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The hydrostatic extrusion of linear polyethylene at high temperatures and high pressures

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An account is given of a series of hydrostatic extrusion experiments which has been carried out on linear polyethylene over a wide range of extrusion temperatures and environmental pressures. The results of pressure-to-pressure hot extrusions, which have been performed on melt crystallised polyethylene and also on pressure crystallised extended chain polyethylene, are discussed, with particular reference to the physical properties of the extruded products.

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1. Introduction

During the last decade, there has been a substantial amount of research devoted to the preparation of very highly oriented flexible polymers, especially linear polyethylene [1]. There have been two major approaches: (a) the production of fine fibres from polyethylene solutions either directly under conditions of extensional flow [2] or by gel-spinning and drawing [3]; and (b) the deformation of the bulk polymer by tensile drawing [4], ram extrusion [5, 6] hydrostatic extrusion [7] or die-drawing [8]. In all cases the experimental situation has been fairly well-defined and the mechanism of molecular alignment and production of high-modulus materials is, therefore, reasonably well understood. There are also some rather more complex situations, notably pioneered by Porter and his colleagues [9], where oriented polyethylenes have been produced under conditions of high pressure and high temperature, where the experimental conditions have not been so clearly defined. Consequently, the relationship of the structure and properties of the extrudates to the extrusion conditions is less well understood.

The present paper describes research which has been carried out in this rather complex regime of high pressure and high temperature, with complete monitoring of the pressure and temperature at all times. The basic experiment is a pressure-to-pressure hydrostatic extrusion of either conventional melt-crystallized polyethylene or pressure-crystallized chain-extended polyethylene to a fixed extrusion ratio. A particular point of interest has been to try to perform the hydrostatic extrusion under conditions where the polyethylene is maintained in the hexagonal phase identified by Bassett and co-workers [10, 11], i.e. at temperatures above about 230° C, at a pressure greater than about 4 kbar.

These experiments have, therefore, produced oriented polyethylenes by three routes:

1. hydrostatic extrusion, at a range of ambient hydrostatic pressures and different extrusion temperatures, of melt-crystallized polyethylene;
2. hydrostatic extrusion, where melt-crystallized polyethylene is taken into the hexagonal phase regime, where a pressure differential is then created, so that deformation occurs within this regime;
3. hydrostatic extrusion of pressure-crystallized chain-extended polyethylene.

In all cases the extruded products have been characterized by determination of axial Young's modulus, density, melting point, long period and

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the average crystal length. These results will be discussed in the light of previous results obtained for materials produced by the deformation of bulk polyethylene crystallized at atmospheric pressure [1].

2. Experimental procedure

2.1. Extrusion equipment

A special purpose high pressure/extrusion facility was designed and developed for all the polymer deformation studies described in this paper. The original design specification for this facility was that it should be capable of containing and controlling pressures up to 5 kbar at working temperatures up to 275° C. In the actual test programme it was not required to operate beyond pressure and temperature levels of 4.8 kbar and 235° C, although it operated satisfactorily under these conditions.

A diagram of the principal high-pressure tooling, as set up for a pressure-to-pressure hydrostatic extrusion experiment is shown in Fig. 1. It comprises two pressure vessels, one to contain the billet and the second to receive the extrudate. Both of these vessels have threaded connections so that they can be screwed together and thereby clamp the extrusion die firmly in place. Relatively easy separation of the two vessels is required in order to provide ready access to the die and the polymer workpiece. Each of the vessels is shrouded in a separately controlled heater band which enables a uniform billet and tooling temperature within ± 2° C to be maintained. The main dimensional details of the pressure components are:

