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Preparation of ultra-oriented, high-strength filaments of polyethylene

TOKIO NIIKUNI,* ROGER S. PORTER
Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts, USA

A strong, transparent high-density polyethylene morphology has been produced in an Instron capillary rheometer by orientation and pressure near the polymer ambient melting point, 130 to 136°C. The multiple and interrelated variables for extrusion of this special morphology have been considered and tested. Capillaries of four different dimensions were employed. The formation of the transparent polyethylene was found to be the result of neither molten-state shear nor simple cold-drawing. It is initiated by the transition from molten flow to cold-drawing in which pre-oriented crystals are drawn within the capillary and entrance region under pressure and shear. Long strands of high perfection have been produced. Prior art, however, has not permitted continuous production. Differential Scanning Calorimetry on the transparent strands shows the existence of a higher melting structure in an inner core, and that a higher extrusion pressure and temperature gives a higher melting ultra-oriented polyethylene strand.

1. Introduction

Highly-oriented, strong, high-melting and transparent high-density polyethylene morphologies have been produced under combined shear, extension, and pressure in an Instron capillary rheometer [1-6]. The crystalline orientation along the *c*-axis (filament length) of this special morphology can be virtually perfect. Prior results indicate an X-ray orientation function of 0.998 and a crystallinity of 86% [4, 6].

Takayanagi *et al* [7-9] and Ward [10] have also obtained transparent polyethylene by variations of conventional drawing. The orientation and the crystallinity of their high density polyethylene samples are 0.996 and above 80% respectively. The difference in the morphology is as follows: in the Instron process used here, the polymer is initially in the molten state and orientation takes place during crystallization and deformation of pre-oriented, ductile crystals. In the latter case, and typical of other workers [11-14], the polymer is in the solid state throughout processing, i.e., conventional cold-drawing. Pressure and sample geometry are also independent variables in studies described here.

The extrusion temperature for production of clear, strong polyethylene in the Instron has been 130 to 136°C, whereas, it was 70 to 120°C in Takayanagi's experiments. In the latter experiments, the transparent polyethylene strand was produced continuously, whereas, before this, only filaments of limited length have been obtained in this laboratory using the Instron method.

In the present study, the first systematic study of the growth mechanism for transparent polyethylene strands has been conducted. The purpose was to understand the basis for preparation of these special morphologies which have the highest polyethylene tensile moduli and highest crystal orientations yet achieved [1-10]. The results may also aid in the development of a continuous preparation process which, hitherto, has been impossible. The results may also be of use to many other workers who have now initiated programmes in this area.

The effects of extrusion temperature, back pressure, flow rate, and capillary geometry on the growth of transparent filaments are discussed. The specific objective is to extrude rapidly and continuously a high melting, ultra-oriented, transparent morphology of high-density polyethylene.

The special strands have been previously

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*On leave from Mitsubishi-Monsanto Chemicals Company, Mie, Japan, studied in a number of ways, including thermal analysis, using the Perkin-Elmer DSC 1B [1-6]. These data show that the transparent polyethylenes have an equilibrium melting point ranging from 138 to 140.5°C depending on preparation conditions. Cold-drawn samples at ambient pressure show lower melting points, 135 to 138°C [7-9]. In our hands, higher melting points correspond to higher clarity. For simplicity samples melting above 138.0°C will be called "transparent" and those melting below 138.0°C, "translucent".

Strands, which do not readily transmit visible light, such as conventional, spherulitic polyethylene morphologies are called "opaque". Visual observations thus provide a qualitative scale for the structures of interest here. In some preparations, the transparent and translucent strands contain fracture planes. These are subsequently called "fracture-transparent" and "fracture-translucent".

2. Experimental

2.1. Instron model, capillary geometry and samples

The instrument used was a floor model Instron Tester TT-BM with a push-button selector for crosshead speeds of 0.05 to 50 cm min^{-1} and equipped with an MCR capillary extrusion rheometer. Four different tungsten-carbide capillaries were used. All capillary entrance angles were 90° and the dimensions are shown in Table I.

TABLE I The tungsten carbide capillaries, all 90° entrance angle

Number	Diameter, D_c (cm)	Length, L (cm)	L/D_c	Drawratio* D_r^2/D_c^2
I	0.0770	2.545	33.1	152.0
II	0.0766	5.098	66.5	154.5
III	0.1280	4.989	39.1	55.5
IV	0.1530	5.080	33.1	38.6

*D_r = 0.953 cm; the capillary reservoir diameter.

