Extrusion and Orientation
of
Higher Molecular Weight Polyethylenes

by

Kenneth Roy Tate

A thesis submitted in conformity with the requirements
for the Degree of Doctor of Philosophy,
Department of Metallurgy and Materials Science,
in the University of Toronto.

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The die design, lubrication, resin molecular weight and other processing conditions all interact to determine the eventual properties of extruded polyethylenes with molecular weight of 0.5 Mg mol\(^{-1}\) to 6 Mg mol\(^{-1}\). The principal objective of this work was to develop an extrusion-orientation process. To fulfil this objective, it was necessary to extrude higher than conventional molecular weight polyethylene resins. This type of extrusion required the investigation of lubrication methodology and controlling the rate of deformation. Continuous screw extrusion, of these higher molecular weight resins, was carried out using conventional and controlled elongational velocity gradient dies. This work established that the elongational velocity gradient imposed upon the polymer melt must be maintained at a specified value to prevent melt fracture and to obtain the desired degree of chain orientation in the extrudate.

The practical accomplishments of controlling the elongational velocity gradient and lubrication conditions were the development of a process to extrude ultra high molecular weight polyethylene at rates of 4 to 20 times that of commercial ram extrusion. Another achievement was a unified process to extrude oriented very high and ultra high molecular weight resins directly from the die. It was also possible to extrude ductile very high molecular weight polyethylene which could be drawn to elongation ratios of 10 to 200, depending upon the draw temperature.
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1 Introduction

Extrusion-orientation is a technique used to increase the strength and tensile modulus of polymeric macromolecular solids. The technique involves uncoiling, extending and aligning the polymer chains and then inducing crystallization to trap the orientation.

The principal focus of this thesis was to develop extrusion-orientation methodologies for polyethylenes using screw extrusion apparatus. To accomplish these objectives, it was first necessary to screw extrude very high molecular weight polyethylene (VHMWPE) and ultra high molecular weight polyethylene (UHMWPE)\(^1\). UHMWPE is generally considered to be unextrudable by conventional capillary extrusion \([1]\), but as was found in this study, these resins can be readily screw extruded with lubricated dies operated at an appropriate elongational velocity gradient (EVG). Once it was possible to screw extrude these higher molecular weight polyethylenes, successful extrusion-orientation experiments were conducted.

This thesis displays that it is possible to screw extrude partially oriented VHMWPE and UHMWPE extrudates, with increased strength and modulus, which have molecular draw ratios near the limit of the die extrusion ratio. This can be considered the first step towards a commercial extrusion-orientation process. The thesis also shows that it is possible to extrude substantially unoriented higher molecular weight resins. Some of the unoriented VHMWPE extrudates can be subsequently extended to draw ratios greater than 200 at temperatures

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1 VHMWPE has a molecular weight of about 1 Mg mole\(^{-1}\). UHMWPE has a molecular weight of 2 Mg mole\(^{-1}\) or greater.
near the melting point. (Please note that the drawing of the extrudates to increase the strength and modulus is not discussed in this thesis.) Screw extrusion of unoriented UHMWPE shows the possibility of replacing the very slow ram extrusion process normally used for these resins. For UHMWPE, the extrusion rates achieved were 4 to 12 times greater than conventional ram extrusion.
2 Review of the Background and Theory

2.1 Rationale

Much of this thesis is concerned with the development of extrusion-orientation processes for the self-reinforcement of polyethylene (PE). These processes depend upon macromolecular extension to achieve chain orientation and increased mechanical properties. As the literature review illustrates much of the knowledge required for extrusion-orientation of polymers is well understood, yet, because of the challenges of trapping the orientation by crystallization, practical extrusion-orientation has been difficult to achieve.

This literature search focuses upon some of the concepts required for self-reinforcing polymers by extending and orienting the macromolecules in the melt or the solid state. It also illustrates some potential polymer processing techniques which acted as the nuclei for the new processes introduced in this thesis.

