Direct ram extrusion of polyethylene; a correlation between chain-folding and tensile modulus

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The paper concerns the production of highly oriented polyethylene by means of pressing the softened but essentially still solid material through a reducing capillary between 90 and 120° C. The objectives were to explore this route towards the achievement of high tensile modulus and to assess its practicability, both of which are presented in the paper. In addition, however, information was obtained relevant to deformation processes and to the relation between tensile properties and microstructure in general. Thus the induced deformation in the solid state and its dependence on processing variables was found to be interpretable in terms of Eyrings theory of viscosity with simple shear as an important element. Both changes in the fold length and fold content could be followed most informatively by low frequency Raman spectroscopy and it was observed, in the course of the present solid-state deformation, that the chains partly refolded to a fold length appropriate to the processing temperature, and partly unfolded. The former is in accord with earlier analogous observations on cold-drawing [13], the latter, as assessed through the reduction of fold content, correlated in an apparently uniquely defined way with the measured tensile modulus where the lowering of the fold content corresponds to an increase in modulus. Thus, this Raman spectroscopically determined fold content represents a promising new parameter in the correlation of structure with properties, it is applied further in the present paper for assessing modulus variation across the width of the extrudate. Other observations on the extrudate include a quantitative analogy with wood, the fibrous structure element being the common denominator.

1. Introduction

The extrusion of solid polymers derives from traditional metal-working techniques. Early results, Imada *et al.* [1], suggested that solid-state extrusion could produce a product with enhanced mechanical properties although this particular study concentrated on orientation and morphology. However, Predecki and Statton [2], using very high pressures, reported very little product enhancement. In both these studies the process was a direct ram extrusion in which the polymer makes direct contact with the walls. At about the same time Bunney and Cassin [3] and Williams [4] investigated the process of hydrostatic extrusion, in which the pressure is transmitted to the polymer by oil which extrudes with the polymer producing continuous lubrication of the polymer-die interface, a line of work being followed up by Gibson *et al.* [5]. The present study on direct ram extrusion concentrates on the dependence of mechanical properties of the extrudate on the processing conditions for the purpose of evaluating the prospects of this process in the production of high modulus polyethylene. As will be seen, in the course of it, information was obtained which may be of general interest for the correlation between orientation, modulus and microstructure.

2. Experimental

The extrusion apparatus consisted of a barrel and ram. The barrel, 1 cm diameter, held at its lower end a die of conical profile ending in a short 5 mm capillary. The cone half-angle was 30°. The dies were characterized by the reduction in cross-sectional area they imposed on the polymer, which is called the deformation ratio (DR). Three values were used in this study, 12, 16 and 20.

High density polyethylene BP Rigidex 50 was used throughout. Compression moulded into rods, the polymer fitted the barrel closely, making direct contact with the walls and the ram tip. No lubricant was used. A band heater, connected to a Eurotherm temperature controller was capable of maintaining the barrel temperature within a degree and the variation of temperature along the barrel length was not more than 2° C.

The apparatus was mounted on an Instron with the cross-head pressing down onto the plunger. As the polymer was extruded beneath, a wire held under tension by a 1 kg mass kept it straight. No die swell was observed in the extrudate. All extrusions in this study were conducted under uniform ram speed, at elevated temperatures between 90 and 120° C.

3. Results
3.1. Rheology

As the ram pressed on the polymer billet the pressure rose gradually to a steady value, which was then maintained during the extrusion. At DRs of 16 and 20 the pressure trace showed a distinct yield point and then often oscillated between a maximum and minimum pressure, resembling a sine curve, the average pressure being taken as the extrusion pressure. If the cross-head is set too fast, the pressure continues to rise during the extrusion and at high speeds the polymer extrudes with a helical fracture scoring its surface. The measurements of this study are confined to regions of stable extrusion pressure.

