y/ϵ_Y ratio? It might be expected that the yield strain would increase progressively as the energy conditions for plane formation became more favourable. To answer both these questions it must be postulated that the conditions for the formation and growth of these planes are very critical, and that these conditions only occur at a limited minimum spherulite radius range. This in turn implies a large degree of reproducibility and uniformity of structures resulting from the moulding technique.

As the spherulite radius increases, the σ_Y/ϵ_Y ratio starts to increase again because the amount of plastic yield prior to failure decreases. However, it must be remembered that the yield stress is also dropping, though more slowly. Eventually, the stiffness is very high because there is very little plastic deformation before fracture. Unfortunately, the yield stress is then so low as to make the material worthless, but it does perhaps indicate the high stiffness and associated probable yield stress of the individual spherulites when cooled slowly.

The yield stress curve is thus considered to be a result of two contributions; the microstructure effect, in which slower cooling results in greater crystallinity and so greater spherulite strength; and the spherulite boundary effect, whereby the boundaries become progressively weaker owing to impurity segregation and voiding. This is shown diagrammatically in Fig. 11.

6. Conclusions

The work reported here shows that under

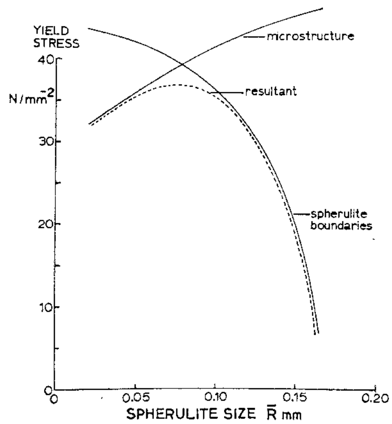

Figure 11 Graph showing the possible component parts of the yield stress versus spherulite radius curves.

normal cooling conditions an average spherulite radius $\bar{R} = 0.08$ mm, produced by a cooling rate of 0.03° C sec^{-1}, gives the optimum tensile properties for this variety of isotactic polypropylene. Slower cooling rates result in the segregation of impurities and the formation of contraction voids at the boundaries, consequently weakening these regions and having a detrimental effect on the whole structure. Increasing the moulding pressure from 1.4×10^7 to 3.5×10^7 N m^{-2} did not significantly reduce this voidage. The implication is that the potential strength of slow-cooled spherulites is large but the problem is boundary cohesion. Various heat-treatments have been tried to strengthen the boundaries but only with moderate success. There is a basic incompatibility between a slow growth rate to produce a highly crystalline material, and a large number of spherulites (and hence, less segregation at any one boundary). Another approach is to use nucleating agents. However, nucleation and growth would then start at a higher temperature and one would not get the slow-cooled "cross-hatched" microstructure that has been shown previously [6] to be advantageous.

Thus, it has been shown that for polypropylene the yield stress goes through a maximum when plotted against the spherulite radius for the radius range 0.04 to 0.16 mm. We believe this to be a general effect which will occur for any crystalline thermoplastic which has a nucleation rate sufficiently low to produce relatively large spherulites. The highest value for the yield stress will then occur at the crossover point of the two effects shown diagrammatically in Fig. 11. For the polyethylenes, the spherulites are so small that there is no significant segregation of impurities or voids. For the nylons, the reported drop in yield stress with spherulite diameter could be because the maximum in the curve has been passed.

It might be thought that the spherulite size in polymers is equivalent to the grain size in a metal and that the variation in yield strength at the large spherulite size is analogous to the Hall-Petch relation for metals [8]. This relation states that the yield stress is inversely proportional to the square root of the grain size. However, a metal can be considered as a continuous matrix with the grain size representing free slip distances. The deformation mechanism in polymers is quite different since the long chain nature and low crystallinity of these materials prevent the kind of dislocation movement that is prevalent in the deformation of metals. For polymers the decrease in yield strength represents a gross weakening of the boundaries rather than an easing of the deformability of the spherulite; in fact the opposite is considered to be happening: spherulites get progressively stronger with size.

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