2.2 Literature Reviewed

Maertin and Ehrenstein[2] delineated how polymer processing can produce self-reinforced partially crystalline thermoplastics. In a review of literature they stated that the following conditions are necessary to produce high strength parts in the injection moulding process:
1. The die must generate elongational flow to ensure chain extension and orientation. Figure 2-1 shows accelerated elongational flow produced by a positive velocity gradient parallel to the axis of flow (ie. \( dV/dx > 0 \)).

2. The polymer should be linear and have a high molecular weight to effect orientation and permit the chains to become parallel to one another.

3. Crystallization must be induced during the final holding phase.

![Figure 2-1](image)

Figure 2-1  Extensomal (ie. elongational flow is an accelerated flow with a flow gradient of \( dV/dx > 0 \)). The accelerated flow is created by the nozzle geometry.


Marrucci [3] indicated that extensional flow has the potential to impart a stable oriented structure to the macromolecules in polymer solutions and melts. In his paper, Marrucci critically reviewed the limiting conditions that must be satisfied to produce oriented
structures in polymeric liquids. He also discussed the difficulties which must be overcome if the oriented structure is to be frozen into a high-strength material. Marrucci cited the early work of Ziabicki et al [4] on fiber spinning to develop a list of relevant insights. These insights are:

1. During fiber spinning some of the orientation in the final product is a result of orientation imparted to macromolecules while in the liquid state.

2. Uniaxial extensional flow causes the orientation of the macromolecules in fiber spinning. Extensional flow selectively orients the particles in the direction of the flow.

3. Spontaneous relaxation of the macromolecules, because of entropy considerations, opposes the orientation imposed by the elongational flow. The processing conditions determine whether the macromolecules are oriented or disoriented when crystallization occurs.

4. Cohesive failure of the fiber limits the processing conditions (ie. tension on the fiber) in spinning. Changing conditions in an attempt to promote fiber orientation may result in fiber breakage.
Marrucci stated that the elongational viscosity, \( \eta_{\text{elong}} \), can be related to the first normal stress difference \( \sigma_{yy} \), in the following manner.

\[
\eta_{\text{elong}} = \frac{\sigma_{xx} - \sigma_{yy}}{G}
\]

Marrucci argued that in order to provide a sufficient parallel velocity gradient \( G \), the following inequality must be satisfied:

\[
G > \frac{0.5}{\tau}.
\]

Marrucci expressed that the largest relaxation time \( \tau \) is a characteristic time of the material at the given processing conditions. In dilute polymer solutions or low molecular weight polymer melts, the relaxation times are in the order of \( 10^{-5} \) to \( 10^{-4} \) s. In entangled systems, such as concentrated solutions or high molecular weight melts, the relaxation time are much longer and moderate values of \( G \) are sufficient to orient the macromolecules. Rouse [5] theory has been used to predict the largest relaxation time for unentangled low molecular weight melts and dilute solutions. This theory related the zero shear viscosity \( \eta \), molecular weight \( M \), polymer density \( \rho \), and temperature \( T \). The relaxation time is given by

\[
\tau = \frac{6 \eta M}{\pi^2 \rho RT}.
\]
Marrucci stated that Rouse's equation underestimated the relaxation times of real polymer systems and can be explained in two ways. 1) Chain entanglements in the melt greatly increased the relaxation time. 2) Larger units with long relaxation times are formed at the beginning of crystallization.

Marrucci stated that the amount of time $t$, the macromolecule spends in the orienting field also determined degree of orientation. The molecule must remain in the flow field for sufficient time to become oriented and stretched. The following inequality relates the parallel velocity gradient and the time in the flow field to a particular constant $\alpha$. The value of $\alpha$ is 4 or greater and depended upon molecular weight, temperature, internal viscosity and other factors.

$$Gt > \alpha$$

Marrucci also stated that polymers with high internal viscosities (ie. high MW) are candidates for flow orientation and crystallization. High viscosities would increase the relaxation time of the polymer, such that recoil of the macromolecules is minimized prior to crystallization. The time in the flow field needed to orient a high molecular weight polymer should not be very long since each portion of the macromolecule chain between entanglements was small. By analogy with small molecules, the short regions between entanglements would also orient quickly.

