Structure and properties of linear polyethylene crystallized by rapid cooling of melts: 3. The effect of shear

J. Akhavan, P. J. Hendra and H. A. Willis
Department of Chemistry, The University, Southampton, SO9 5NH, UK
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This paper investigates the relationship between the mechanical performance of an injection moulded product and the flow and temperature characteristics within the mould during manufacture. This has been achieved by devising a laboratory experiment involving production of a thin moulded rod. We have shown that the modulus in linear polyethylene is anomalously high when the polymer melt is rapidly solidified whilst being exposed to a high shear gradient. We have related this observation to the morphology of the solid product.

(Keywords: linear polyethylene; quenching; high modulus; orientation; moulded polyethylene)

INTRODUCTION

Injection moulding is probably the most important fabrication method for the production of a wide variety of thermoplastic articles and sections. It is generally recognized that the final properties of injection mouldings are strongly dependent on the design of the mould and its runners, the flow patterns adopted by the melt inside the mould and the precise processing conditions on the injection moulding machine. It is clear that all of these parameters in turn influence or even control the morphology and orientation of the polymer in the moulded product and that the mechanical performance of the product depends on the molecular structure[1-3].

Examination of injection mouldings for many polymers has shown that they frequently possess a skin of highly oriented molecules[4], the molecules being oriented along the direction in which flow had occurred immediately prior to quenching. The central bulk region, or core, on the other hand is often less oriented than the skin. This morphology has been observed in mouldings from both glassy and semicrystalline polymers. The higher molecular orientation in the skin is thought to cause dimensional instability and premature fracture under impact and flexure[3,5]. During moulding by injection, the polymer flows under considerable pressure and hence within a large and disparate shear field into a space where it rapidly cools to produce an object which is solid at the surface with a molten core, the latter eventually cooling to produce an inhomogeneous object. The experiment related here involves forcing a polymer melt through a cylindrical die under defined conditions (flow rate, pressure, temperature, shear etc.). After a stable flow of melt has been established the die is then rapidly cooled, the polymer freezing and blocking the tubular hole producing a cylindrical moulded object which is subsequently removed and examined. This note contains an account of the properties of such a polymer cylinder and the way its mechanical performance and molecular properties depend on the processing conditions.

EXPERIMENTAL

High density commercial polyethylene used in this investigation was supplied by British Petroleum and is graded Rigidex 50[7].

The polymer melt was extruded using a standard Baughan $1\frac{1}{4}''$ extruder fitted with a general purpose screw having a length:diameter ratio of 20:1. On the discharge end of the extruder is a pressure monitor and a long heated melt reservior containing a 90 degree elbow which directs the molten polymer downward, see *Figure 1*. The latter is used to control temperature. The polymer then flows downwards through a tapering hole and into a stainless steel capillary tube (which acts eventually as our mould). It has a length of 40 mm and an internal diameter of 1 mm and is surrounded by a cooling jacket as shown in *Figure 2*. The moulding produced when the polymer is frozen inside the capillary die is rod shaped with a large diameter end piece at the downstream end (as shown in *Figure 3b*).

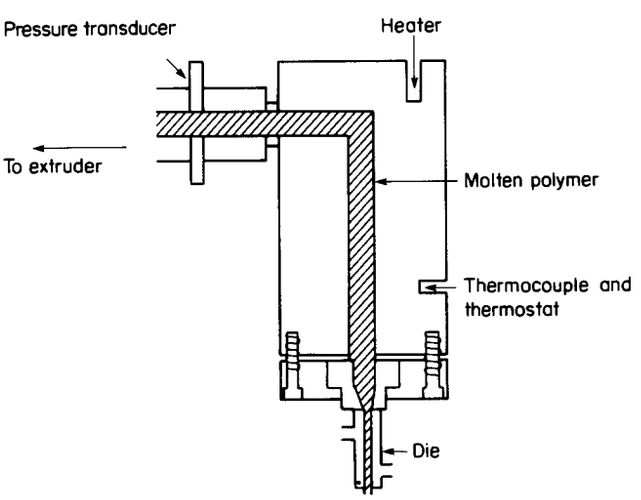

Figure 1 Schematic diagram of endpiece attached to the discharge end of the extruder

