

Properties of Oriented Polyethylene Bars of Large Cross Section

GREGORY COURVAL,¹ LI-HUI WANG,² and ROGER S. PORTER^{*,2}

¹Alcan International Limited, Kingston, Ontario, Canada and ²Polymer Science and Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003

SYNOPSIS

The solid-state extrusion technique has been used to prepare uniaxially oriented polyethylene bars with rectangular end cross sections of $6 \times 50 \text{ mm}^2$. They were extruded at 110°C from billets of high density polyethylene. The tensile modulus and strength for the extrudate with a draw ratio (DR) of 14 were 17.9 and 0.32 GPa, respectively. The mechanicals were also measured in the transverse direction by means of the proportional elastic limit (PEL) bending test. The PEL results do not change after DR 14 due to the fibrillate structure formation. Crystallinity and shrinkage tests were made on samples taken over the bar cross section. They show that uniform properties were achieved across the width of the bar with proper die design. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Various workers have studied the uniaxial draw of polyethylene (PE). A common goal has been to increase tensile properties.¹⁻¹³ Property development on drawing is found to depend on the extent and efficiency of deformation; that is the fraction of applied energy stored (that is, goes into chain orientation and extension) versus the energy dissipated (i.e., the energy converted to heat). In consequence, properties are expected to build in terms of molecular draw ratio, rather than the measured draw ratio. Processes for efficient molecular draw are thus desired for property development. From this view, the draw of macromolecule in the solid state has been found to be more effective than in the molten state. Indeed, solid-state draw below the melting temperature is more efficient and relaxation of drawn samples is more restricted. By solid-state extrusion, it has been found that polymers can be effectively subjected to elongation in a tapered entrance zone of a capillary extruder. On drawing in a single extrusion pass, the tensile highest modulus and draw ratio

(DR) attained for PE in small cross sections have been 70 and 45 GPa, respectively.²

All prior solid-state extrusion studies conducted at UMASS have been performed within a capillary rheometer of an Instron Test Machine.^{1,2,10-13} Although this technique produces efficient draw, the dimensions of the extrudate are limited by the $\frac{3}{8}$ -in diameter of the rheometer reservoir. For practical applications, the extrusion of high density polyethylene (HDPE) to much larger dimensions by similar techniques, has now been also successfully performed.¹⁵ The mechanical properties achieved in the large dimension extrudate for PE resin are reported here. The relationships between the properties of the extrudates and the molecular and processing parameters will be discussed. Comparisons may be made with rolled PE.

EXPERIMENTAL

Materials and Preparation

The PEs were purchased from Du Pont Inc. The resins were designated 2909 and 98A, having a nominal molecular weight (MW) of 60,000 and 190,000, respectively. The as-received samples were compression-molded into billets 10 cm in diameter

* To whom correspondence should be addressed.

and 40 cm in length, appropriate for direct solid-state ram extrusion.

Extrusion

All extrusions were carried out at 110°C in a specially designed temperature controllable cylinder with an inner diameter of 10 cm. The prepared HDPE billets were preheated in an oven, transferred to the extruder reservoir barrel, and then pushed out through a die by an hydraulic piston. Several different tapered dies were used. The extrusion DR was calculated as the ratio of the cross-section area of the extrudate ($6.0 \times 50 \text{ mm}^2$) to that of the extruder reservoir barrel, 10 cm in diameter.

Due to the large cross sections of the extrudates, the uniformity of deformation across the extruded bar in the transverse direction is very important. For this evaluation, three different types of die were designed: a straight taper die (STD), a constant width die (CWD), and a constant aspect ratio die (CARD).¹⁶ The bars extruded with these dies were studied.

Sampling

The solid-state extrudates studied in this work were cut 5-m long, all with a rectangular cross section of $6.0 \times 50 \text{ mm}^2$. For the purpose of measuring properties across the profile, extrudate sample with lengths of 10 mm were cut in a transverse direction from the length of the extruded PE bars (Fig. 1). Each of these sections was further cut transversely into five smaller and equal specimens with a thickness of 0.5 mm. Such sections were obtained from each sample cut at five equal spacings and numbered by sample position. Only the center portions from the pieces were taken for the thermal analyses made on samples taken across the extrudate bar width. (One such sample is shaded in Fig. 1.) The results from these specimens represent the properties across the bar profile.