Southern and Porter [6] crystallized commercial high density polyethylene (HDPE) with melt flow index of 0.9 and 2.1 under the combined orientation and pressure effects avail-
able in an Instron capillary rheometer. The samples formed consisted of fibrils oriented parallel to the axis of flow with an extended-chain component in the crystal structure. The specimens were clear with a high degree of crystal perfection and significantly higher melting point than the melt crystallized polymer. Southern et al introduced an empirical equation for HDPE which relates the degree of supercooling to the static pressure of a quiescent melt. The degree of supercooling was given by
\[ \Delta T = T_M + (0.02^\circ C/atm)P - T_c \]
where \( \Delta T \) was the degree of supercooling, \( T_M \) was the equilibrium melting point of a perfect polyethylene crystal in \( ^\circ C \), \( T_c \) was the temperature of crystallization in \( ^\circ C \) and \( P \) was the static pressure in atmospheres. This equation predicted a supercooling of 20 \( ^\circ C \) for a static pressure of 900 atmospheres (91 MPa). Since entropy effects of the oriented chains were ignored, the degree of supercooling should be greater than the equation predicts. Southern and Porter concluded that:

1. the orientation of the polymer chains was attributed to the velocity gradient parallel to the axis of flow. The larger the velocity gradient along the centre axis of flow, the higher the melting point of the crystallized polymer after extrusion was completed.

2. the velocity gradient perpendicular to the axis of flow did not seem to be the significant factor in producing the oriented chain structure.
3. Crystallization in the entrance region of the capillary was a direct result of the longitudinal velocity gradient, in the entrance region of the capillary, compounded with the applied pressure.

4. Pressure increased the degree of supercooling and aided in the formation of crystals which resulted in a sluggish extrudate that was accompanied by an increase of pressure.

In a later paper, Crystal and Southern [7] confirmed that these specimens, produced by the combination of orientation and pressure in the Instron capillary rheometer, did contain a chain-folded lamellae and extended-chain structures. They based this conclusion on microscopy and electron diffraction studies. Southern and Porter [8] collected thermal data to accentuate the extraordinary melting behaviour of the oriented polyethylene samples produced by crystallization in the Instron capillary rheometer. They found that the melting point was sharp and high and that the crystals could be superheated. They also concluded after comparison of thermal properties with other known structures, that an extended chain crystals were inferred.

Tam [9] produced transparent highly oriented polyethylene fiber by a continuous polymer melt extrusion process. The process combined flow orientation, temperature gradients and drawing to achieve highly oriented fibres at low pressures. The prime

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1 The melting of the extended chains is believed to result in an extension of the differential scanning calorimetry (DSC) tail which was observed by Southern and Porter. The tails are similar to those observed for shish-kebab structures.
conclusion drawn by Tam was that flow orientation of the polyethylene melt and shear induced crystallization produced highly oriented transparent fibers. These fibers consisted of extended chain crystals. The extended chain crystal structure was indicated by the high Herman-Stein orientation function of 0.9966 in the extrusion direction and by elevated melting temperature. Tam also concluded that continuous production of oriented fibers can be produced by controlling the temperature gradient along the die, the flow conditions into the die orifice and the draw rate. The fibers produced in this process were more oriented on the outside shell and less oriented in the core.

Collier, Tam, Newcome and Dinos [10] extruded highly oriented polyethylene and polypropylene fibres by uniaxial elongational flow and oriented crystallization. The experimental apparatus and choice of HDPE were similar to Tam’s earlier work. No melt flow index was given for the polypropylene. Collier et al argued that the melting temperature of the flow oriented polymer must be greater than that of the non-oriented coiled polymer. The change in Gibbs free energy in a polymer system was given by

\[ \Delta G = \Delta H - T \Delta S. \]

