Letters

Fibrillar structure of ultra-oriented polyethylene

It has been reported recently[1–3] that by a novel approach to the drawing process of polymers ultra-high modulus polyethylene can be prepared. The discovery raises the very important question of the structure of the new products and how this compares with that of conventional (low draw) materials. Experimental evidence has been produced suggesting that for drawn as well as hydrostatically extruded[4] ultra-high modulus polyethylene the deformation pattern is consistent with the Peterlin model for the plastic deformation of semicrystalline polymers[5]. According to this model a major morphological transition occurs in the early stages of the deformation when the original spherulitic texture is destroyed and replaced by a new fibrillar structure. Further straining of the sample results in chain unfolding and increased orientation of both crystalline and non-crystalline material. Previous work has already shown that the uniqueness of the relationship between Young's modulus and draw ratio established for low draw samples[6] is surprisingly maintained even at the highest draw ratios now attainable[1,3]. Furthermore it has been proved that this relationship does not depend in first approximation on molecular weight, the thermal history of the polymer and the processing conditions[3]. However it has also been demonstrated that the large strain properties such as creep are extremely sensitive to the details of the sample structure which in turn relate to differences in molecular weight and processing route, i.e. a unique relationship between mechanical properties and draw ratio no longer applies[7]. For this reason it is necessary to extend the characterization of these materials as far as possible. It is of particular value to examine these high stiffness fibres with the electron microscope in order to obtain indications on the bulk morphology as well as direct information on the surface topography; the latter may be of direct interest in view of the possible applications of these products for reinforcement.

In this Letter we wish to report the most significant findings of a preliminary investigation using the scanning electron microscopy (SEM) technique. The linear polyethylene (LPE) used was Rigidex type 140–60 (BP Chemicals); the preparation and properties of samples drawn to different draw ratios ($\lambda = 14$ to 30) have been described in an earlier publication[1]. The free surface of the sample was coated with Au/Pd; electrical contact between the metal holder and the sample surface was accomplished by a thin film of aluminium paint (such a procedure is necessary to prevent charging up effects). A JEOL JSM 15 electron microscope was used and the scanning frequency on observation was 0.1 sec^{-1}. Magnifications up to 10K were obtained.

The first important feature highlighted by the results in *Figure 1a–1f* is that all the samples exhibit a clear fibrillar structure and in general the fibrils do not exceed 1 μm in diameter. Secondly it is noted how the average size, size distribution and uniformity of such fibrils are markedly dependent upon the draw ratio. At low λ the fibrils appear more homogeneous in diameter, with a smoother surface and a high degree of longitudinal continuity. By contrast at the highest λ (*Figures 1e, 1f*) much finer fibrils are present which are also characterized by an amazingly

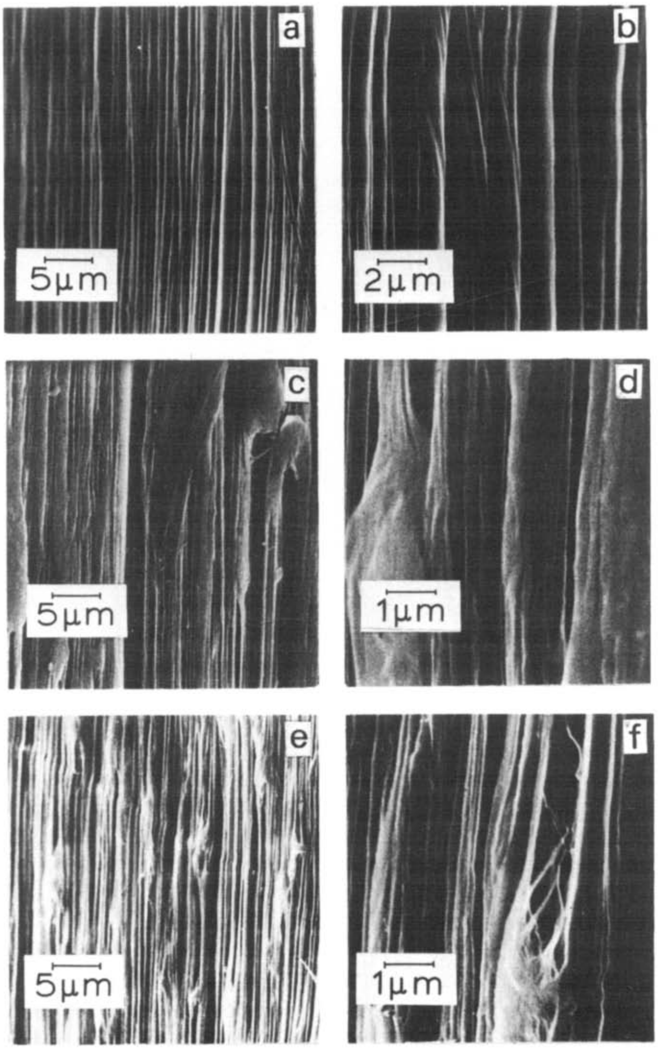

Figure 1 Scanning electron micrographs of LPE samples drawn to $\lambda = 14$ (a, b); $\lambda = 20$ (c, d); $\lambda = 30$ (e, f)

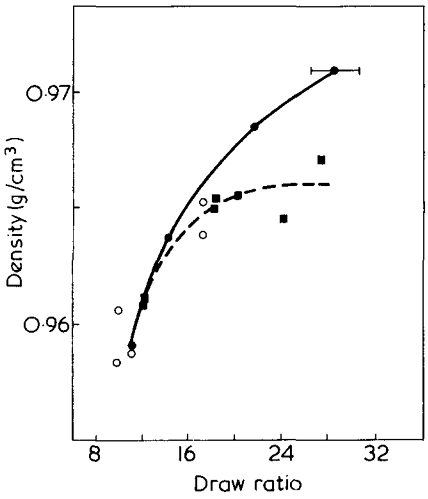

Figure 2 Density (at 23°C) vs λ for samples of Rigidex type 140–60 (●); 50 (■); 25 (○)

high concentration of longitudinal discontinuities in the form of ruptures.