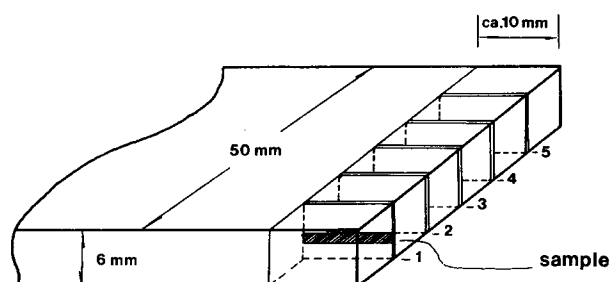


Figure 1 The schematic diagram of sampling.

Thermal Analysis

The peak melting temperature (T_m) and heat of fusion of sample taken from the drawn HDPE bars were measured on a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate of $20^\circ\text{C min}^{-1}$. The sample weights were known precisely and in the range 2–4 mg. The DSC instrument was calibrated with indium for both the temperature and heat of fusion. The 69.2 cal/g taken as the heat of fusion of the perfect PE crystal was used for calculation of fraction crystallinity in the samples.¹⁷

Thermal Shrinkage Measurements

For shrinkage tests along the draw direction, specimens with dimensions of $10 \times 1 \times 0.5 \text{ mm}^3$ were cut along the drawn direction as described above. The samples were wrapped with a thin layer of aluminum foil. They were quickly heated above the HDPE melting point by being placed for 1 min in a hot silicone oil bath held at 170°C . The efficiency of draw (ED) was calculated from the known original extrusion draw ratio of the samples and from the change of dimension on shrinkage, by the equation¹⁸:

$$\text{ED} = \frac{L_t - (L_s - L_o)}{L_t} \times 100\% \quad (1)$$

where L_t , total sample length of extrudate; L_o , the original length of test sample before drawing; and L_s , the sample length after shrinkage.

Mechanical Properties

The tensile moduli and strength of drawn bars were measured at room temperature at conditions as per ASTM D-638-88. Transverse samples were too short for reliable tensile testing so that bending tests were carried out to measure the transverse properties of uniaxially oriented HDPE bars. Specimens for this test were cut out from across the width of the full HDPE bar, providing specimens of about $50 \times 13 \times 6 \text{ mm}^3$. A standard 3-point bending testing method, ASTM C-947-81, was performed at room temperature in an Instron tester. The (major) bending support span was 30 mm of the 50-mm width and the cross-head speed of the Instron test machine was 1.0 mm/min. From these measurements, the stress for the proportional elastic limit (PEL) was calculated by the following equation:

$$\text{PEL} = \frac{P_e L}{bd^2} \quad (2)$$

where: P_e , force at the point on the force-deflection curve where the force-strain curve deviated from linearity, N ; L , major support span, mm; b , width of specimen, mm; and d , depth of specimen, mm. All specimens tested were found to be brittle in the direction parallel to orientation, so the measured PEL is equal to the transverse modulus of rupture (MOR).

The ASTM test requires specimens having a ratio of the specimen major span length to the specimen depth between 16 : 1. In this bending test, extrudate geometry precluded use of the standard sample size. Nonetheless, all measurements were carried out under the same conditions, so that the results are comparable.

RESULTS AND DISCUSSION

On solid-state extrusion, the morphology of the PEs was found to have been changed dramatically. In the initial morphology before draw, isolated crystalline spherulites dominate, which consisted of folded chain lamellae arranged radially about a center. On solid-state extrusion, the spherulites first elongate in the draw direction. At high draw, spherulite deformation results in the orientation of the crystalline lamellae in the stretch direction.² Thus as the spherulites deform, lamellae reorient themselves along the stress direction; and at a yield stress, when necking occurs, the spherulitic morphology converts to a fibrillar structure. At this stage, the initial opaque spherulitic structure becomes transparent and fibrillar.

As can be seen in Figure 2, an extrudate of DR 14 exhibits good transparency even at the thickness of 6 mm. Thus means that a fibrillar structure has



Figure 2 Photograph of extruded PE bar.