The relationship between extrusion pressure, ram speed and temperature is a simple one. At a given temperature the extrusion pressure increases with the log of the cross-head speed, as shown in Fig. 1a and, if a constant cross-head speed is maintained, the extrusion stress σ reduces in proportion to increased temperature (Fig. 1b). This behaviour obeys the yield theory of Eyring [6] quite closely.
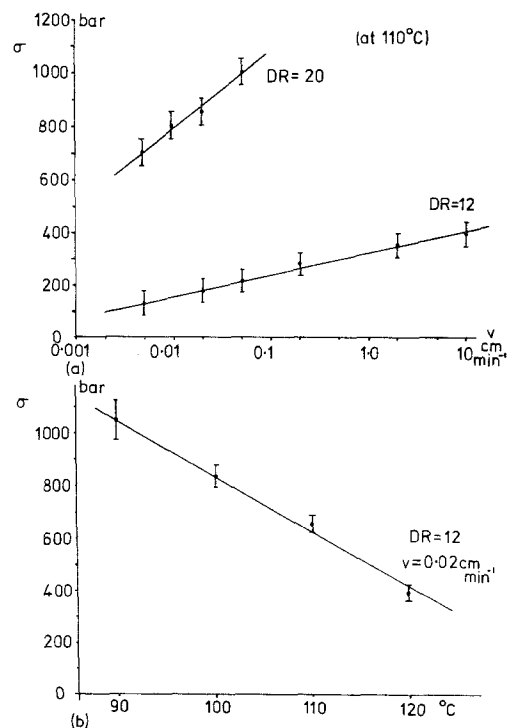

Figure 1 (a) The variation of extrusion pressure with the ram speed at two deformation ratios at 110° C. (b) The variation of extrusion pressure with temperature at DR 12 for a fixed ram speed.

This theory of plasticity has already met with considerable success in explaining the plastic yield of polymers [7] through its prediction that the flow shear stress τ is given by

$$\tau = 2\eta k_1 \sinh \frac{\tau V}{2kT} \qquad (1)$$

where η is the viscosity, V the activation volume and k_1 a temperature-dependent constant. The theory is based on the idea that the application of a directional shear stress τ, aids yield by reducing the energy barrier to be surmounted in that direction. Writing $\eta = \tau/\dot{\gamma}$, where $\dot{\gamma}$ is the shear rate, we have from Equation 1

$$\dot{\gamma} = 2k_1 \sinh \frac{\tau V}{2kT} \qquad (2)$$

For polymers, the volume V is interpreted as the volume of the statistical link in the polymer chain in dilute solution [7]. Extending this to solid polymers, and for the purposes of an estimate, this volume can be taken as the volume occupied by a chain stem between folds. This puts the value of $\tau V/(2kT)$ at an order of magnitude of 10, in which

967

region sinh $[\tau V/(2kT)]$ is very closely approximated by $\frac{1}{2}\exp[\tau V/(2kT)]$ so that from Equation 2

$$\dot{\gamma} = k_1 \exp \frac{\tau V}{2kT}.$$

The shear rate in the die is proportional to the cross-head speed v and the shear stress to the extrusion pressure σ so

$$v = k' \exp \frac{A\sigma}{2kT}$$

with A constant. This relationship predicts the logarithmic dependence of v on σ and the proportionality between σ and T at constant v. Suffice it to remark that, although in theory k' is temperature dependent its variation with temperature appears to be small.

The applicability of a theory containing the idea of shear activation leads one to imagine that through a lowering of energy barriers, a greater chain mobility occurs in the die than might be expected from considering the die temperature alone.

3.2. Extrudate features

The most striking feature of the extrudate is probably its transparency, caused by the breakdown of the spherulite morphology at the micron level which gives bulk-crystallized high-density polyethylene its characteristic whiteness.

The extrudate is remarkably tough normal to its axis but it is weak parallel to it. It cleaves easily, revealing a fibrous substructure from which individual fibres may be pulled away with tweezers.