If the system was melting, then the change in free energy was zero and the equation above can be rewritten as

\[ T_m = \frac{\Delta H}{\Delta S}, \]

where \( T_m \) was the melting temperature. Since the entropy of the oriented polymer chains was less than the corresponding random configuration, Collier et al hypothesized
that the entropy was inversely proportional to the elongational velocity gradient.

\[ \Delta S \propto \frac{1}{\left( \frac{\delta v}{\delta z} \right)} \]

The enthalpy of a polymer melt was believed to be insensitive to chain configuration. Thus the effective melting point must be elevated because of the reduced entropy as shown below.

\[ T_m \propto \frac{1}{\Delta S} \times \frac{\delta l}{\delta z} \]

The supercooling of the melt increased with the elongational velocity gradient. At greater extensional flow rates, the decreased entropy caused the effective melting temperature to increase which also increased the free energy of the system (ie. the driving force for crystallization). The resistance to crystallization was also reduced since the chains were more ordered (ie. parallel orientation). Collier et al stated that increased free energy and resistance leads to rapid crystallization. Collier et al used this concept to explain the orifice plugging observed by Southern and Porter and others. At the entrance to the orifice the elongational velocity gradient was the largest. If the melt, in the reservoir, was near the melting point it will become supercooled and less resistant to crystallization. As a result, massive crystallization suddenly occurred at the entrance to the capillary. Collier et al concluded:
1) The temperature in the converging zone should be greater than the melting point of the polymer to prevent crystallization in the converging zone and ensuing blockage. The temperature in the die-land should be low enough to ensure crystallization in this region.

2) Crystallization should occur in the die land region and not in the entry region to the capillary to ensure continued polymer flow at low pressures. The temperature of the reservoir zone must be maintained at a temperature higher than the effective melting point of the polymer to prevent massive crystallization from plugging the capillary and increasing the extrusion pressure.

3) Extrusion of polyethylene melts are not dynamically stable, as crystallization can occur inside the die and plug the capillary. Greater extrusion rates may be more stable than slower extrusion rates. Polypropylene melts are dynamically more stable than polyethylene melts.

Collier, Chang and Upadhyayula [11] extended the previous work on fibers to oriented ribbons using HDPE (MFI 2.6) and Polypropylene (MFI 5.0). The extrusion operation was intermittent. The die was initially cooled until the orifice was plugged and then it was reheated to permit extrusion. The speeds ranged from 2.5 cm/min (1 inch/min) to about 30 cm/min (one foot per minute). It was possible to extrude a maximum of about 60 cm of extrudate before plugging of the die terminated the process. The screw speed was only 2 rpm. The structure of the polypropylene and polyethylene ribbons were highly oriented
and fibrillar when examined by scanning electron microscopy (SEM). Differential scanning calorimetry (DSC) thermal analysis at 10 °C/min found that the melting peak temperature was increased by 8.5 °C for the polypropylene and 10 °C for the polyethylene. The Youngs modulus of the polypropylene extrudate was reported to be 8.76 GPa, the yield strength was 317 MPa, and elongation at break was 9.5 percent. The failure surface exhibited a multiple layer delamination.

Collier, Perez, Ghosh and Sierra [12] developed the melt transform coextrusion (MTCE) process. MTCE consisted of orienting and crystallizing a centre core of polypropylene by hydrodynamic means in the die, while the outer sheath is made up of lower melting point unoriented polyethylene which crystallized outside the die. The molten polyethylene skin acted as a lubricant for the oriented polypropylene core. This core-sheath structure allowed much faster production rates. Perez and Collier [13] continued the work on MTCE and have found that the tensile strength, tensile modulus and melting point elevation increased with increasing extrusion pressure and with flow channel reduction ratio. The authors introduced a take-up device to pull the extrudate from the die. Collier [14] stated that the skin layer in the MTCE process acted as a lubricant and a crack inhibiting layer.