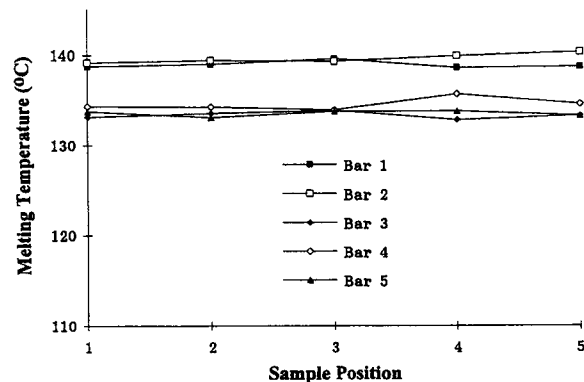


Figure 3 The peak temperature profile across the bar.

been developed with high chain orientation. Importantly, this morphological change is also associated with enhanced longitudinal mechanical properties.

It is obvious that the physical and mechanical properties of the extrudate, such as the melting temperature, crystallinity, and tensile properties are related to the degree of chain orientation and extension. Thus a study of the profile of the physical properties in the transverse direction across the bar can examine the uniformity of deformation. The melting temperature and crystallinity data of the HDPE bars extruded at $\sim 110^\circ\text{C}$ taken from different sample positions as shown in Figure 1, are presented in Figures 3 and 4. From these figures it can be seen that the average crystallinity for all these bars is about 80%. These data are equivalent with those obtained in our previous solid-state extrusion study of PE at the same temperature using the capillary rheometer of an Instron when compared at the same DR.²

The change of T_m and crystallinity on deformation depends mostly on the PE chain orientation. From this view, the ED in the present study is re-

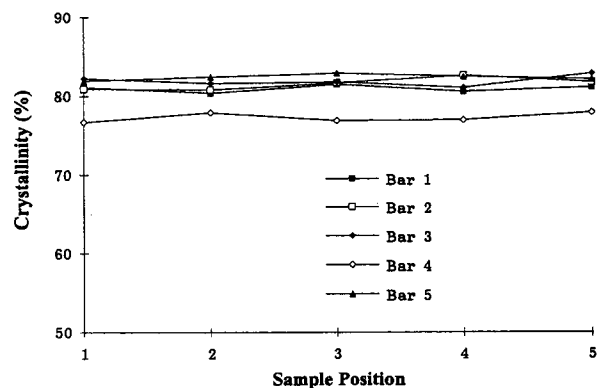


Figure 4 The crystallinity profile across the bar.

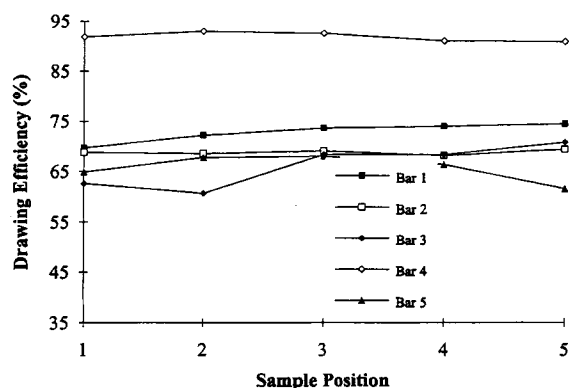


Figure 5 The drawing efficiency profile across the bar.

ported subsequently to be almost the same as in our previous studies. The relative fluctuation of crystallinity in the profile is less than 0.8, and the fluctuation of melting temperature is $\pm 0.5^\circ\text{C}$, less than 0.5%. This indicates an effective and uniform extensional deformation in the taped die entrance zone and independent of the die design chosen.

It has been shown that the elastic recovery of drawn PE can be a sensitive and quantitative measure for the ED. The correlations of this property with morphology and tensile modulus have been discussed.¹⁻¹³ We thus measured the thermally induced elastic recovery for each sample extruded at 110°C . When a specimen was immersed in a silicon oil bath kept at 170°C for 1 min, elastic shrinkage quickly occurred, being complete within seconds. The ED was evaluated in terms of the ratio of molecular draw ratio (MDR) from shrinkage defined in eq. (1) to the macroscopic deformation of original draw. The measured data are depicted in Figure 5. From this figure it can be seen that in most of the

extrudates the ED is not as uniform across the width of bars as suggested by melting temperature and crystallinity measurements. The exception is bar 2, extruded with the CWD die from which the relative difference of ED across the width of bar 2 is less than 0.2%, but for the others it is larger than 2–3%. It can thus be concluded that among all the designs the CWD gives the most uniform deformation.