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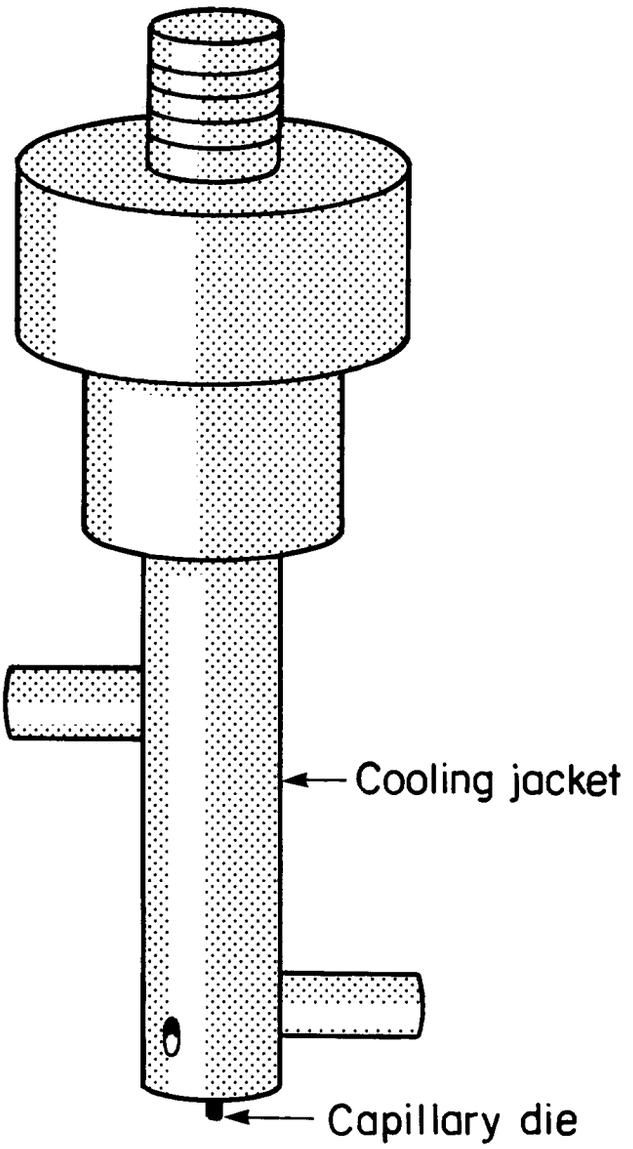

Figure 2 Diagram of the capillary die

The capillary die is divided into two sections to enable the solid polyethylene rod to be removed conveniently from the capillary mould after quenching. The polymer rod is removed by unscrewing the cooling jacket, hence also removing the lower part of the die. The rod, which is held tightly in the lower part of the die, detaches itself from the upper part at 'A', as shown in *Figure 3*. The polyethylene rod is then removed from the lower capillary tube by careful extraction.

Stage 1 of the experiment involved the establishment of stable extrusion of the molten polymer. The speed at which the polymer travelled through the capillary and its temperature could be adjusted over a wide range (see *Figure 4*). Pressure was monitored upstream of the capillary die but was not controlled.

Initial measurements of output and pressure were noted as the flow rate and reservoir temperature were increased. The results are given in *Figure 4*. The values of shear at the wall, quoted in *Figure 4* are calculated from the conventional equation[8].

$$r_w = \frac{4Q}{\pi R^3} \quad (1)$$

where Q is the flow rate and R is the die radius. From *Figure 4* it can be seen that the flow rate is controlled by the extruder screw since it is not significantly affected by temperature changes in the reservoir; however, increases in flow rate increase both pressure of the molten polymer and of course the shear rate at the die walls. An increase in temperature of the die head reduces the measured pressure of the polymer, presumably due to a reduction in melt viscosity.

The next stage in this investigation was to study solids produced by quenching the flowing polyethylene within the capillary die.

The flowing polyethylene melt was quenched by immersing the die head in iced water and at the same time forcing cold water to flow through the cooling jacket. Rapid cooling was achieved because the capillary die has thin stainless steel walls. A rapid flow of water was maintained for an ample time for complete solidification to occur. The quenched rod was then removed while the assembly was immersed in iced water, thus ensuring that heat from the aluminium block did not rewarm the rod. The experiment was conducted at various flow rates and die head temperatures, see *Figure 4*.