Mackley, Frank and Keller [15] conducted work on flow induced orientation of polyethylene melts. They showed that fibres could be formed when a melt flowed through a single 0.35 mm diameter orifice at a relatively low pressure of 5 MPa (50 bar). The melt temperature was 140 °C with a mean velocity of 2.6 cm s\(^{-1}\). They emphasized that the
continuous crystal formation only occurred for a specific set of conditions. If the temperature was raised or the flow rate reduced, then no crystallization took place. Alternatively, if the temperature was lowered or the flow rate increased, then the orifice was blocked by overwhelming crystallization.

Odell, Grubb and Keller [16] discontinuously extruded oriented polyethylene plugs using a capillary rheometer. The resin used was BP Rigidex 9 with Mw of approximately 130 000 g mol\(^{-1}\). The plugs were of approximately 0.8 mm diameter and 5 cm long with a tensile modulus which ranged from about 10 to 100 GPa. The structure formed by this process is shown in Figure 2-2. It consisted of chain extended core fibrils, probably formed by flow orientation, which acted as a framework for the interlocking parallel overgrowths. If the core fibrils were close enough, the overgrowths would crystallize with chain folding parallel to the flow direction. This was further enhanced by the interlocking mesh of transverse folded lamellae. If the distance between core fibrils was large then the chain folding habits would twist and weaken the structure.
Figure 2-2  Schematic diagram of the interlocking shish-kebab morphology. The structure consisted of chain extended core crystals (ie. the shish) and interpenetrating tapered lamellar over growths (ie. the kebab).

Bashir, Odell and Keller's [17] task was to take the batch orientation process of Odell and develop a similar continuous direct extrusion-orientation process. Bashir realized that conventional melt spinning produced orientation in the melt. This orientation was lost because of the high extrusion temperatures and slow quenching which allowed significant remelting and relaxation to occur. He then proposed using the a blend of 3% GUR 415 and Rigidex 006-60. This blend would allow the formation of oriented UHMW polyethylene crystals which were stable in the melt (up to 160 °C) and did not remelt like normal polyethylene crystals at this extrusion temperature. The method of spinning involved extrusion with an Instron capillary rheometer at a temperature just greater than the self-blocking temperature. The filament was quenched with cold air 2 cm from the
die exit and then wound upon a drum. Bashir found that a conventional resin (ie. Ridigex 006-60) did not have the ability to support the required drawing tension slightly above the self-blocking temperature, it would fracture. In contrast, the blended melt behaved in a much different manner than the corresponding neat resin melt. The blended melt had the ability to support a "very high tension" and allowed the polymer to be drawn from the die with little or no extrudate swell. The high tension prevented self-blocking and the extrudate pressure from rising. Bashir reported extensional modulus of 3-10 GPa, depending on extrusion speed. Transmission electron microscopy (TEM) showed a shish-kebab morphology for the blended resins. DSC indicated two peaks for these extrudates, one peak at approximately 134 ºC and another at 138 ºC. The dual peak behavior suggested a composite of the chain extended material and chain folded materials which had different melting temperatures. In addition the wide angle X-ray diffraction (WAXS) pattern suggested a two component material, with arcs from the oriented material superimposed upon rings from disoriented materials. Bashir explained the process in simple terms. The extensional flow field from the converging region formed the extended chain cores from the UHMW polyethylene component and tension on the extrudate prevents these cores from retracting. These extended chain cores are capable of being superheated and were metastable in the melt. The remainder of the melt, which has lower molecular weight, nucleated upon the extended chain crystals to establish the folded chain lamellae (ie shish-kebab structure). Bashir, Odell and Keller [18] continued to develop their direct extrusion-orientation process.
Bashir and Keller's [19] research into continuous extrusion-orientation took a new and unexpected turn to developing ultimate properties. Previously, Bashir had studied direct extrusion-orientation of filaments (Bashir et al 1984 and 1986), but in 1989 he abandoned the direct extrusion-orientation approach and proposed an alternative method of "melt drawing". Melt drawing makes use of elongational flow to orient the polymer by stretching the melt outside the die. Bashir's rationale for deserting the direct method was that direct extrusion-orientation required very close control of the processing conditions, while melt drawing allowed much greater latitude during processing. Melt drawing consisted of extruding an unoriented polymer and then drawing it while it was still in the melt state. The pure extensional flow field generated during deformation is used to form and orient the core crystals. Bashir stated that the conditions necessary for melt drawing are:

