STRUCTURAL CHANGES IN THE PREPARATION OF ULTRA-HIGH MODULUS POLYETHYLENE

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Abstract - The attainment of ultra-high moduli in polyethylene is characterised by drastic changes in the crystal size distribution. As the deformation ratio increases, the original crystalline lamellae become linked by an increasing number of crystal bridges. Results from GPC and shrinkage experiments were used for the detailed structural analysis of products with different draw ratio and processing history.The implications of the findings in terms of an improved understanding of the deformation process were also discussed.

INTRODUCTION

In the past decade the preparation of ultra-high modulus polyethylene has been achieved by a variety of processes including solid-state deformation and solution spinning (1). The results to be presented in this note relate specifically to two processes of the former class i.e. cold drawing and hydrostatic extrusion.

A common feature of the ultra-high modulus materials produced by these two routes is the extremely high levels of plastic deformation, typically of the order of 20:1 or greater. The achievement of these remarkable deformation ratios prompted a revision of the traditional concept of "natural" draw ratio as a parameter which depended solely on the nature of the polymer and assumes values in the range 4 to 10. Also it became soon apparent that the properties of the ultra-drawn products could not be interpreted simply in terms of molecular and crystal orientation. Drastic structural changes were to be identified as the cause of their peculiar processing behaviour and performance.

DEFORMATION AND STRUCTURAL CHANGES

Broad-line NMR (2), birefringence (1) and X-ray diffraction (2) measurements indicate that significant changes in amorphous and crystal orientation only occur up to deformation ratios of approximately 15. Thus orientation effects cannot explain the linear dependence of the modulus upon draw ratio (3) up to draw ratios (λ) as high as 40. On the other hand Clements et al. (4) found that a correlation exists between λ and the longitudinal crystal thickness as determined by wide-angle X-ray diffraction experiments. The most surprising aspect of the finding was that the average crystal size can be well in excess of the "long period" which is calculated from the small-angle X-ray scattering pattern. Crystal sizes of the order of 600 Å i.e. over three times the value of the "long period", were measured for the highest draw ratio samples. The results were also consistent with the melting behaviour of the ultra-drawn products (5).

On the basis of the X-ray evidence,a structural model was proposed (6) which associates the deformation process with the development of crystal continuity. The conventional crystalline lamellae, which give rise to the "long period" are still present throughout the process. However, as the deformation proceeds, crystalline bridges are formed between adjacent lamellae and their concentration increases with draw ratio. Such a structural model can explain satisfactorily not only the draw ratio dependence of the Young's modulus but also the high thermal conductivity of ultra drawn products (7). Moreover it provides a new framework for analysing the process of plastic deformation.

A limitation of the X-ray diffraction method is that it can only provide the weight-average crystal size. Attempts to measure the full crystal size distribution were therefore made using other techniques i.e. low frequency laser Raman spectroscopy (8) and nitric acid etching (9) combined with gel permeation chromatography (GPC).
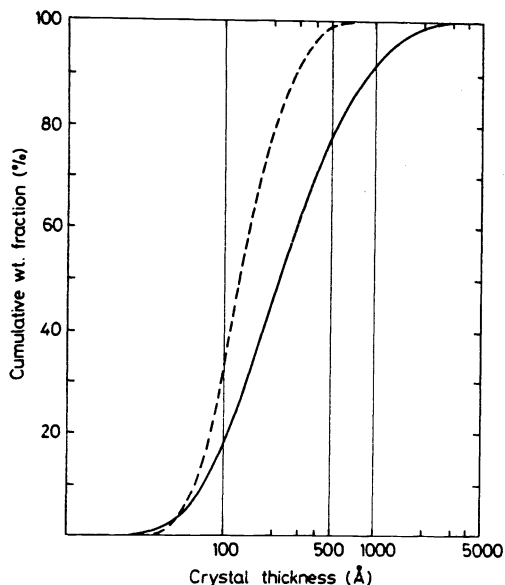
Fig. 1 GPC crystal thickness results for a Rigidex
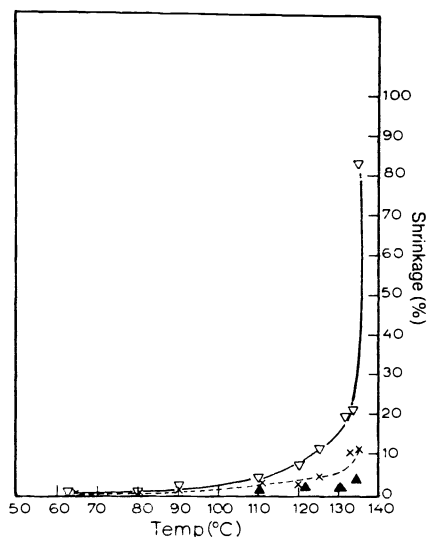50 sample drawn to (- - -) λ = 11 and (——) λ = 20
(Ref. 9)

Fig. 2. Shrinkage behaviour of Rigidex H020-54P
samples drawn to (∇) λ = 11, (χ) λ = 20 and (Δ)
λ = 25-30 (Ref.10).