The molecular weight of PE resin can have a significant influence on the draw and property of extrudate, as shown in the crystallinity and draw efficiency of extruded bar 4. For the resin with the higher molecular weight, the crystallinity obtained is lower (see Table I). On the other hand, the more molecular chain entanglement will be favorable to the elastic recovery, that is, higher drawing efficiency is obtained.

For practical application of highly oriented polymers, a major problem is the possible reduction in strength in the transverse direction. Therefore the mechanical strength across the bars was studied. The results on mechanical properties of solid-state extruded bars are shown in Table I. The PEL values for different extrudates are listed in the last column of this table. It does not change very much for the bars with the same DR. It drops down for the bar with the higher DR. This behavior is anticipated, due to the fibrillar structure formation. For highly oriented chains, only the van der Waals forces in the transverse direction provide integrity. The PEL values show no major difference for all these samples of the same DR, except for the bar with DR of 23. It is obvious that extreme orientation does not favor transverse strength. Thus could be mitigated by flash melting and cooling of the bar surface to produce a tough skin on the bar.

Table I Physical and Mechanical Properties of Uniaxially Oriented Polyethylene Drawn at 110°C to Make Bars

Sample Bar I.D.	Molecular Weight ($\times 10^{-4}$)	Die Used	Draw Ratio	Cryst. % After Draw (Average)	Mechanical Properties		
					Machine Direction		Transverse Direction
					Tensile Modulus (GPa)	Tensile Strength (MPa)	PEL (MPa)
1	6	STD	14	81.0	13.7	267	18.5
2	6	CWD	14	81.6	16.0	251	22.0
3	6	CARD	14	81.9	17.9	280	26.2
4	19	CARD	14	77.3	10.4	321	23.6
5	6	CARD	23.4	82.4	16.4	273	19.9

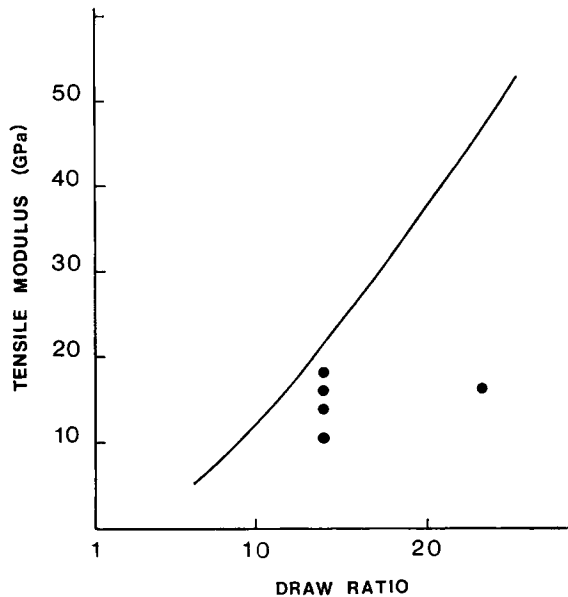


Figure 6 The modulus–draw ratio data comparison of present data with that in our previous study. The solid line is from Zacharides et al.² drawn at 120°C; the solid circles are from the present work.

The tensile modulus of these bars do not match our previously published modulus–DR curve, as shown in Figure 6. This is most likely caused by the low ED in the region of 65–75%. A higher ED was obtained for bar 4, ~ 90%, but the lower apparent is associated with a lower tensile modulus. The effect may be due to defects and notch sensitivity. Nevertheless, it can be seen from Table I that the tensile modulus and the strength are much higher than the conventional HDPE spherulitic morphologies reported in the literature. The tensile modulus and strength of the conventional HDPE are in the range of 413–1,030 and 17.9–33.1 MPa, respectively.¹⁷ Comparing these data with those listed in Table I, shows that the tensile properties of the extruded bars are improved tremendously, about 10–15 times.

CONCLUSIONS

The solid-state extrusion technique has been successfully performed on PE samples of large cross-section dimension, 5-cm wide and 0.6-cm thick. The tensile properties and the crystallinity of the solid-

state extruded PE bars are markedly higher, about 10–15-fold, than for the same PE conventionally crystallized. For most of the bars studied, the properties across the bar width are remarkably constant, indicating uniform draw. Thermal shrinkage tests appear to be more sensitive to profile differences than are measurements of melting point and percent crystallinity. From all data developed, it can be concluded that properties across the bar are not overly sensitive to die design.

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