When the extrudate is bent between the fingers white crazes are observed appearing at about $45°$ to the fibre axis (Fig. 2) and occurring only on the compression side in bending. An electron micrograph showing an inclined row of kinked fibrils is given by Imada et al. [1], which can be identified as a craze. In all, the crazes show a remarkable similarity to the features observed in the compressional failure of wood by cell-wall kinking. This failure of wood has been studied by Dinwoddie [8], who observes that the angle α between the kink band and the grain depends on the temperature of testing. In the present study $\tan\alpha$ is measured because it is simply related to the geometry of the kink. Approximating the kink by part of a sine wave of amplitude a (Fig. 3), the slope of the sine wave at its origin is $2\pi a/\lambda$, but
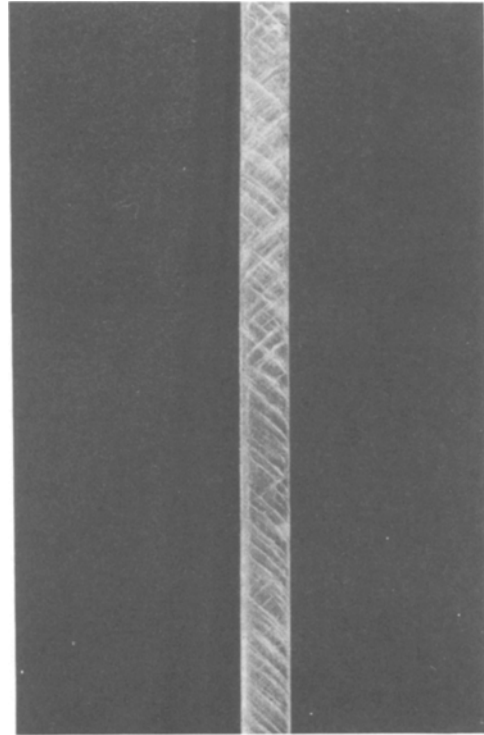

Figure 2 White crazes form at about $45°$ on the compression side of the extrudate in bending.

$a = \rho$, the fibre radius, so $\tan\alpha = \lambda/(2\pi\rho)$. The parameters are not elaborated on here; the important point is that the function of α to be considered is $\tan\alpha$. For the extrudate in compression tests, $\tan\alpha$ varies with log strain-rate in the same way as $\tan\alpha$ with temperature for wood (Fig. 4a and b, Table I). This similarity is striking and suggests that this failure is not peculiar to polyethylene extrudate but is a fundamental mode for such aniso-
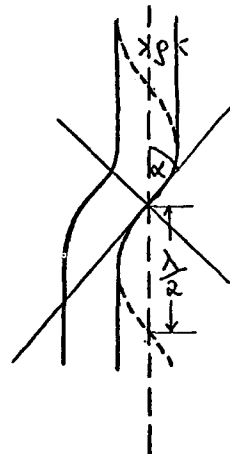

Figure 3 The geometry of the kinked fibres.

TABLE I Values of kink angle α

	Polyethylene			Wood		
$\dot{e}$ (sec^{-1})	10^{-1}	10^{-2}	10^{-3}			
T(°C)				-147[*]	20[*]	105[*]
T(°K)				126	293	378
average α	45.2	47.9	50.4°	54.2[*]	59.2[*]	61.2°[*]
tan α	1.007	1.107	1.209	0.387	0.678	0.819

[*] From [8].

tropic materials. Indeed, it has been observed in such diverse materials as oriented nylon and cadmium single crystals.

The melting point endotherm for the extrudate was compared with that for the unextruded billet. The extrudate endotherm becomes more highly peaked and less symmetrical and is shifted upwards by a few degrees. There is no evidence of a high melting point fraction such as would be observed if a portion of extended chain crystallization had occurred.

Wide-angle X-ray photographs confirm the crystal orientation investigated exhaustively by Imada et al. [1], that is good uniaxial c-axis orientation. Small-angle X-ray photographs were taken, using a Franks camera, at the centre and edges of the extrudate with the beam normal to the fibre axis. The diffraction peaks are quite diffuse but they do reveal a degree of lamella stacking order with lamella interfaces at right angles to the chain direction at the centre and edge of the sample.

3.3. Laser Raman spectroscopy
3.3.1. Introduction
Some aspects of the morphology of the extrudate were studied through its Raman spectrum. Two Raman active modes were of interest. Firstly, the
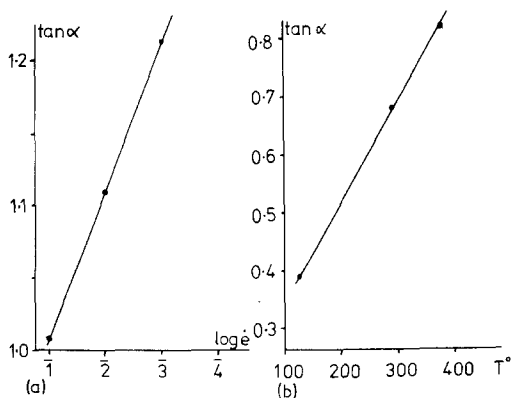

Figure 4 (a) A plot of tan α against log strain-rate for the extrudate. (b) A plot of tan α against T for Norway Spruce Wood Table I (adapted from Dinwoodie [8]).