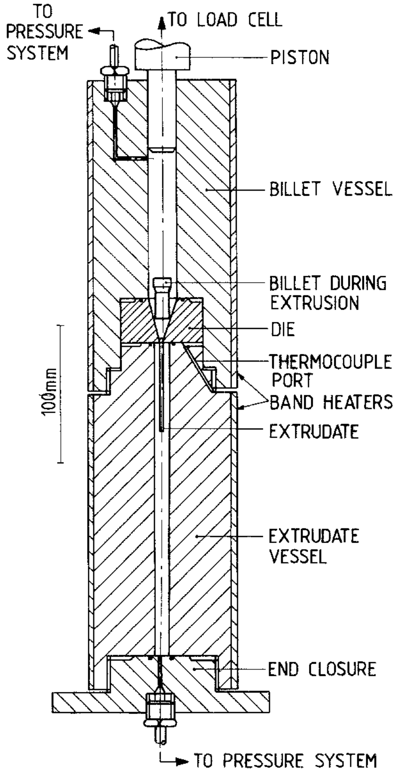

Figure 1 Apparatus used for pressure-to-pressure hydrostatic extrusion.

billet vessel:	bore diameter 20 mm, active bore length 170 mm;
extrudate vessel:	bore diameter 8 mm, active bore length 220 mm;
extrusion dies:	three dies having bore diameters of 2.5, 3.1 and 5 mm have been used, the die semi-angle is 15° in each case.

The above dimensions accommodate the production of extrudates of up to 170 mm reliable length produced at extrusion ratios up to 20:1 and with diameters in the range 2.5 to 5 mm.

Two pressurizing fluids have been used throughout; castor oil for the lower temperature work (i.e. up to 200° C and silicone fluid (DC 550) at higher temperatures. The pressurization of these fluids is achieved in two ways. An air-driven hydro-pump, capable of producing a stall pressure of 5 kbar when using air at 8.5 bar, is used to prime the system, i.e. to create an appropriate starting pressure in both vessels with a billet held in the die by a slight pressure drop across the die. A piston mounted in the upper vessel closes off this vessel and is used to generate the additional differential pressure across the die which is required in order for extrusion to occur. Since the whole apparatus is mounted in the compression zone of a 500 kN screw-driven universal testing machine, the displacement of the piston can be set at a controlled rate and both displacement and the compressive load on the piston can be accurately monitored. Transducers and instrumentation are also provided to continuously record the pressure in each of the vessels and the tooling temperatures, particularly in the vicinity of the die. A system of small-bore high-pressure piping together with control valves enables separate parts of the high-pressure system to be isolated as necessary. A high-pressure reservoir connected to the extrudate vessel ensures that the pressure rise in this vessel as a result of the fluid being displaced by the extrudate is negligible.

The relatively high temperatures and pressures used in the apparatus represent severe conditions for the static and dynamic seals used around the die and piston, respectively. The solution chosen for both of these problems is to use an O-ring/mitre ring combination and to accept that one or more of these rings may require replacing after a few operations. The O-rings are manufactured from Viton which is capable of withstanding temperatures up to 250° C.

A typical experiment with the high-pressure facility commences with the assembly of the tooling with a billet pressed lightly into the die and the system filled with oil and suitably bled. The hydropump is then used to raise the oil pressure in both vessels to the required mean value; always ensuring that the billet vessel holds a slightly higher pressure than that in the extrudate vessel. The band heaters are then energized and controlled to achieve the desired operating temperature. During this period the piston is held at a fixed position and the tendency for a rise in the fluid pressure in both vessels, due to thermal expansion, is offset by the use of the relief valves. On achieving the desired temperature and mean pressure conditions – generally after a period of 3 to 4 h – the extrusion is performed by movement of the piston. The piston speed can be set at any value up to 20 mm min^{-1}, but for the benefit of the present experiments it was usually held at > 1 mm min^{-1}. The travel of the piston is the only means of interpreting the progress of an extrusion since it is not feasible to fit displacement transducers within the pressure vessels. However, this indirect method proves adequate for most extrusion conditions. In the particularly difficult situations, when, because of a large extrusion ratio, the extrudate length needs to be limited so as not to reach the bottom of the extrudate vessel, the expedient of giving the billet a stepped larger diameter at its rear end is used. On completion of the extrusion the pressures in both vessels are equalized to the original mean back-pressure value and the heaters are switched off. The whole assembly is allowed to cool at constant pressure by moving the piston so as to overcome the pressure drop due to thermal contraction. Once the temperature has reached 80° C the pressure is released and on removal of most of the pressurizing fluid the vessels can be separated and the die and polymer sample can be retrieved.