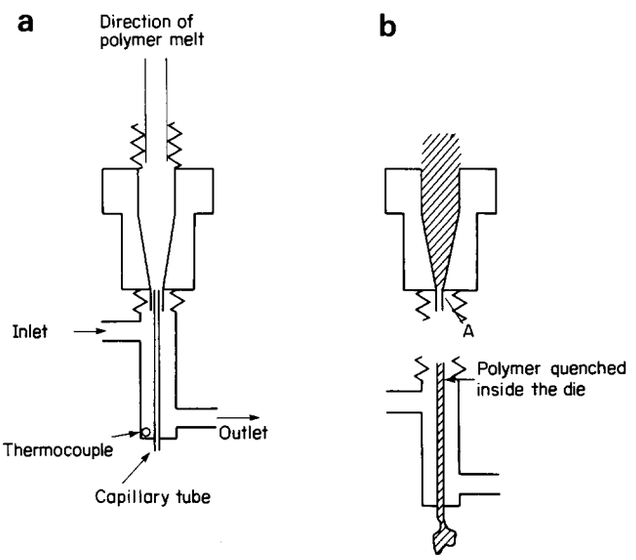

Figure 3 Schematic diagram of the capillary die (a) before quenching and (b) after quenching with the lower part of the die removed

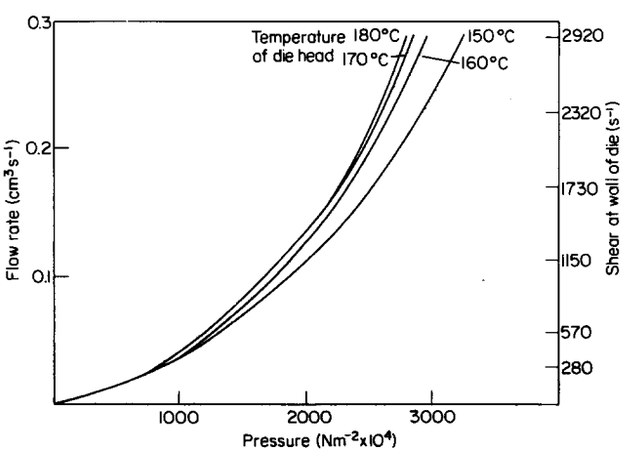

Figure 4 Dependence of the melt pressure and shear at the die wall on the flow rate and injection temperature

Table 1 Optical birefringence measurement ($\times 10^{-3}$) of linear polyethylene mouldings quenched inside the capillary

Section of rod	Flow rate (± 0.002 cm^3 s^{-1})	Temperature of capillary die before quenching ± 1°C: 150°C Skin	150°C Core	160°C Skin	160°C Core	170°C Skin	170°C Core
Centre	0.056					9	11
	0.168	23	21	14	13	10	12
	0.280					31	21
Downstream	0.056					5	4
	0.168	15	9	6	7	9	6
	0.280					27	9

SAMPLE ANALYSIS

Raman active longitudinal acoustic modes were measured using a Coderg T800 spectrometer powered by a Spectra Physics model 170 argon ion laser, operating at 514.5 nm.

The relationship between the longitudinal acoustic mode (the LA mode) and the length of the regular chain segments[9] is

$$v = \frac{M}{2L}\left(\frac{E}{\rho}\right)^{1/2} \tag{2}$$

where E = effective modulus of the crystalline core
ρ = density of the vibrating helix
L = length of the regular segment
M = order of the mode
v = bandhead frequency of the LA mode.

The values of E and ρ are 2.90×10^9 Nm^{-1} and 1×10^3 kg m^{-1} respectively[10]. Melting points and d.s.c. endotherms were recorded on a Perkin Elmer DSC 2B differential scanning calorimeter. The rate of heating was 20 deg/min and the rate of cooling was 80 deg/min.

Densities were measured on a standard density gradient column using a mixture of 2-butoxyethanol and 2-(2-methoxyethoxy)ethanol.

Degree of orientation of the polymer was determined from optical birefringence[11]. A Leitz polarizing microscope, fitted with a Berek quartz compensator and using the Köhler method of illumination was used. Microscopic measurements were taken on microtomed specimens from two regions, in the downstream part of the rod which is nearest the exit of the capillary tube and the centre of the rod. The samples, of 10 μm thickness, were microtomed parallel with the cylindrical axis. The first slice was labelled as the skin and the 50th microtomed slice was labelled as the centre.

