JOURNAL OF MATERIALS SCIENCE 11 (1976) 2057–2060

The crystal modulus of ultra high modulus linear polyethylenes

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Attempts have been made to determine the longitudinal crystal modulus for linear polyethylene by studying the change in the 0 0 2 reflection with load for a series of uniaxially oriented films. The specimens examined covered a wide range of draw ratios, and included a number of ultra high modulus films. In low draw ratio specimens, the assumption of homogeneous stress gave a value for the crystal modulus in good agreement with previous work. The results for the ultra high modulus specimens, on the other hand, were more consistent with continuity of strain, although there were still discrepancies which require further study.

1. Introduction

The question of the "crystal modulus" of a crystalline polymer, i.e. the modulus of a perfect polymer crystal is of considerable theoretical and practical interest. Most attention has been given to the longitudinal crystal modulus, which is usually parallel to the molecular chain axis, and therefore the largest in value. Theoretical calculations of this modulus have been made for most of the well-known crystalline polymers, usually based on force constants obtained from spectroscopic data [1–3]. For linear polyethylene (LPE) values ranging between 150 and 350 GPa have been obtained [4, 5], with most recent figures falling around 270 GPa [6].

Several experimental techniques have been used in attempts to measure the crystal moduli. These include Raman scattering [7], inelastic neutron scattering [8], and X-ray diffraction. The X-ray method was first applied by Dulmage and Contois [9], but has subsequently been used by Sakurada and co-workers [10, 11] to measure the crystal modulus of many crystalline polymers, including LPE. In all these studies with the X-ray diffraction method, it has been assumed that the stress applied to the crystalline region is identical with the macroscopic stress applied to the bulk specimen, i.e. that there is homogeneity of stress throughout the specimen. With this assumption the crystal modulus can be immediately calculated from the relationship of the measured crystal strain to the applied stress. For the oriented polyethylenes examined by Sakurada, the results showed good internal consistency and a value of 240 GPa was obtained for the longitudinal crystal modulus, which is in reasonable agreement with the theoretical values quoted above.

These values for the longitudinal crystal modulus of LPE are somewhat higher than the modulus of steel, and have therefore given stimulus to attempts to produce oriented products of this polymer with ultra-high stiffness. Recent work in our laboratory [12–14] has shown that practical methods can be devised for the production of oriented films, fibres and extruded shapes in LPE with longitudinal Young's moduli as high as 160 GPa, measured as a dynamic modulus at 20 Hz and −160° C. It is also possible to produce small strands of polymer with similar properties in an Instron rheometer [15].

This paper describes X-ray diffraction studies, similar to those of Sakurada and co-workers, on a number of oriented films of LPE, including some drawn to very high draw ratios with very high Young's moduli. The results are of interest in providing further information on the crystal modulus, and also because they throw light on the structure of these very highly oriented materials. Wide angle X-ray diffraction and broad line NMR studies [16] show that the crystalline regions of these products are very highly aligned, and that there is a very small mobile fraction. Small-angle X-ray diffraction studies [17] show that the long spacing remains constant with increasing draw ratio, but that the intensity of the diffraction pattern is progressively reduced.

These results suggest that with increasing draw ratio the structure may be changing from the initial sandwich type structure of alternating crystalline and amorphous material (a parallel lamellae structure) to a continuous crystal with defects distributed throughout the material, rather than being concentrated between the lamellae. Alternatively, we can imagine that the interlamellar material is densifying due to the pulling out of chain folds and the production of many tie molecules. It is therefore of particular interest to examine the validity of the assumption of homogeneous stress.

2. Experimental

A stretching jig was designed and built to fit onto the diffractometer table. The experiment required that a load of several kilograms be applied axially to a short tape specimen whose position must not change on application of the load. To this end the loading arrangement consisted of a lever arm and pulley acting through a load cell to the specimen grip, the whole being kept in alignment by linear bearings. The specimen grips were faced with fine emery paper to provide a firm, even grip on the specimen and to prevent it from slipping. For the low temperature measurements a small enclosure of rigid polyurethane foam was mounted around the specimen which was then cooled with a cold nitrogen gas.

The specimens tested were of three different grades of Rigidex linear polyethylene (B.P.C.I. Ltd) of draw ratios and grades as specified in Table I and all were in the form of tapes of cross-section approximately 1.0×0.1 mm and about 40 mm long. Density was determined by direct weighing and measurement and the accuracy in the quoted value was limited by the small size of the specimens.

The basic technique of the X-ray measurements was to determine the Bragg angle of the (0 0 2) reflection as a function of applied load. Difficulties arose owing to the fact that the changes which occurred were only of the order of 0.1%, i.e. changes in 2θ of less than 0.1° which may be compared with the natural line width of around 0.5°.

Fluctuations in the direction of the primary beam during the course of protracted measurement were found to lead to apparent changes in the Bragg angle of the same order as that which would arise from straining the specimen and hence a technique had to be devised to circumvent this.

Time is the essential element here and the following method was used to determine changes in Bragg angle rapidly after applying a load. The counter was set on the side of the diffraction peak at about half maximum intensity and the change in counting rate observed upon application of the strain. In the absence of any change in line intensity and width the change in line position may be determined directly from an analysis of the initial line shape. The line intensity did not remain generally constant, however, owing to beam fluctuations and changes in crystal orientation. There was also the possibility that the line width might change. If, however, two measurements of counting rate change are observed, one on each side of the line, a simple analysis shows that the true shift may be deduced directly from the two observations providing that only the three above effects occur and that they are of small magnitude – which they were.

A series of loads was used with each specimen and the lattice strain determined, being equal to $-\cot\theta \, d\theta$.