The third feature worth noting is the presence of longitudinal voids of up to 0.5 μm in width which appear to be present at both low and high λ.

The latter observation has particular relevance in the assessment of density measurements obtained by any flotation method. As shown in *Figure 2* different density/λ relationship is found for samples of different molecular weight (samples 2–4 in ref 1); this is either related to the actual molecular characteristics of the drawn samples or is just a consequence of differences in void size and distribution. The results in this case would merely reflect variations in the diffusion pattern of the solvents used into the loosely packed structure.

A reliable determination of the density is necessary whenever this parameter is used for estimates of sample crystallinity for instance and the present results underline the need for further investigations before a conclusive assessment of the general validity of the density determinations as a means of structural evaluation.

In conclusion we can say that a clear indication has been found for the presence of a fibrillar texture even in ultrahighly drawn samples of LPE. The observed differences in size and homogeneity of the fibrils are consistent with the established views of the plastic deformation of semicrystalline polymers[5] and hence no difference in kind has to be invoked between these samples and conventional highly drawn LPE (λ = 9–10).

The limitations of the SEM technique are obvious and do not allow us to state conclusively to what extent the observed features are part of the surface topography or representative of the bulk morphology. In either case however we believe that they must be taken into account for the important consequences that they can have on other physical measurements.

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References

1 Capaccio, G. and Ward, I. M. *Nature Phys. Sci.* 1973, **243**, 143; *Polymer* 1974, **15**, 233
2 Smith, J. B., Davies, G. R., Capaccio, G. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1975, **13**, 2331
3 Capaccio, G., Crompton, T. A. and Ward, I. M. *J. Polym. Sci. (Polym. Phys. Edn)* 1976, **14**, 1641
4 Gibson, A. G., Ward, I. M., Cole, B. N. and Parsons, B. *J. Mater. Sci.* 1974, **9**, 1193
5 Peterlin, A. *J. Mater. Sci.* 1971, **6**, 490
6 Andrews, J. M. and Ward. I. M. *J. Mater. Sci.* 1970, **5**, 411
7 Capaccio, G. and Ward, I. M. *Proc. PRI Int. Conf. Deformation, Yield, Fracture Polymers Cambridge, UK* 1976

Fluorescence and photooxidation of commercial polypropylene

Recently, using luminescence techniques we established the presence of α,β-unsaturated aldehydic and ketonic carbonyl impurity groups in commercial unstabilized polypropylene[1–4]. These groups absorb light in the wavelength region above 290 nm which is the region relevant to the mechanism of the sunlight-induced oxidation of the polymer[5], (see *Figure 1*). In *Figure 2* we show a direct correlation between the concentration of these groups and the resultant light stability of the polymer.

In contrast Chakraborty and Scott[6] reported no correlation between polymer photooxidation rate and the initial concentration of α,β-unsaturated carbonyl groups as determined by infrared spectroscopy. Clearly therefore, there is some disagreement as to the exact nature of the α,β-unsaturated carbonyl impurities in the polymer and the role that they play in polymer photooxidation.

From their data Chakraborty and Scott[6] maintain that the main photoinitiating species in polypropylene are α,β-unsaturated hydroperoxide groups and these in turn are photolysed to α,β-unsaturated carbonyl groups. If this mechanism is valid, therefore, it might be expected that in the early stages of photooxidation, or indeed thermal (anaerobic) degradation there should be an increase in the concentration of α,β-unsaturated carbonyl groups. However, *Figure 3* shows that when these processes are monitored by fluorescence spectroscopy a decrease in the concentration of α,β-unsaturated carbonyl impurity groups is observed. At present we suggest that the failure by Chakraborty and Scott[6] to observe

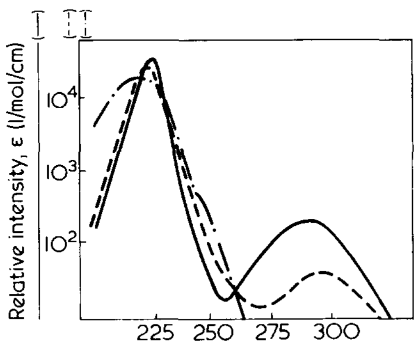

Figure 1 Comparison of the fluorescence excitation spectrum of unstabilized polypropylene film (200 μm thickness) (———) with the absorption spectra[8] of pent-3-ene-2-one (– – –) and 2-butenoic acid (— · — ·) in n-hexane. Fluorescence spectrum was obtained using a double beam Hitachi Perkin–Elmer MPF-4 spectrofluorimeter