The test method for Young's modulus is based on that given by Bonnin, Dunn and Turner[12]. The quenched polymer rods were cut into two pieces of length 20 mm. Each rod, in turn, was supported by two parallel knife edges cut with V-notches to prevent the rods from rolling. The knife edges were placed 15 mm apart. The applied load was hung from the specimen half way between the supports and the specimen deflection was measured by observing the centre of the rod through a travelling microscope. All deflections were measured after 100 seconds under load. In all cases loads were limited to 80% of the elastic limit. Experiments were conducted at a constant temperature of 22°C.

Table 2 Young's modulus (± 100 MPa) of linear polyethylene mouldings quenched inside the capillary

Section of rod	Flow rate (± 0.002 cm^3 s^{-1})	Temperature of capillary die before quenching ± 1°C: 150°C	160°C	170°C	180°C
Upstream	0.056	3070	2250	2120	1970
	0.168	3350	3070	2960	2440
	0.280	4160	3670	4680	3410
Downstream	0.056	2720	2540	2040	1970
	0.168	3410	3150	3050	2520
	0.280	4500	5110	4680	5620

Young's modulus was calculated using the equation[13]

$$E(t) = \frac{4L^3}{3\pi D^4}\frac{\omega}{\delta(t)} \tag{3}$$

where $E(t)$ = Young's modulus
L = distance between supports (in this case 15 mm)
D = diameter
W = applied load
$\delta(t)$ = deflection

RESULTS AND DISCUSSION

As shown in *Table 1*, the values of birefringence for the skin and core of the quenched rods (a) increase with increasing flow rate, (b) decrease along the length of the rod, in a downstream direction and (c) decrease with increasing temperature of the molten polymer prior to quenching.

It is also evident from *Table 1*, that the birefringence values for the skin of the quenched rod are larger than those of the cores particularly at high flow rates.

We can conclude that the degree of orientation tends to (a) relax with distance, (b) increase with increasing flow rate and (c) decrease with a decrease in viscosity. At high flow rates the molecular chains become more aligned at the capillary walls.

The Young's modulus values calculated from equation (3) are given in *Table 2*. It is clear that the Young's modulus for both parts of the quenched rod:

(1) increases with increasing flow rate;

(2) decreases with increasing temperature, except at the higher flow rates.

It can also be seen that the Young's modulus values do not change along the length of the rod for a given flow rate

or temperature. Increasing the melt temperature (and hence reducing its viscosity) reduces both the consequent orientation and rigidity of the rod. The fact that we note no change in modulus along the rod may be because Young's modulus is only measured by deflection at the centre of each piece. At high flow rates the values obtained for Young's modulus do not vary with viscosity; one possible explanation is that the flow pattern has changed. The presence of orientation is reflected also in die swell measurements[14], (see *Table 3*), in that the amount of die swell increases with increasing flow rate, although the effect of temperature is not discernable.

The optical and mechanical results indicate that the molecular chains are aligned in the capillary mould and that flow rate and die head temperature all significantly affect these properties.

White and his coworkers[6] have shown that the stream lines for the flowing melt when entering the capillary die have a 'wineglass stem' appearance. According to White, the chains are highly oriented in the entrance to the capillary die, but tend to disorientate once they enter the die.

Southern and his coworkers[15-17] have produced highly oriented fibres by solid state extrusion of polyethylene is a capillary rheometer. The fibres produced were found to consist of essentially continuous crystals. Similarities were found between the continuous crystals developed in the capillary rheometer, with the 'shish kebab' crystals studied by Pennings and Kiel[18] and Keller *et al.*[19,20], and the pressure induced crystallized morphology reported by Wunderlich and his coworkers[21-26]. Our results indicate that the quenched polymer rods are oriented and hence they might conceivably possess an extended chain or 'shish kebab' morphology. However, if we compare our melting point data, presented in *Table 4* and crystallinity values calculated from density (see *Table 5*) with those given for extended chain structure (i.e. melting point 146°C[11] and crystallinities by density as high as 97%[19]), it is clear that both sets of our figures are too low to justify any proposal of extended chain structures.

Calculated lamellar thickness in our quenched rods are presented in *Table 6*. It is evident from *Table 6* that an increase in flow rate of molten polymer leads to an increase in thickness of lamellae in the quenched rod. It is also clear that the lamellae in the rods tend to decrease in thickness downstream, all of which would be consistent with the views of White[6] referred to above.