2.2. High-temperature high-pressure experimental programme

The polyethylene material used throughout the experimental programme has been Rigidex R006-60, which is a Phillips-type ethylene homopolymer manufactured by BP Chemicals Ltd. It has a melt flow index of 0.6 with $\bar{M}_n = 25\,000$ and $\bar{M}_w = 135\,000$. This grade of linear polyethylene has been widely used for solid state deformation studies.

The programme of extrusion experiments was comprised of two parts:

1. a series of extrusions at medium temperatures in the range 100 to 200° C using back pressures capable of ensuring that solid-phase extrusion occurs. The aim of this work has been to study the effect of under cooling due to environmental pressure on both the extrusion process and the extrusion products;

2. a series of experiments performed at temperatures above 200° C to study the extent to which extended-chain crystallization might be achieved in or influenced by the high-pressure hydrostatic extrusion process. The experiments in this series can be further categorized into two classes: those which have been aimed at extending the high-pressure high-temperature conditions of (1) in an effort to obtain solid phase extrusions with the polymer material in what is deemed to be the hexagonal phase, and those aimed at studying the effect of a pre-extrusion or post-extrusion high-temperature, high-pressure anneal on the properties of the extrusion products.

2.3. Testing of extrusion products

Characterization of the products of the various extrusion experiments is an important feature of the experimental programme. This has been achieved through performing a series of standard mechanical and physical tests on the extrudates. These tests include three-point bend tests for evaluation of axial Young's modulus, techniques of density gradient column and differential scanning calorimetry (DSC) for density and melting point determination respectively, wide-angle X-ray scattering (WAXS) for assessing orientation and crystallite thickness, and small-angle X-ray scattering (SAXS) for measurement of long period.

3. Experimental results

3.1. Extrusions with back-pressure at intermediate temperatures

The criterion for a successful extrusion for this range of temperatures (100 to 200° C) is that the back-pressure, and hence the mean hydrostatic pressure superimposed on the deforming workpiece, should

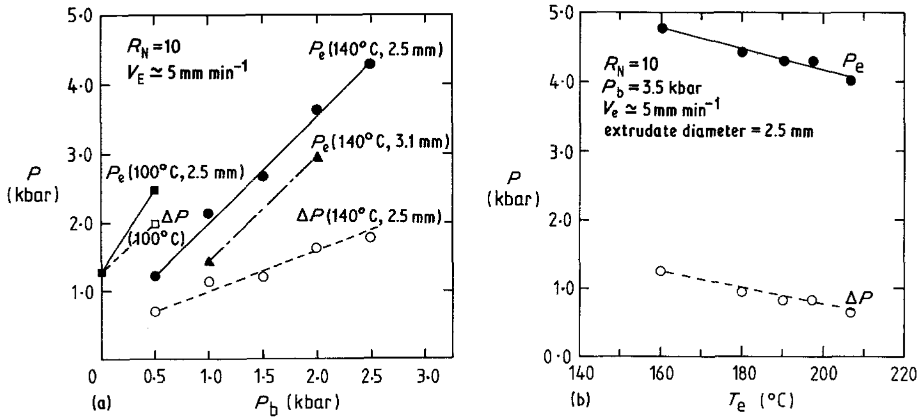

Figure 2 (a) Extrusion pressure, p_e, and differential pressure, Δp, plotted against back-pressure, p_b, at different temperatures and extrudate diameters. (b) Extrusion pressure p_e, and differential pressure, Δp, plotted against extrusion temperature, T_e, for constant back-pressure $p_b = 3.5$ kbar.

be sufficient to ensure that the polyethylene remains in the solid state regime. At least 30 extrusion experiments have been performed within this regime, covering back-pressures up to 3.5 kbar. This series of experiments was prefaced by a number of extrusion experiments with and without back-pressure at temperatures below the melting point of the polyethylene. These serve to provide datum information on the extrusion behaviour of the 006-60 polymer.