The sample used throughout was a high-density polyethylene (duPont Alathon 7050, weight average molecular weight ($\overline{M}w$) = 52500, number average molecular weight ($\overline{M}n$) = 18400). The physical and processing characteristics of this polymer have been previously described [1-6].

2.2. Standard preparation procedure

The polyethylene pellets were melted in the reservoir of Instron capillary rheometer at 150°C. The polymer was then extruded at a controlled temperature (130 to 136°C) and at volumetric flow rates of 0.36 to 1.44 cm^3 min^{-1} (0.5 to 2.0 cm min^{-1}, Instron crosshead speed). Considerable extrudate expansion is observed at the start of flow. At lower temperatures and high flow rates, the extrusion back pressure readily exceeds the equilibrium value for steady flow because of partial polyethylene crystallization in the reservoir. Concomitantly, the extrudate expansion becomes more pronounced. Finally, at the same temperature and crosshead speed, polymer flow is greatly retarded because of the massive reservoir crystallization, the pressure thus builds, and the transparent strand starts to form in the capillary entrance region which results in elimination of extrudate expansion.

The back pressure is then set near the maximum allowable Instron value and the transparent polyethylene strand is subsequently produced at one of the slowest rates possible with this Instron. Fig. 1 shows the pressure versus time relationship in the extrusion process of transparent strands. From time 0 to t_c, the crosshead is kept in motion at a speed of 0.5 to 2.0 cm min^{-1}. From time t_d, the pressure is kept constant and just below the Instron limit by controlling the crosshead at near the minimum speed. The crosshead speed is in the range of 10^{-3} cm min^{-1} or near 7×10^{-4} cm^3 min^{-1} volumetric flow rate, depending on capillary. The transparent polyethylene starts to grow in the capillary entrance at a time later than t_c.

To improve this standard procedure, the following variations were tried with the goal of making continuously and at high rate a transparent, ultra-oriented, unflawed, high tensile modulus polyethylene strand.

2.3. Tests at higher temperature

In the standard process, polyethylene, originally as melt, is crystallized by the extrusion stress (pressure) in the reservoir. This is because the extrusion pressure, up to 2 kbar, elevates the polyethylene melting point by about 40°C. The crystallization occurs in seconds after extrusion is started. The polymer is then extruded through the reservoir, the capillary entrance region and the capillary by a cold-drawing mechanism to make the transparent strands.

The high-speed deformation of aged reservoir crystals can be so severe as to produce extensive fractures. Thus to draw the polymer from a more ductile crystalline state, a yet higher extrusion temperature seemed desirable. Above 136°C, however, a flow rate higher than presently achievable is required to produce the pressure needed to arrest the flow by crystallization. To surmount this, the polymer in the reservoir was first crystallized by the process previously described. The temperature was then raised to 138°C and the pressure kept at about 2 kbar. This approach for preparation of transparent, unflawed strands was limited for the following reasons: (a) the Instron crosshead speed had to be moved discontinuously in order not to exceed the 2.4 kbar pressure limit; (b) the transparent polyethylene, once formed in the capillary, remelted because of the residence time at this temperature and lower pressures down the capillary.

2.4. Tests at reduced pressure

After achieving steady-state cold-drawing by the standard method, the back pressure was reduced to 500 atm by stopping the crosshead. This reduces the polyethylene melting point. The pressure was then kept constant by periodically starting and stopping the crosshead to achieve extrusion at a reduced rate. A supercooling effect prevents the crystalline material from melting at the reduced pressure. By this method, continuous extrusion of unflawed, but less-perfect, translucent polyethylene was accomplished. This suggests that for the production of transparent, ultra-oriented polyethylene crystals a higher pressure is required. Transparent strands could be re-established, however, in the same experiment by again increasing the pressure to the Instron limit, 2.4 kbar. The Instron has now been modified to operate at higher pressures. Fig. 1, shows the pressure-time relationship for the process. The transparent polyethylene starts to grow again at the time between t_g and t_h. During the time t_f to t_g the pressure was kept at 200 to 300 atm and less-perfect translucent polyethylene was extruded. The polymer in the reservoir remains crystalline throughout this process, this is why the peak t_c in Fig. 1, found in the first pressure increase curve (the standard process), is not observed during the second pressure increase process.