The GPC cumulative crystal thickness distribution for a low (λ = 11) and a high (λ = 20)
draw ratio samples are shown in Fig. 1. Whereas at λ = 11 the maximum crystal thickness
is 600-700 Å, values as high as 4000 Å are measured for the λ = 20 material. The marked
divergence of the two curves suggests that during the drawing process the small crystals
present at low λ melt and recrystallise to form larger crystals. Some amorphous material
must also undergo crystallisation to account for the increase of crystallinity on drawing
(2).

An important implication of these structrual changes is the enhanced dimensional stability
of the ultra-drawn samples (10). The shrinkage behaviour of high molecular weight samples
(M_w = 312000) is plotted in Fig. 2, as a function of temperature and draw ratio. At the
highest draw ratios (λ = 25-30) the shrinkage at 135°C is a mere 5-7% compared with 85% for
the low draw samples. Also, the shrinkage stress is very high i.e. 15 MPa, and practically
complete reversibility is observed in cycles with an upper temperature limit of 80 - 100°C
(10).

Within this context it is interesting to note that full reversion is achieved when the
samples are exposed to a temperature (150°C) well in excess of the crystalline melting
temperature (Fig. 3). This memory effect indicates that at least part of the molecular
network has undergone the same deformation as the bulk sample (10).
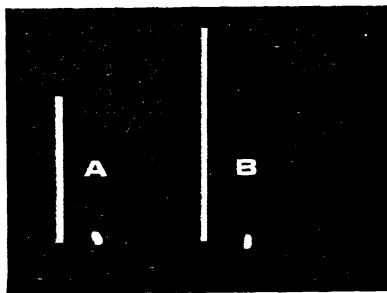

Fig. 3. Results of the reversion experiments at 150°C
on samples of Rigidex 140-60 drawn to (A) λ = 11 and
(B) λ = 20 (Ref.10).

POLYMER AND PROCESSING PARAMETERS

The crystal thickness distribution for a low ($\overline{M}_w$ = 101000) and a high ($\overline{M}_w$ = 312000) molecular weight sample drawn to λ = 25 in identical conditions is shown in Fig. 4. The data were derived from GPC measurements (9).
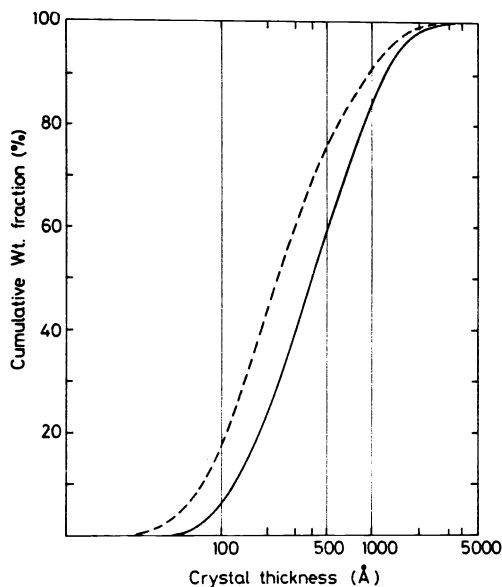

Fig. 4.   GPC crystal thickness distributions for
(---) low and (——) high molecular weight samples
drawn to λ = 20-25.

There is a significant difference between the two sets of results, the higher molecular weight sample exhibiting a broader distribution of crystal thicknesses .It has been suggested (9) that the effect could be a consequence of differences between the original crystal size distribution of the samples. This in turn would relate to the molecular weight dependence of the crystallisation kinetics. The GPC evidence is in accord with the melting and superheating behaviour of these samples (5) and with spectroscopic determinations (8).

The features described above do not seem to affect the small-strain mechanical properties (3). Nevertheless the polymer molecular weight has a great influence on the drawing behaviour (3) and on the tensile creep properties of the ultra-drawn samples (11). Therefore the results just described could be relevant to a fine analysis of the latter properties.

No appreciable variation of the crystal thickness distribution with draw temperature was found (9). It is well known the "long period" (small-angle X-ray scattering) increases with draw temperature (12) and this is often interpreted as a sign of an increase in average crystal size. However it was pointed out (9) that the interpretation of the small-angle X-ray diffraction pattern is not without ambiguity. It was therefore concluded that the draw temperature though not affecting the general features of the "crystalline super-structure", influences the large scale reorganisation of the crystalline and non crystalline phase in a way which is reflected by the changes in "long period".

CONCLUSIONS

The production of ultra-high modulus polyethylene by solid state deformation is linked to profound structural changes. As the draw ratio increases, an increasing number of crystal bridges develops between adjacent lamellar crystals. The resulting crystalline continuity explains some of the remarkable properties of these materials e.g. stiffness, thermal conductivity and high melting temperature, and hence it should be seen as a key element of an effective deformation.

Some general considerations about the plastic deformation process can also be made in the light of findings described above. It is established that for a highly crystalline polymer - like polyethylene - it is advantageous to perform the deformation in the region of the α-relaxation. The purpose is to exploit the enhanced plasticity of the crystalline regions. Thus a first criterion is automatically introduced to choose a reasonable processing"window" i.e. a temperature and rate regime, for good deformability. The structural changes discussed above, on the other hand, mainly depend upon selective crystallisation and provide a very effective means of locking extremely high levels of crystal and amorphous orientation. Therefore the competition between the crystallisation kinetics and processes of molecular relaxation as well as the crystal-crystal interfacial morphology should also be considered in the search for the optimum polymer-processing combination.

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