In evaluating the influence of the back-pressure on the hydrostatic extrusion process, one of the most significant process variables is the relatively steady-state differential pressure (Δp) which is required in order for extrusion to occur. Figs. 2a and b show examples of how this differential pressure varies as a function of back-pressure (p_b) and extrusion temperature (T_e), respectively, for constant values of extrusion ratio (R_N). In both cases the variation is approximately linear and shows the expected trends implied by undercooling. i.e. at constant temperature higher back-pressures lead to increasing values of Δp. This same linear variation with increased temperature is shown in Fig. 3, although this graph also indicates the influence of extrusion ratio and back-pressure. The influence of undercooling on the differential pressure Δp is summarized in Fig. 4 for two different extrusion ratios ($R_N = 10$ and $R_N = 20$) and for a range of different combinations of extrusion temperature and back-pressure. In order to derive the appropiate values of the undercooling ($T_m - T_e$) advantage has been taken of the work of Bassett and Turner [10] who have produced experimental values for the variation of melting point (T_m) with pressure for a similar grade of polyethylene to that used in the present work. The results presented in Fig. 4 suggest that the different temperature and back-pressure conditions can be reduced to a single parameter – that of undercooling. When the degree of undercooling is very low (< 10° C), the extrusion behaviour becomes virtually independent of extrusion ratio and a small differential pressure of less than 0.75 kbar is sufficient to cause extrusion to occur.

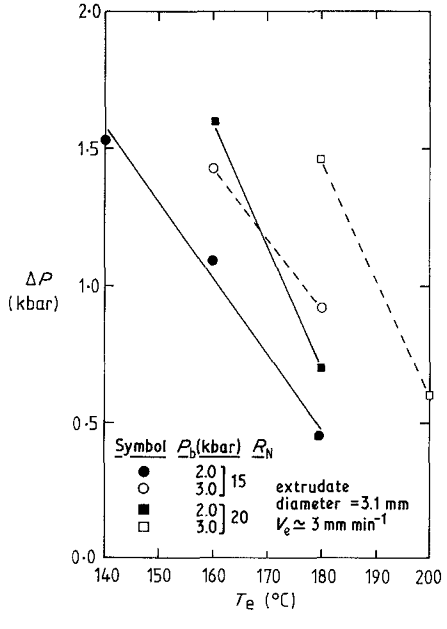

Figure 3 Differential pressure Δp as a function of extrusion temperature, T_e, for different extrusion ratios and back-pressures.

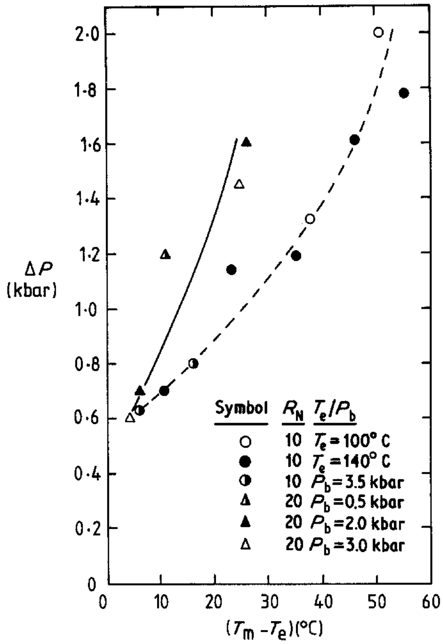

Figure 4 Influence of undercooling ($T_m - T_e$) on differential pressure, Δp, for different extrusion conditions.