LA mode in which the chains in the crystal region between fold surfaces execute an accordion-like vibration which has been found to obey the classical vibrational behaviour of an elastic rod. [9, 10]. Thus, by measuring the fundamental frequency and assuming values of Young's modulus and density for the crystal, the fold or stem length can be found and is given by the formula $l = (3183/\nu)$ Å where ν is the Raman shift in cm^{-1}. An instrument of high resolution is required to resolve the LA mode which occurs at small wavenumbers. A Coderg T800 spectrometer was used in these experiments.

The validity of stem-length measurement by the laser Raman method has been established by comparing with the traditional low-angle X-ray method [11].

The second vibration band of interest is one in which the C–H bonds along the chain become active. This occurs at $\nu = 1294$ cm^{-1}.

3.3.2. The change in fold length during extrusion
The fold length of the extrudate is found to depend on only one processing parameter, the extrusion temperature T_E and it increases with T_E as shown in Fig. 5a, where each point on the curve is an average of values for different DRs and plunger speeds (Table II) and the error bars represent errors in the mean. A plot of fold length against the inverse of supercooling $T_M - T_E$, where T_M corrected for pressure (by 17° C/kbar pressure applied [12]), shows the standard relation well established for crystallization from the melt and from solution (Fig. 5b) providing evidence that "melting" and "recrystallization" occur in the die despite the fact that the die temperature is always below the normal melting point of the material.

Similar behaviour has been observed drawing by Corneliussen and Peterlin [13] and they also attribute this to melting and subsequent recrystallization. However, melting in the normal sense does not occur in the die. If a billet severed along its
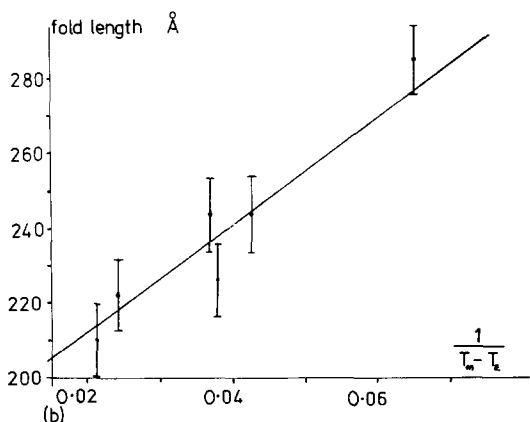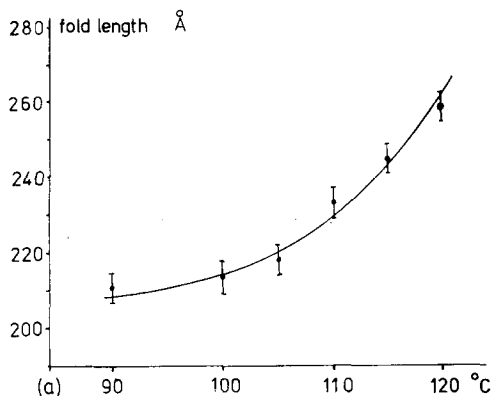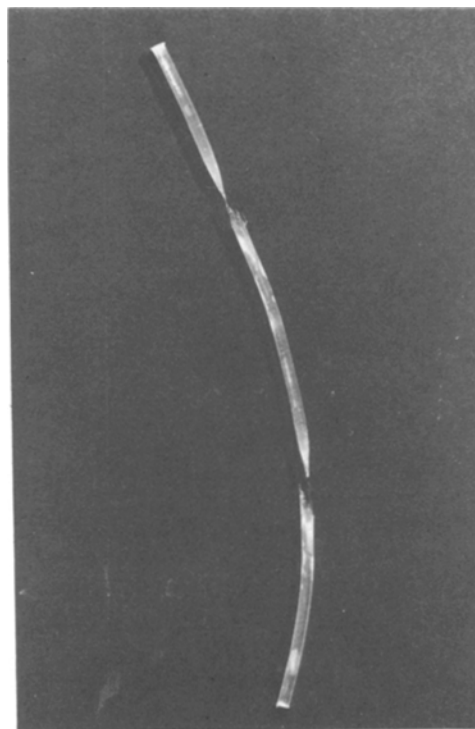
Figure 6 This extrudate came from a sliced billet and has been slightly separated to show the form of the interfaces.