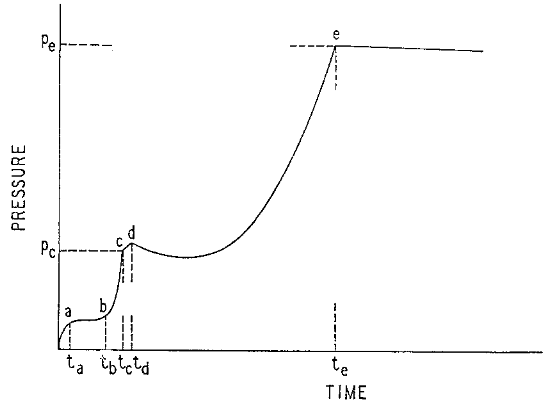

Figure 2 Instron rheometer pressure trace, combination method.

2.5. The standard procedure plus pressure relief

Fig. 2 shows the time versus pressure curve for a combination process. At time t_d, immediately after reaching the crystallization pressure at t_c, the crosshead speed was reduced to decrease the

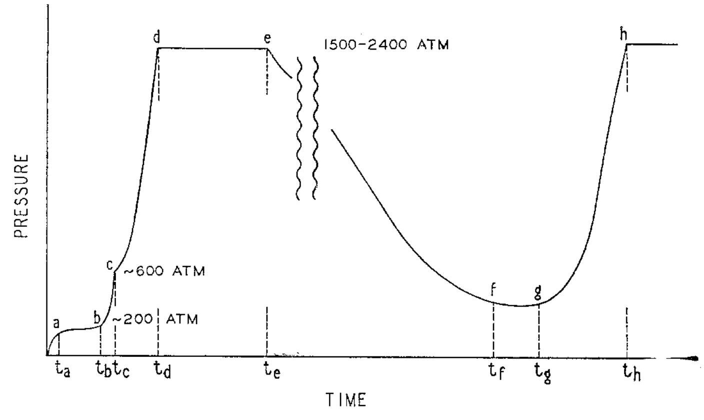

Figure 1 Instron rheometer pressure trace.

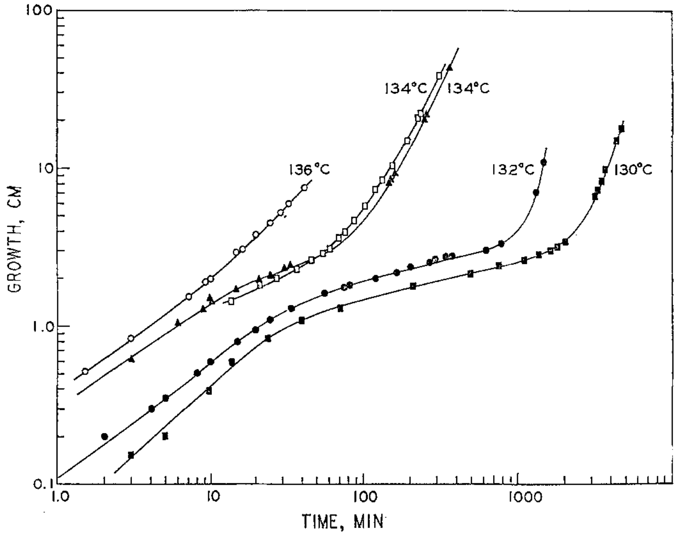

Figure 3 The growth of strands with time, capillary I.

rate of pressure increase which eventually reached the Instron limit and the experiment consequently stopped. By this method, an unflawed, transparent polyethylene segment, 6.5 cm in length, was obtained. This was the longest continuous unflawed transparent strand produced in this laboratory to date. It may be noted that the time for the pressure to increase from P_e to P_c in this case is much longer than in the standard method.

3. Results and discussion

3.1. Growth rates

Representative data and repeat experiments at 134°C are plotted in Fig. 3. It may be seen that the curves for transparent strand production can be divided into three regions corresponding to an initial slope, a plateau and finally a steady state where only fractured transparent strands are observed. Takayanagi *et al* have also reported that the solid state (cold-drawing) extrusion of polyethylene reaches a steady state [13-14]. The growth rates for transparent strands under different conditions are plotted in Figs. 4 and 5.