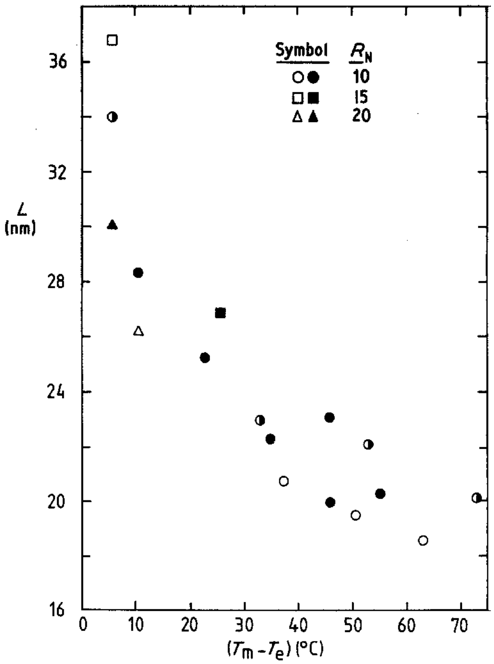

Figure 6 Influence of undercooling ($T_m - T_e$) on long period, L, for different extrusion conditions.

Characterization of the extrudates achieved in this regime of temperature and pressure shows considerable similarity with the products achieved in conventional hydrostatic extrusion (i.e. 100° C and zero back pressure.) Some of the principal features of the product properties are shown in Figs. 5 to 7 and in Table I. The results of axial modulus measurements as obtained from three-point bend tests performed on extrudates produced under different conditions of pressure temperature and die size are shown in Fig. 5. The variation of modulus is seen to be principally a function of the extrusion ratio and is almost independent of other process

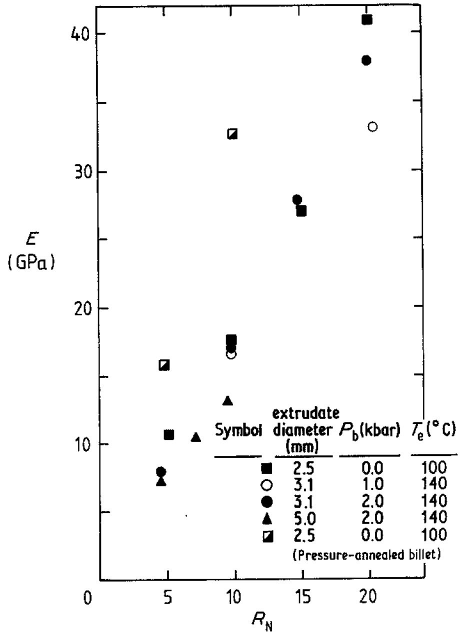

Figure 5 Variation of axial Young's modulus, E, with extrusion ratio, R_N, for various extrusion conditions.

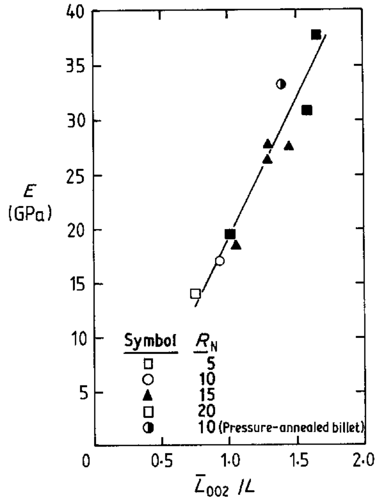

Figure 7 Variation of axial Young's modulus, E, with crystal thickness/long period ratio $\bar{L}_{002}/L$ for various extrusion ratios.

TABLE I Summary of properties of some extrudates of low pressure-to-pressure extrusions

Sample	R_N	Extrusion conditions		Modulus, E (GPa)	Melting point, T'_m (° C)	Density (g ml^{-1})
		P_b (kbar)	T_e (° C)			
L1	10	0	100	17.5	136.5	0.976
L2	10	0.5	140	15.9	136.5	0.971
L3	10	2.0	140	18.5	136.3	0.967
L4	10	3.5	180	17.1	135.9	0.968
L5	10	3.5	216	*	139.1	0.981
L6	20	2.0	140	37.8	137.8	0.973
L7	20	2.0	160	34.7	138.0	0.975
L8	20	2.0	180	19.4	139.2	0.976

*Extrudate unsuitable for modulus measurement using three-point bend method.

variables. The modulus values achieved are typical of those achieved in conventional hydrostatic extrusion, although at the higher extrusion ratios, in particular, some diminution in stiffness occurs if the degree of undercooling is too small.