Figure 5 (a) A plot of average fold length against extrusion temperature for extrusions at three different DRs and five different ram speeds (Table II). (b) The variation of fold length with reciprocal supercooling.

TABLE II Variation of fold length with extrusion temperature.

$T_E(°C)$	DR	ram speed (cm min^{-1})	fold length 1 (A)	average 1 (A)
90	12	0.02	211	211
100	12	0.02	224	214
	16	0.02	204	
105	20	0.02	227	219.5
	16	0.02	212	
110	12	0.02	240	233.5
	12	0.2	226	
	12	2.0	244	
	20	0.005	236	
	20	0.01	230.6	
	20	0.02	227	
	16	0.02	227	
115	12	0.02	244	244
120	12	0.02	262, 275	257.7
	16	0.02	255	
	20	0.02	253	
	20	0.01	236	
	20	0.005	265	

length is extruded, the extrudate preserves the interfaces which become sharply pointed. Fig. 6 shows a length of polyethylene extruded from a severed billet. It has been separated to show the "pencil profile" given to the interfaces by extrusion. For the low melt viscosity polymer used, this would not happen in the presence of wholesale melting.

The change in fold length during extrusion could not be examined *in situ* but was determined by removing a partly extruded billet and examining slices from it. The sample used was extruded at 110° C and 0.02 cm min^{-1} (Fig. 7). The change is a continuous decrease through the deformation zone, apparently occurring beyond the die exit too. For drawn polyethylene Kasai and Kakudo [14] have measured the "crystal block size" by X-ray line broadening and find it to decrease continuously through the neck.

3.3.3. A new structure sensitive parameter
In the study of polymer processing it is of considerable interest to find parameters which correlate with mechanical properties and which can be interpreted in simple morphological terms. In the
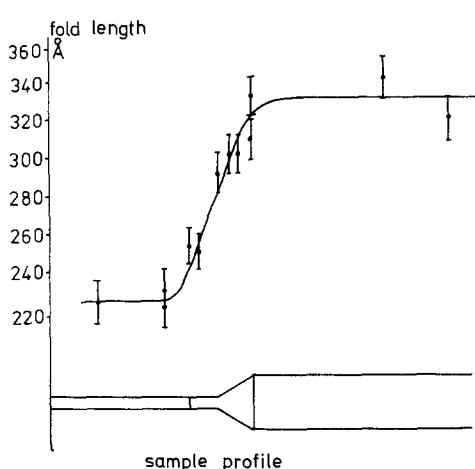
Figure 7 The fold length variation along a partly extruded billet at 110° C. The billet was originally crystallised at a higher temperature during slow cooling, hence the higher initial fold length of 330 Å.

Figure 8 A typical Raman spectrum and, below, the Raman peak after subtraction of the background.

laser Raman method, not only can the positions of the peaks be determined but also their integrated intensity. The integrated intensity of the LA mode is related to the distribution of chain folds in the sample. If the distribution is completely random then it is anticipated that there will be no distinct LA mode. An intense LA mode is expected when there are a large number of folds having nearly the same stem length. Thus if, for each specimen, one takes the integrated intensity of the LA mode and divides it by the integrated intensity of an internal standard, such as the Raman C–H bending mode at $\nu = 1294 \, \text{cm}^{-1}$, this leads to a parameter D_F defined by

$$D_F = \frac{\text{integrated intensity of LA mode}}{\text{integrated intensity of 1294 peak}}$$

so that

$$D_F \propto \frac{\text{number of folds at the given fold length}}{\text{total chain length}}.$$

This new parameter should be a measure of the extent of chain folding in the structure and it is proposed that it be called the "degree of folding".