The transparent strand starts to grow in the capillary at time t_0. After a length of about 3.0 cm, the formation of unflawed strand ceases and a fractured transparent strand starts to grow. These features are general for tests at 130 to 134°C. At 136°C, only fractured transparent strands were obtained. Unfractured transparent samples at 136°C have, however, been obtained by an alternate procedure. This extrusion, shown in Fig. 3, did not show the plateau region. A plot of the transparent strand growth rate of temperature is shown in Fig. 4. It may be noted that growth rate exhibits a remarkably linear and sensitive dependence on temperature, increasing five times for only a 6°C temperature increase.

TABLE II Minimum flow rate (cm^3 min^{-1}), for reservoir crystallization

Temp. (°C)	Capillary no.			
	I	II	III	IV
138	2.0	1.0	5.0	5.0
137	1.0	0.5	2.0	5.0
136	1.0	0.5	2.0	2.0
135	1.0	0.5	2.0	2.0
134	0.5	0.5	1.0	2.0
133	0.5	0.2	1.0	1.0
132	0.2	0.2	1.0	1.0
131	02.	0.1	0.5	0.5
130	0.1	0.1	0.5	0.5
129	0.05	0.05	0.2	0.2

The minimum flow rate required to arrest the flow (to generate crystals) at each temperature, and thus to initiate the process, is shown in Table II. The trend is to lower flow rates for production of transparent strands in capillaries of higher "draw ratio", i.e., higher pressure drops. At extrusion temperatures below 132°C, lower flow rates give only steady state flow and conventional opaque strands. Extrusion temperature and capillary geometry dictate the extrusion rate for obtaining polyethylene crystallization in the reservoir and thus the minimum conditions for formation of transparent strands.

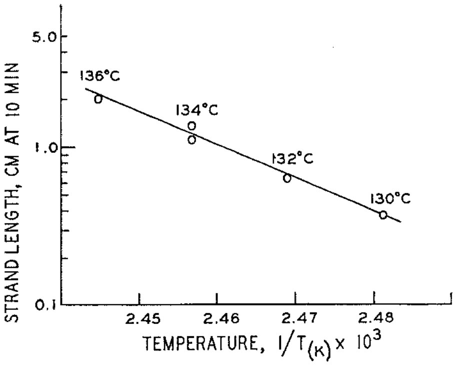

Figure 4 Growth rate of transparent polyethylene strands, capillary I.

3.2. Extrusion speed and growth rate

Fig. 3 suggests that the initial crosshead speed does not affect the growth rate. The importance of the initial speed is, thus, to develop the pressure and shear to induce polyethylene crystallization in the reservoir. The rate of production is limited by fracture of the transparent morphology. The cause of fracture in the steady state region is not well understood. It does appear to occur above a critical draw rate in the capillary entrance region. This critical rate may correspond to a limiting rate for the smooth conversion of the conventional to an ultra-oriented morphology. An activation energy for this process can be estimated from Fig. 4. Fracture of the strands occurs when pressure exceeds a critical rate for cold-drawing. The pressure, however, has two distinct effects causing (a) an increase in the melting point and (b) an increase in the draw rate.

Takayanagi *et al* [9] have also reported fracture formation at higher pressures corresponding to relatively high deformation rates. The point where the steady state cold-drawing starts is affected by temperature, pressure and capillary geometry.

The extrusion curves reach the steady state region at different times. For example, at 132°C, the sample prepared at 2400 atm yielded a transparent segment 5.7 cm in length whereas the 1500 atm sample formed a 5.0 cm transparent segment.

The conclusion, then, is that the most probable method for producing transparent polyethylene continuously is to extrude the polymer at higher temperature and by using relatively large diameter capillaries. Pressure can be made an independent variable.

3.3. The reduced pressure method

It may be postulated that the one and only way to extrudate transparent, ultra-oriented polyethylene continuously is to draw the polymer from its molten or from a highly ductile crystalline state. The draw rate cannot exceed the rate for morphological conversion to ultra-orientation or else extensive fracture results, see Fig. 5.