Measurements of the long period of the extrudates as presented in Fig. 6 further confirm the undercooling effect of the back-pressure. In polyethylene drawn at atmospheric pressure the long period has been shown to be essentially a function of drawing temperature with very little effect of draw ratio [12]. From Fig. 6, in which for a wide range of extrusion conditions the long period is plotted against undercooling ($T_m - T_e$), it is evident that, although there is much scatter of the points, lower undercooling or higher temperature yields higher values of long period. At higher values of undercooling (> 60° C) the long period appears to stabilize at a value of 19 to 20 nm.

The similarity of the products obtained in this set of experiments is confirmed by several other observations. First, it can be seen from the results of measurements of melting point and density shown in Table I that these materials are comparable to those obtained in previous conventional hydrostatic extrusion experiments, where extrusion was performed into an atmospheric-pressure environment. In fact, there is a fall in both density and melting point at extrusion ratios around 5:1, with a steady increase to a value 1 to 2% above the isotropic values for extrusion ratios of 20:1.

Secondly, there is the structural information obtained from measurements of the integral breadth of the 002 reflection which is a measure of the average crystal length $\bar{L}_{002}$. In previous studies of very highly drawn polyethylenes it had been noted that $\bar{L}_{002}$ can increase with the increasing draw ratio to values which greatly exceed the long period L. For such samples, it was proposed that the quantity $\bar{L}_{002}/L$ can be used to provide a quantitative measure of the degree of crystal continuity, which was assumed to arise from the presence of randomly placed intercrystalline bridges linking the adjacent crystal blocks of the Peterlin model for a drawn fibre. It was shown that there was a good correlation between the dynamic Young's modulus determined at − 50° C and the degree of crystal continuity as defined by $\bar{L}_{002}/L$, and in some cases detailed modelling led to very satisfactory predictions for the magnitude of the −50° C Young's modulus and its variation with temperature [13, 14].

In the present set of samples, $\bar{L}_{002}$ is always of a similar value to L or exceeds it by a comparatively small margin. It is, therefore, considered more appropriate to deal with the present data by plotting the room temperature Young's modulus, which is available for most samples, as a function of $\bar{L}_{002}/L$, as shown in Fig. 7. It can be seen that there is an excellent correlation, which gives some confirmation for the view that crystal continuity plays a significant role in determining the Young's modulus.

3.2. Extrusion with back-pressure at temperatures above 200° C

As the programme of pressure-to-pressure experiments is extended into the temperature range above 200° C the control of the experiments becomes increasingly difficult. This is principally due to the fact that, as indicated in Figs. 2a and 3, at the higher temperatures the differential pressures required to cause the extrusion to occur are very small. In fact they became so small that they are barely detectable by the pressure-measuring devices used in the extrusion facility. Because of this lack

TABLE II Summary of properties of extrudates produced by pressure-to-pressure extrusions at high temperatures and pressures.

Sample	R_N	Extrusion conditions		Modulus, E (GPa)	Melting point, T'_m (° C)	Density (g ml^{-1})
		P_b (kbar)	T_e (° C)			
H1	10	4.0	227	5.6	140	0.990
H2	10	4.2	227	9.5	139.5	0.985
H3	10	4.5	227	9.5	139	0.983
H4	10	4.5	234	5.6	140	0.990
H5	10	4.6	232	14.5	139.1	0.984
H6	10	4.6	235	7.2	–	0.986

of control, only a limited number of extrusions have been completed within this regime. The principal results of these experiments are given in Table II.

As implied by these results, particularly those for the axial modulus, the extrusions become unstable at temperatures around 230° C and quite different results can be achieved for what appear to be almost identical conditions. At these temperatures the quality of the extrudates is also observed to deteriorate; not only are they less transparent, but they exhibit surface flaws. The latter appear to be the result of stress-cracking attack induced by the silicone fluid since these flaws are somewhat reduced when the billets are given a protective coating prior to extrusion. Wide-angle X-ray diffraction patterns of the samples referred to in Table II showed that, with the exception of sample H5, which was extruded under conditions well below the solid/intermediate phase boundary, a much lower degree of orientation was obtained, compared with those extruded at lower temperatures and comparable extrusion ratios, and in some cases the material is almost isotropic suggesting that the melt phase has dominated.