In all cases the lattice deformation was found to be elastic and immediate; time-dependent effects which are observed in mechanical measurements were not obtained. Recovery was also immediate and complete.

From a graph of lattice strain versus applied stress a value of apparent modulus could be deduced making the initial assumption of continuity of stress throughout the specimen. That this assumption is, in fact, not valid is shown by an examination of the raw results, which is presented in the next section.

3. Results and discussion

The results obtained for the seven specimens tested are shown in Table II. Column 4 shows the values of the apparent crystal modulus calculated from the crystal strain as a function of the load applied and the initial cross-sectional area of the specimen. These values show a very clear decrease with increasing draw ratio, and also vary between the different polymer grades. As discussed previously [18], the highly drawn specimens

TABLE I

Specimen		NMR mass fraction crystallinity	Measured density (g cm^{-3})	Calculated density (g cm^{-3})
R50	12:1	0.78	0.96 ± 0.03	0.965
	20:1	0.84	0.88 ± 0.04	0.971
	30:1	0.88	0.82 ± 0.05	0.981
R140:60	11:1	0.77	0.90 ± 0.04	0.96
	23:1	0.87	0.86 ± 0.04	0.98
	30:1	0.90	0.70 ± 0.06	0.98
R9	16:1	0.80	0.98 ± 0.03	0.97

TABLE II Apparent crystal modulus values assuming homogeneous stress

Material grade and draw ratio (R = Rigidex)		Specimen* modulus (GPa)	Density (g cm^{-3})	Apparent crystal modulus (GPa)	Apparent crystal modulus (GPa) after correction for voiding
R50	12:1	16.5	0.96	260 ± 30	(no voiding)
	20:1	31	0.88	183 ± 20	208 ± 23
	30:1	68	0.82	140 ± 15	171 ± 18
R140–60	11:1	14	0.90	192 ± 25	213 ± 28
	23:1	40	0.96	142 ± 20	165 ± 23
	30:1	61	0.70	107 ± 11	153 ± 16
R9	16:1	22	0.98	226 ± 20	(no voiding)

* Static 10 sec isochronal creep modulus measured at room temperature.

TABLE III Apparent crystal modulus values assuming strain continuity

Material grade and draw ratio		Apparent crystal modulus after correction for voiding (GPa)	NMR crystallinity	Apparent crystal modulus assuming continuity of strain (GPa)	Crystallinity required to give constant crystal modulus
R50	20:1	208 ± 23	0.84	248 ± 27	0.87
	30:1	171 ± 18	0.88	198 ± 21	0.71
R140–60	23:1	165 ± 23	0.87	190 ± 26	0.69
	30:1	153 ± 16	0.90	170 ± 18	0.64

showed evidence of longitudinal voids when examined by optical and scanning electron microscopy. Further indication of voiding is obtained from density measurements. The results in Table I are consistent with considerable voiding in the Rigidex 50 and 140–60 grade specimens at high draw ratios if it is assumed that the density of the amorphous regions is 0.860 g cm^{-3} and the density of the crystalline regions 1.00 g cm^{-3}. Only in the case of the lowest draw ratio Rigidex 50 and the Rigidex 9 specimens are the measured densities in agreement with those calculated from NMR mass fraction data. Even if the use of the NMR data to calculate the expected density is open to some reservation, it is clear that measured densities in the range 0.70 to 0.90 are quite inconsistent with the likely levels of crystallinity in these specimens, which from a variety of evidence is at least 90%.

We have therefore corrected the apparent modulus values for longitudinal voiding, for all the remaining samples, and show these results in Column 5 of Table II. Although it increases the values of the apparent modulus very significantly, it can still be seen that only in the lowest draw ratio specimens do the results come close to the value of 240 GPa reported previously by Sakurada and his co-workers.

Bearing in mind the small-angle X-ray diffraction results which indicate that the clear lamellar texture of the low draw ratios is no longer evident at these very high draw ratios, we have therefore calculated the apparent crystal modulus on a *continuity of strain* model, i.e. assuming that all the non-crystalline material is in parallel and has a Young's modulus which is so low as to be effectively zero in this situation. These values are given in column 4 of Table III and it can be seen that they do indeed increase considerably, approaching the low draw ratio figure for homogeneous stress. There are still sizeable discrepancies for the highest draw ratio samples, particularly in the case of the 140–60 grade. It was considered instructive to calculate the mass fraction of crystalline material which would be consistent with a constant apparent crystal modulus calculated on this strain continuity model, and these results are shown in the final column of Table III. It will be noted that the results for the high ratio samples are not physically plausible. It does not seem likely that the crystallinity falls to ~ 60 to 70% in these specimens.

4. Conclusions

(1) In the low draw ratio specimens, providing that longitudinal voiding is taken into account, the apparent crystal moduli are in good agreement with the homogeneous stress model and the value of 240 GPa reported previously by Sakurada and his co-workers.

(2) In the ultra high modulus specimens, after correction for voiding, the results for the crystal moduli are more consistent with continuity of strain. However, even with this other extreme assumption, the values obtained still show significant discrepancies from the values obtained in the lower draw ratio materials. This suggests that a more detailed examination of the X-ray diffraction patterns under stress may be rewarding in providing information on the structure of these unique materials. It should be noted that the results depend on the structure of the sample, and this observation has led to a more extensive series of measurements which are now being undertaken. It has recently been found that even in low draw ratio samples the assumption of homogeneous stress does not always hold, and the measured lattice modulus can be much lower than the value obtained by Sakurada.

Acknowledgements

We wish to thank Dr G. Capaccio for his assistance in the preparation of the samples. R. N. Britton was supported by the Science Research Council.

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Received 10 February and accepted 30 April 1976.