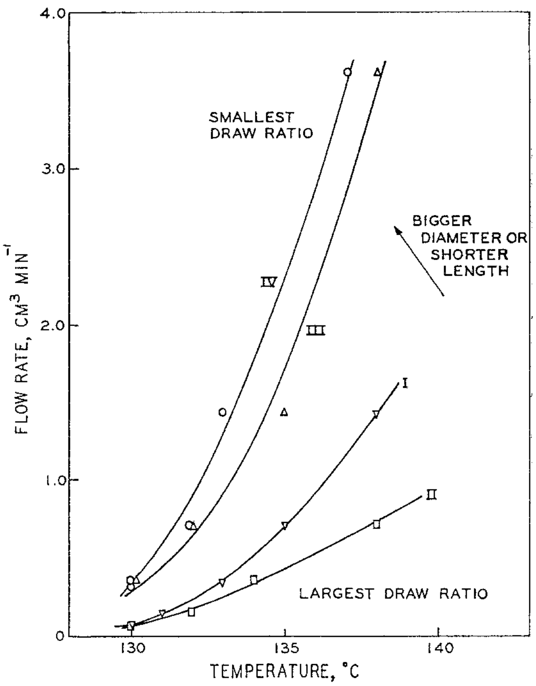

Figure 5 Combination of volume flow rate and temperature needed for reservoir crystallization for different capillary geometries, I, II, III and IV.

By the reduced pressure method, described earlier, a transparent strand of 5 cm length was produced. This sample showed virtually the same melting point and transparency as the sample obtained by the standard method. This supports the idea that ductile crystals, sheared while going through the capillary entrance region, give the transparent morphology.

At relatively low pressure, up to 600 atm, the crystals in the reservoir and capillary entrance are more deformable since the temperature is closer to the equilibrium melting point. Polymer, under this condition, has the potential of becoming highly oriented, the same as the polymer drawn into the entrance region under low-pressure during the initial extrusion by the standard preparation. But if subjected to a yet lower pressure, the extrudate comes out poorly oriented, only translucent, lower melting (137° C) and brittle since it doesn't contain the long fibril structure. This is because the low pressure results in less molecular extension. It should be noted that, in any case, only a part of the polymer which is drawn into the entrance region eventually becomes transparent and unflawed.

3.4. Growth initiation and length of transparent strands

The length attainable for transparent, unfractured strands is controlled by the volume and extent of polymer which has been highly oriented in the capillary entrance region. Table III lists the length of transparent, unflawed segments obtained for several conditions. The length is strongly related to the time t_c to t_d, i.e., from when the polymer is crystallized under pressure and then drawn. The time t_c is not exactly the same as the time that unexpanded solid solid-state extrudate first appears at the capillary exit. The higher the temperature, the longer this interval. For example, at 130° C the solid state extrusion starts in seconds after the pressure reached P_c ,but at 134° C, the soft solid, exhibiting extrudate expansion, continues to be extruded for about 1 min.

TABLE III The length of unflawed transparent strands as obtained by different extrusion capillary conditions

Extrusion conditions		Length of flawless, transparent segment (cm)	Time, sec from t_c to t_d
Temp. (°C)	Pressure (atm)		
130	1000	3.4	18
	1500	4.3	24
		4.5	
	2000	4.4	30
	2400	4.5	45
132	1000	4.2	18
	1500	5.0	33
	2000	5.3	36
	2400	5.7	39
	2000	5.4	36
134	2000	6.0	42

The first solid extruded from the capillary is always opaque, followed by the transparent strand. The opaque section varies in length from 3 cm at 134° C to 5 cm at 130° C for capillary III. The polymer in the reservoir is massively crystallized at t_c; the portion near the reservoir wall is sheared but is not substantially drawn nor stretched. The polymer in the capillary entrance region, however, is stretched (extensional flow) at the centre of the conical axis and partially sheared. The polymer is also crystallized under pressure and additional pressure pushes it into the capillary providing more stretching, drawing and orientation. This is a major difference from other cold drawn procedures. Here, the polymer molecule is not simply sheared nor extended by pressure. The polymer is first sheared and stretched by a molten flow mechanism (i.e., partially crystalline and high viscosity) and then massively crystallized with some orientation under pressure and then drawn in the capillary and entrance region.

The volume of the unflawed transparent segment has never exceeded the volume of the capillary entrance cone. The longest unflawed strand corresponds to 78% of the polyethylene in the capillary entrance cone. Apparently, the polymer in the upper entrance region and reservoir is not well oriented and thus not readily converted to unflawed, transparent strands.