The parameter D_F is sensitive to the subtraction of the background from the observed chart. The LA mode is so near the origin that it occurs on the shoulder of the laser spike and so the background is varying very rapidly. Observations so far, in cases where the LA mode is well resolved have shown that the LA mode is not appreciably asymmetric [15]. Bearing this in mind, a smooth background is subtra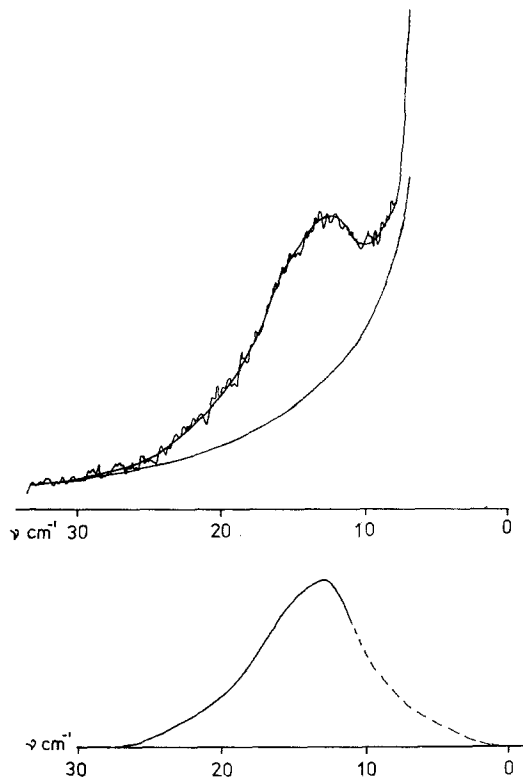cted to give a symmetrical peak. A typical experimental spectrum is shown in Fig. 8, the background is fitted using a flexible ruler and subtraction of the background yields the LA mode shown. The integrated intensities of the peaks are found by tracing the peaks on tracing paper, weighing them, and finding the ratio of weights. Since the intensity of the LA mode depends on its frequency shift, a correction should be applied to compare integrated intensities at different frequencies. However, for the small variation in frequen-
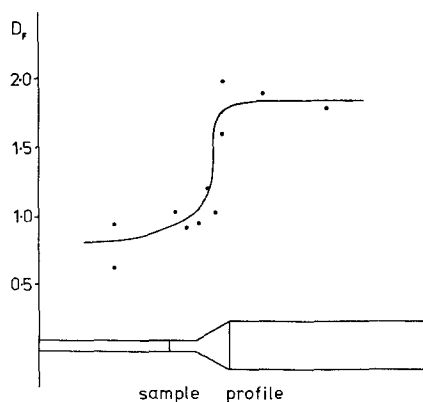

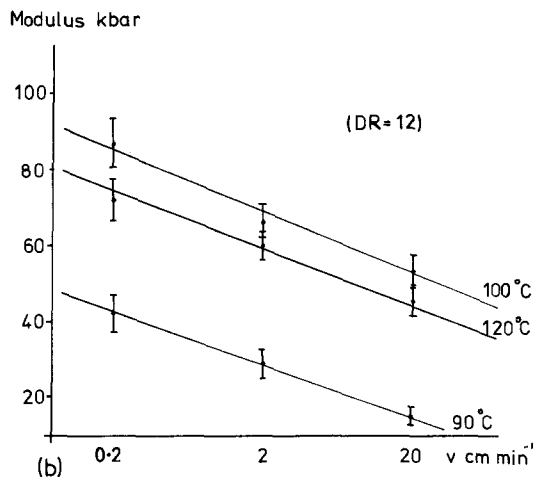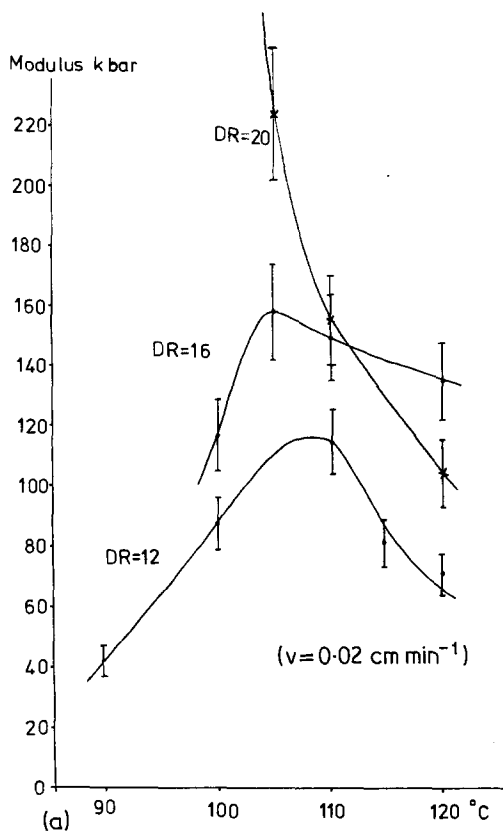*Figure 9* The variation of parameter D_F along a partly extruded billet.