It is of particular interest that the melting points are significantly higher for these samples (cf. Table I) and that the densities are also higher than samples prepared by conventional hydrostatic extrusion (in the range 0.983 to 0.990, compared with 0.968 to 0.981). Small-angle X-ray measurements, using a Franks camera, did not reveal any sign of a two-point pattern, in contrast to conventional extruded samples. All these results suggest that it is likely that these samples were extruded in the hexagonal phase regime. It is interesting to speculate that the low degree of orientation achieved may be due to the molecular mobility in this phase, and it does not appear from these experiments to offer a viable route to ultra-high modulus material.

3.3. Pre- and post-extrusion annealing experiments

These experiments represent further steps in our attempts to understand the significance of the intermediate hexagonal phase and extended-chain crystallization in regard to the possible oriented structure which could be produced by hydrostatic extrusion.

Using the data of Bassett and Turner, a pressure of 4.5 kbar and temperature of 236° C were chosen for the conditions to give annealing within the hexagonal phase. This annealing process was performed within the extrusion facility and was achieved by carefully raising both the pressure and temperature so as to avoid the melt phase. The samples were held at the annealing conditions for 1 h and then the heaters were switched off and the facility allowed to cool naturally whilst the pressure was gradually reduced.

A number of billets were pressure-annealed in this manner in order to produce a chain-extended structure. These billets were then hydrostatically extruded both under pressure-to-pressure conditions and under conventional conditions. It was thought initially that, in view of the potentially brittle nature of the annealed billets, it would be feasible only to extrude under superimposed hydrostatic pressure conditions. However, it was found to be perfectly straightforward to extrude these materials without the back pressure. The results of these extrusion experiments on the pressure-annealed polyethylene are shown in Table III.

The remarkable feature of these results is the high value of stiffness achieved in the extrudates. These values are approximately double those obtained by hydrostatic extrusion of isotropic polyethylene crystallized at atmosphere pressure under the same extrusion conditions, and yet the extrusion pressures required and the general behav-

TABLE III Summary of properties of materials produced by hydrostatic extrusion of chain-extended polyethylene

Sample	R_N	Extrusion conditions		Modulus, E (GPa)	Melting point, T'_m (° C)	Density (g ml^{-1})
		P_b (kbar)	T_e (° C)			
P1	5	0	100	15.9	139.4	0.983
P2	10	0	100	32.6	139.6	0.980
P3	10	2	140	33.8	139.2	0.979
P4	10	3	160	33.7	138.9	0.981

iour of the extrusion process is almost identical for the two types of material. The undercooling effect of the pressure is found to be exhibited for the extrusion of the pressure-annealed material just as for the isotropic material and many of the characteristics of the extrudates are similar apart from the axial modulus.

It is interesting to note that the melting points and densities of the listed in Table III are significantly higher than the conventional extruded materials of Table I, but not so high as pressure annealed materials (Table IV). This suggests that the products of Table III may contain some remnants of extended-chain material. The sample P3 was found to show a long period of 20.2 nm and the corresponding value of $\bar{L}_{002}$ was 29.3 nm. It is shown in Fig. 7 where it can be seen to lie within the range of results for conventional extruded materials. However, it should be borne in mind that the $\bar{L}_{002}$ value is an average value, and does not give any information regarding the distribution of crystal sizes, so that these samples could contain a greater proportion of long crystals than conventionally drawn or extruded polyethylene.

These samples were significantly less transparent than conventionally extruded materials, at comparable extrusion ratios. An equatorial streak, indicative of longitudinal voids, was also observed in the small-angle X-ray diffraction pattern.