Table 3 Die swell measurements (±0.1°C) of linear polyethylene mouldings quenched inside the die

Flow rate (±0.002 $cm^3 s^{-1}$)	Temperature of capillary die before quenching ±1°C			
	150°C	160°C	170°C	180°C
0.028	2.4	1.8	1.9	2.3
0.056	2.1	2.4	2.8	2.1
0.113	2.4	2.4	2.3	2.4
0.170	2.3	2.4	2.2	2.5
0.228	2.6	2.6	2.5	2.6
0.287	2.7	2.4	2.6	2.7

Table 4 Melting temperature (±0.5°C) of linear polyethylene mouldings quenched inside the capillary

Section of rod	Flow rate (±0.002 $cm^3 s^{-1}$)	Temperature of capillary die before quenching ±1°C			
		150°C	160°C	170°C	180°C
Upstream	0.028	127	126	126	126
	0.056	127	127	128	128
	0.113	129	129	128	129
	0.168	129	129	129	129
	0.228	130	130	129	130
	0.280	132	130	130	131
Centre	0.028	126	127	127	126
	0.056	127	128	128	127
	0.113	129	129	129	128
	0.168	129	129	129	129
	0.228	130	129	129	130
	0.280	131	131	131	132
Downstream	0.028	127	127	126	127
	0.056	128	128	128	127
	0.113	128	129	129	128
	0.168	128	129	129	129
	0.228	130	130	129	130
	0.280	130	131	130	131

Table 5 Density ($\rho \pm 0.002$ g cm^{-1}) and crystallinity (±1%) values for linear polyethylene mouldings quenched inside the capillary

Section of rod	Flow rate (±0.002 $cm^3 s^{-1}$)	Temperature of capillary die before quenching ±1°C							
		150°C ρ	150°C Cry	160°C ρ	160°C Cry	170°C ρ	170°C Cry	180°C ρ	180°C Cry
Upstream	0.056	0.947	58%	0.956	63%	0.946	58%	0.947	58%
	0.113	0.953	62%	0.953	62%	0.953	62%	0.952	61%
	0.168	0.948	59%	0.955	63%	0.952	61%	0.953	62%
	0.228	0.953	62%	0.954	63%	0.954	63%	0.954	63%
	0.280	0.948	59%	0.950	60%	0.948	59%	0.954	63%
Centre	0.056	0.948	59%	0.950	60%	0.953	62%	0.948	59%
	0.113	0.950	60%	0.950	60%	0.953	62%	0.947	58%
	0.168	0.950	60%	0.948	59%	0.951	61%	0.956	60%
	0.228	0.952	61%	0.951	61%	0.952	61%	0.953	62%
	0.280	0.953	62%	0.947	58%	0.951	61%	0.954	63%
Downstream	0.056	0.946	58%	0.946	58%	0.948	59%	0.947	58%
	0.113	0.946	58%	0.955	60%	0.948	59%	0.946	58%
	0.168	0.952	61%	0.949	59%	0.948	59%	0.949	59%
	0.228	0.947	58%	0.946	58%	0.947	61%	0.950	60%
	0.280	0.948	59%	0.953	62%	0.952	61%	0.948	59%

Table 6 Calculated lamellar thickness (±2 Å) from the Raman LA modes recorded on linear polyethylene mouldings quenched inside the capillary

Section of rod	Flow rate (±0.002 $cm^3 s^{-1}$)	Temperature of capillary die before quenching ±1°C			
		150°C	160°C	170°C	180°C
Upstream	0.028	177	191	181	183
	0.056	186	186	186	192
	0.113	193	192	183	183
	0.168	196	189	188	183
	0.228	194	196	193	196
	0.280	196	194	194	194
Centre	0.028	168	168	168	176
	0.056	183	172	168	161
	0.113	183	188	176	179
	0.168	188	186	179	182
	0.228	188	192	193	202
	0.280	191	192	194	193
Downstream	0.028	166	162	167	168
	0.056	172	162	162	175
	0.113	174	179	168	168
	0.168	177	170	171	168
	0.228	168	176	182	186
	0.280	184	186	186	191

CONCLUSION

In this investigation we have gained an insight into the relationship between the mechanical performance of an injection moulded product and the flow and temperature characteristics within the mould during manufacture.

We suggest that extension of this work could prove to be of considerable importance to mould designers. Clearly, where changes of section occur shear rate is frequently maximized particularly near the surface of the product. We propose that at these points, so often the ones where stress is high, the modulus will be unfortunately large with the inevitable consequence that cracking of the surface will be a persistent problem.

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