971

Figure 10 (a) The variation of tensile modulus with extrusion temperature at three deformation ratios but with a single ram speed. (b) The variation of tensile modulus with ram speed at three temperatures at a fixed DR.

measured at 0.1% strain. the strain was found from the displacement between the grips, with a correction for machine softness. The temperature of the room was $23 \pm 2°$ C.

3.4.2. The effect of processing conditions on the extrudate modulus

The extrudate modulus is dependent on both temperature and plunger speed at a given DR and there is an optimum temperature at each DR for obtaining the highest modulus (Fig. 10a). Also, if the plunger speed is increased in ratio, the modulus reduces linearly (Fig. 10b). In addition, increasing the deformation ratio increases the upper limit of modulus obtainable.

This general behaviour contrasts sharply with tensile "drawing" for which the modulus is a unique function of the deformation ratio, [18, 19].

The observation of a maximum modulus suggests that two competing processes might be involved, one increasing and one descreasing with temperature so that the peak represents an optimum. The highest modulus obtained was 220 kbar which is a 36-fold increase on the bulk-crystallized starting material and we note that the optimum modulus obtained at each deformation ratio is broadly equivalent to that obtained by drawing or hydrostatic extrusion at similar deformation ratios [5, 19].
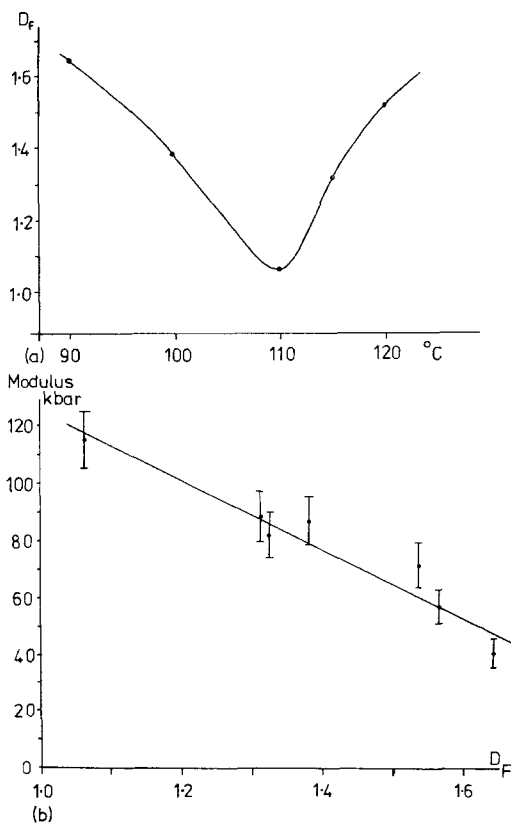
cies of these LA modes, this correction is much less than experimental error and was not applied.

The change in D_F during extrusion was studied using a partly extruded billet and slicing it. The result is shown in Fig. 9. It can be seen that most of the change in D_F occurs as it enters the conical part of the die and the decrease in D_F can be attributed to the decrease in the percentage of material folded at the characteristic fold length.

The correlation between D_F and the mechanical properties of the extrudates is discussed in Section 3.4.3.

3.4. Mechanical properties
3.4.1. Measurement of tensile moduli

The tensile moduli of the extrudates were measured in an Instron tensometer. The aspect ratio of the samples were over 100, so as to avoid the end-effect which occurs in the modulus measurement of anisotropic materials [16, 17]. The samples were gripped in close-fitting copper tubes crimped onto the specimen ends. Unless otherwise stated, the tests were carried out at a strain-rate of $10^{-4} \sec^{-1}$ and secant moduli were

Figure 11 (a) The variation of D_F with extrusion temperature (cf. lowest curve Fig. 10a). (b) A plot of tensile modulus against D_F for a variety of samples prepared at DR 12.