A simple post-extrusion annealing was carried out on a conventionally extruded product. As shown by the results summarized in Table IV the annealing process markedly increases the density and melting point, but the orientation is found to be retained and the axial modulus is little affected. This experiment was undertaken essentially to confirm the uniqueness of the pressure-annealing/extrusion route exemplified by the samples of Table III in contrast to the lower stiffness properties of the extrusion/pressure annealing route, and merely confirms previous more extensive studies of the latter by Bassett and co-workers.

4. Discussion

The results described above for the pressure-to-pressure extrusion of conventional bulk polyethylene crystallized at atmospheric pressure show no remarkable features. It is clear that the key variable is the degree of undercooling, and that the results should be considered in terms of $(T_m - T_e)$ the difference between the polymer melting point at the ambient pressure and the extrusion temperature. It is very satisfying that both the processing parameters (e.g. the differential pressure required to sustain extrusion) and the structural parameters relevant to the extrudate (e.g. long period and crystallite size), relate directly to the degree of undercooling for a given deformation ratio.

For this processing route, the unique relationship between the Young's modulus of the extrudate and the extrusion ratio is maintained, as established by previous work. It is also found that the Young's modulus relates to the ratio of average crystal length to long period $\bar{L}_{002}/L$.

The attempts to carry out the hydrostatic extrusion process in the hexagonal phase regime

TABLE IV Properties of isotropic material and $R_N = 10$ extrudate before and after pressure annealing. Annealing conditions: pressure = 4.5 kbar; temperature = 236° C; time = 1 h

Sample	Modulus, E (GPa)		Melting point, T'_m (° C)		Density (g ml^{-1})	
	Before	After	Before	After	Before	After
Isotropic	–	–	137.5	141.5	0.973	0.991
$R_N = 10$	17.2	16.0	135.5	139.8	0.962	0.990

did not lead to any outstanding products, although it does seem probable that at least one sample (H5 in Table II) was oriented in this regime.

The comparative failure of these experiments led us to explore the possibility of hydrostatic extrusion of pressure-annealed extended-chain material, with most interesting consequences. It appears that much higher Young's moduli can be obtained for a given draw ratio than is the case for hydrostatic extrusion or die drawing of bulk polyethylene crystallized at atmospheric pressure. Structural measurements suggest that these materials are not very different in some respects from those produced by the more conventional routes. In particular the value of the long period (about 20 nm) corresponds with that expected for the temperature of extrusion and the average crystal lengths are again similar to those for conventional oriented materials of comparable Young's modulus. The densities and melting points of the pressure annealed/extruded materials were somewhat higher than conventional oriented materials.

It is notable that substantial lengths of unflawed extruded product (~ 30 cm) were obtained. This raises the possibility of producing high-modulus polyethylenes from a wider range of molecular weights, for example, from high molecular weight material where the deformation ratio is limited to about 10. This possibility is at present being explored, and also the extension of the principle to other polymers.

5. Conclusions

1. Well-controlled pressure-to-pressure hydrostatic extrusion of conventional melt-crystallized polyethylene has been achieved throughout the extrusion temperature range 100 to 200° C and extrudates of consistently sound quality have been produced. The most significant feature of both the extrusion operations and their products is their direct dependence on the degree of undercooling which is introduced. Orientation of the products as identified by the axial Young's modulus shows a similar dependency upon extrusion ratio as that observed in previous work on extrusion and drawing.

2. The matching of the extrusion pressures and temperatures in order to achieve extrusion whilst in the so-called hexagonal phase regime (i.e. ~ 4.5 kbar and ~ 230° C) has proved to be difficult mainly because of the extremely low differential pressures required for extrusion under these conditions. The products of satisfactory extrusions achieved within this regime exhibit lower Young's moduli than is achieved in more conventional solid-phase extrusions and confirm the structural indications of only limited orientation.

3. Hydrostatic extrusion of the pressure-crystallized chain-extended polyethylene, both with and without back-pressure, produces extrudates having considerably enhanced stiffness. This is a route which offers potential for the production of higher modulus within a number of additional grades and types of polymer.

4. Post-extrusion annealing of conventionally extruded products, whilst enhancing properties such as density and melting point, cannot be used to improve the stiffness properties.

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