In the standard method, the transparent morphology does not begin to form before massive crystallization occurs. Thus, in Fig. 3, t_c is taken as the origin. The key point in producing transparent strand continuously is, thus, to know how to supply a pre-oriented, soft crystalline state continuously into the capillary. One possibility is considered in Section 2.3. The idea is to maintain the soft crystalline state of polyethylene in the reservoir, and to impose an appropriate pressure. Poor orientation and poor transparency was obtained, however, at low pressures. Another possibility is to draw the polymer down through several stages as in metal processing. Temperature gradients are also an obvious future try.

Fig. 6 shows the growth rate in the plateau region where the unflawed, ultra-oriented transparent polyethylene strands are produced. Growth in this region is sensitive to the temperature but relatively independent of pressure

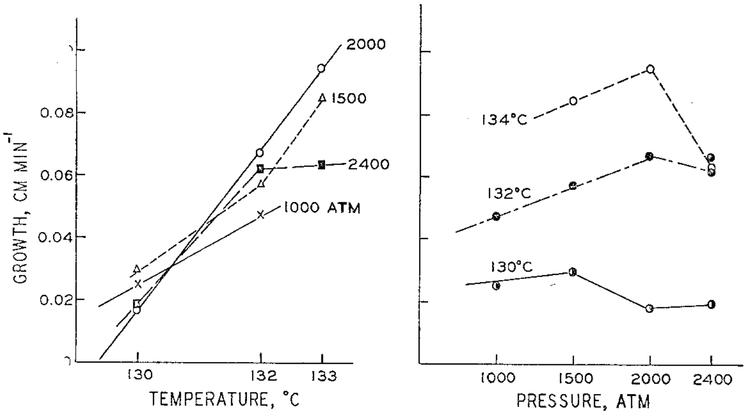

Figure 6 Growth of transparent, unflawed strand (plateau region). Influence of temperature and pressure.

especially at the lower temperatures. The initial growth of transparent strands is formed directly from the melt [15]. The major production is formed from a deformed morphology in the second stage. In the third, i.e., steady-state, region less-oriented reservoir morphologies are deformed (cold-drawn) into highly oriented but fractured polyethylene strands. In all three regions, temperature dramatically affects the growth rate.

TABLE IV Transparent polyethylene extrudate formed at 132° C, 2000 atm, in capillary III

Extrusion order	T_m (°C)	ΔH (cal g^{-1})
1	137.2	45
2	138.2	53
1	138.9	54
3	138.8	57
5	140.5	60
6	139.5	—

3.5. Thermal analysis

The sample obtained using the 0.128 cm diameter capillary III, were tested with Differential Scanning Calorimetry, Perkin-Elmer DSC-1B. Indium, with a melting point of 156.3° C was used for calibration. The heating rate used throughout was 2.5° C min^{-1}.

Samples were prepared by cutting small longitudinal sections from extruded polyethylene strands. Cutting was done with a razor blade. This is simple since the filaments readily fibrilate. The weight of each section was about 5 mg. For a study of possible variations in crystal perfection, sections were also sliced across the strand axis. Fig. 7 shows the position of the sample taken along and across the strand.

Table IV shows the changes in melting point,

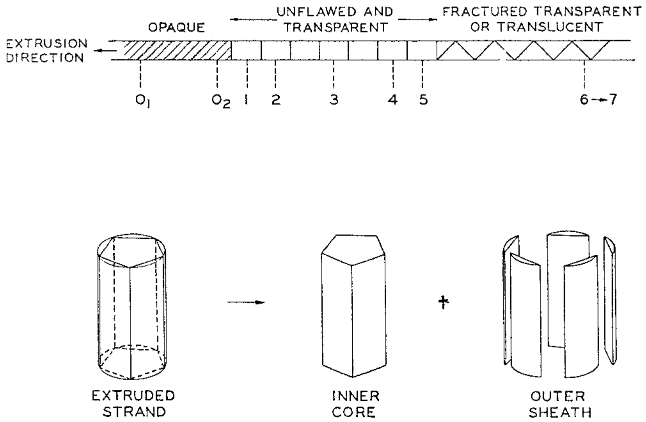

Figure 7 Sections of special polyethylene morphology.

T_m, and % crystallinity for sample from different positions along the strand axis. The T_m (positions 1 to 5) varies significantly from 138 to 140.5° C. This may be due mainly to more effective drawing down the strand since this part, which is closest to the fracture region, is subjected to higher pressures and larger draw ratios. Annealing could also play a role since the fractured end stays in the capillary at least 1 h longer than the lead end.