3.4.3. Correlation between tensile modulus and D_F

A set of samples at DR 12 and plunger speed 0.02 cm min^{-1} but at increasing temperatures was prepared. These samples are characterized by a modulus which goes through a maximum as the extrusion temperature is increased (Fig. 10a). Fig. 11a shows a plot of D_F against extrusion temperature and should be compared with the lowest curve in Fig. 10a showing the moduli as a function of the same temperature.

It can be seen the D_F falls to a minimum when the modulus is a maximum. A further plot of D_F against tensile modulus of samples prepared in a wide variety of conditions at DR 12 is shown in Fig. 11b showing that the tensile modulus depends only on D_F at a given DR. This implies that it is the portion of the material which is not folded at the length characteristic of the extrusion temperature which determines the stiffness of the sample as a whole.

If the line in Fig. 11b is extrapolated to $D_F = 0$, a modulus of about 300 kbar is obtained. This may represent the maximum stiffness obtainable at this deformation ratio.

3.4.4. The variation of modulus across the specimen diameter

The possibility of a variation of stiffness across the extrudate was investigated by using the parameter D_F. Six specimens were cut from a long length of extrudate (prepared at 110° C, DR = 12, $v = 0.02$ cm min^{-1}) and a central longitudinal slice was removed from each. By further slicing a set of specimens were obtained at five positions across the diameter. The average values of D_F (assuming cylindrical symmetry) are plotted in Fig. 12. The smaller value of D_F at the centre should mean that the modulus is greater at the centre of the specimen than at the edge which, using Fig. 11b, amounts to 20 kbar, or about 20%.

This variation implies that a modulus measurement made in three-point bending would be less than that in tension if measured under similar conditions. Simple calculations show that the expected difference in measured moduli is quite small, about 2 to 3% for a 20% variation in modulus across the sample. Unfortunately, this proved too small a variation to measure with confidence, although preliminary results do indicate a trend in the expected sense.

4. Conclusions

The deformation of HDPE by direct ram extrusion through a conical reducing die at elevated temperatures produces a highly oriented fibrous product of enhanced stiffness.
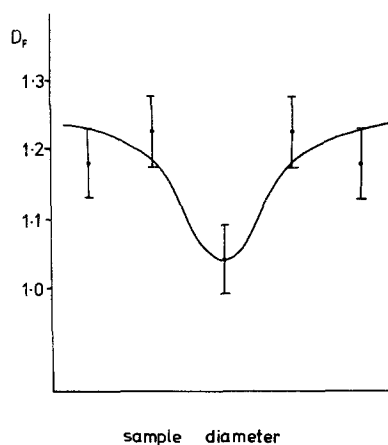

Figure 12 The variation of D_F across a sample diameter.

973

The deformation in the die is thought to be dominated by simple shear, arising from frictional contact at the walls as shown by the profile given to an initially flat interface (Fig. 6). This sets it apart from hydrostatically lubricated extrusion.

It is thought that the polymer remains solid in the die but has a greatly enhanced molecular mobility by Eyrings shear activation mechanism. The mobile chains refold according to their new temperature environment while some others simultaneously unfold, especially near the centre, away from the wall. These partially unfolded chains are thought to be responsible for the increase in stiffness as they contribute to the continuity of the structure. They scatter laser light at a lower frequency shift than the refolded material and do not contribute to the Raman LA mode, causing the observed decrease in the folding parameter D_F. The tendency for the chain unfolding is enhanced at the centre where the flow is accelerating producing a higher modulus at the centre of the extrudate than at the edge. The parameter D_F, the degree of folding, which is proposed as a measure of the folded chain content of a sample, is sensitive to only the crystalline fraction and is found to relate directly to the measured moduli at DR 12 which was chosen for this examination. Furthermore, it is independent of the processing conditions used to achieve those moduli. It has been used to measure modulus indirectly, where a direct measurement would be very difficult.

Finally, we note that to achieve the highest moduli requires an optimum temperature, the highest deformation ratio and the slowest extrusion speed and, although the product improvement compares favourably with other reported processing methods at similar deformation ratios, it is obtained only at the expense of a reduction in the processing speed.

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