TABLE V Extrusion at 132° C under reduced pressure. All fractured and all measurements in steady state extrusion (position 7)

Pressure (atm)	T_m, °C
2000	139.5
1500	139.0
1000	137.8
250	137.0

Table V shows the effect of extrusion pressure on the T_m of the transparent extrudate at 132° C. A similar trend was observed at 130° C. Those samples were all fractured and either transparent or translucent. Obviously, low pressure gives less crystalline perfection to the extrudate. Table VI shows the difference in T_m and degree of crystallinity in the extrudate prepared at different conditions. All samples were cut from position 5, see Fig. 7. This means all samples were unflawed and transparent.

TABLE VI Polyethylene properties at different extrusion conditions

Temp. (°C)	Pressure (atm)	Melting point (°C)	Heat of fusion (cal g^{-1})
Capillary III			
130	2400	140.5	58
	2000	139.9	56
	1500	140.2	56
	1000	140.1	56
132	2400	140.5	58
	2000	140.5	56
	1500	140.5	57
	1000	140.5	55
133	2400	140.5	56
	2000	140.6	53
	1500	140.1	61
134	2400	140.5	58
	2000	140.5	57
Capillary I			
132	2000	139.5	59

The pressure does not significantly affect melting above 1500 atm where a T_m limit of 140.5 to 140.6° C is observed. The % crystallinity is 82 to 86% assuming that the perfect crystal has a ΔH of 68 cal g^{-1}. Table VII shows differences in T_m for different sample positions and for preparations at different temperatures. Table VIII shows differences in T_m for the inner core and outer sheath. It is significant, about 1.5° C. The weight of the inner core to outer sheath is about 4 to 3.

These tests are the first calorimetric documentation of morphological differences between the inner and outer sheath as previously observed microscopically [2] and suggested by other measurements. It can be said that the higher the extrusion temperature and pressure, the higher the melting point, i.e., the more perfect the crystal. Neither temperature nor pressure of preparation have a dramatic effect on T_m as it appears to approach an upper limit.

4. Conclusions

1. Over the measured range, 130 to 136° C, transparent and ultra-oriented polyethylene is obtainable with any of the capillaries tested. The appropriate pressure and flow rate, however, must be determined.

2. Transparent strands are obtainable at a faster rate at higher temperatures and at smaller capillary draw rates. Detailed studies have been made [13, 14]; pressure effects are not paramount.

3. The transparent polyethylene is obtained essentially as a result of a cold-drawing process in which partially crystalline polymer (a ductile crystal) is sheared through the reservoir exit and drawn down (or stretched) by pressure in the capillary entrance region. After massive reservoir crystallization, the polymer subsequently drawn into capillary remains transparent but contains fractures. When the pressure is low, ≥ 300 atm, only poorly oriented, opaque or translucent strands are obtained.

4. Thermal analysis by DSC shows that the inner core of the strands has a distinctly higher, 1.5° C, melting point than the outer sheath. Strands prepared at higher temperatures and pressures generally showed higher melting points.

5. The degree of crystallinity for the transparent strands is in the range 80 to 86% a few percent higher than for the same polyethylene conventionally crystallized.

6. Pre-oriented polyethylene morphologies are

TABLE VII Melting point of transparent strands prepared at 2000 atm

Extrusion Temp. (°C)	Run No.	Strand position by extrusion order				
		1	2	3	4	5
130	1	138.1	—	—	—	139.7
132	1	138.0	—	—	—	139.9
	2	—	138.8	—	140.3	—
	3	138.5	—	139.9	—	140.5
134	1	138.4	—	—	—	139.8
	2	—	139.5	—	140.7	—

TABLE VIII Melting point of inner core and outer sheath

	Strand position by extrusion order				
	1	2	3	4	5
Sample prepared at 132°C, 2000 atm					
T_m of inner core	138.3	139.4	—	140.2	140.3
T_m of outer sheath	137.5	137.8	—	138.2	138.9
Sample prepared at 134°C, 2000 atm					
T_m of inner core	138.7				140.0
T_m of outer sheath	138.7				139.1

a prerequisite for capillary production of ultra-orientation transparent strands. This occurs naturally in the conical capillary entrance region.

7. A smooth, clear capillary surface is necessary to produce the special morphology. The production of this transparent, unflawed material is generated at rates below a critical rate of morphological conversion which is shown to increase systematically with decreasing draw ratio (area ratio of reservoir to capillary) and with temperature.

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