1. Strain rate must be great enough to overcome the relaxation forces of the chains in the melt, but not so extensive, as to trigger an elastic response. The elastic

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2 Nadkarni and Schultz presented very similar work, conducted 12 years earlier, in a paper entitled "Extensional Flow-Induced Crystallization in Polyethylene Melt Spinning", Journal of Polymer Science, Polymer Physics Edition, vol. 15, 2151, (1977). This work was carried out with the spin-line controlled at temperatures of 90 - 120 °C. The polymer for these studies was a high density polyethylene with relatively low molecular weight of 177 000 g/mol. Bashir's and Nadkarni's groups observed similar morphologies when high stretch rates were used to spin the fibres. Nadkarni et al showed row nucleated structures where the row nuclei acted as a reinforcement frame in the fluid. They also show secondary lamellar crystallization occurred on the row nucleated crystals. They described these structures as shish-kebabs. Nadkarni and Schultz stated, "There was an indication in the case of fibers spun at high take-up speeds, that a fibrous entity occurred in greater mass and provided a higher elastic modulus".
response occurs when the melt is deformed at too fast a rate, to allow the molecules enough time to disentangle and flow. It is believed that entanglements in the melt may act as temporary cross-links within the time scale of the stretch rate.

2. Adequate strain (i.e. draw ratio) to completely elongate the chains.

3. Correct temperature regime (130 - 160 °C) to induce flow crystallization.

4. Rapid cooling after drawing to capture the orientation by crystallization.

Bashir and Keller found that Hizex 145 (Mw of 950 000 g/mol.) was the most successful polymer for melt drawing. Compression moulded Hizex 145 had the ability to be melt drawn at 145 °C to extensions of 60-80 times. This resulted in excellent mechanical properties, with a tensile modulus of 60-80 GPa and strengths of 700-1500 MPa. The morphology, as determined by TEM, appeared to be very similar to the structure produced by extrusion-orientation of BP 006-60 (Bashir 1984 and 1986), but with more core fibrils spaced more closely together. A DSC thermogram showed regions of low melting point (127-133 °C) which resulted from the melting of the lamellar folded chain overgrowths. The thermogram also showed peaks above 140 °C which were attributed to melting of the core crystals.

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3 The greater concentration of the core fibrils is a result of the higher concentration of chains with Mw greater than 10^6 g/mol.
Hare and Cuculo [20] used convergent capillary dies to produce transparent oriented polyethylene in the manner developed by Southern and Porter. The technique involved hydrodynamic orientation coupled with controlled crystallization. The objectives of their study were to determine 1) the effect of the interior die angle on the production and properties of highly oriented polyethylene strands, and 2) the effects of a temperature gradient on the rate of production of the strand. The dies had included angles of 15, 30 and 45°. An Instron capillary rheometer with crosshead speeds of 0.05 to 50 cm/min was employed for these experiments. Du Pont Alathon 7030 polyethylene (MFI 3 and average MW of 115 000) was chosen for these trials. The authors stated that capillary design, temperature, polymer type and MW contributed to the degree of orientation. They found that the capillary would block when certain extrusion rates were exceeded and lower extrusion temperatures were used for a particular polymer. Several explanations were offered for this blockage: 1) massive crystallization had occurred in the capillary and 2) elastic compression of the melt limited flow. The explanation favoured by Hare and Cuculo involved massive crystallization due to the elevation of the melting point by pressure. The researchers found that massive crystallization occurred more easily with the small angle dies. The extrudates were of poor quality with an irregular surface and little transparency (ie. translucent). Exerting a tensile force, by suspending a weight on the strand, or lubricating the die with Teflon aerosol spray, both improved the strand quality. The poor appearance of the strand was felt to be a result of 1) high pressures forcing a solid plug through essentially zero length (ie. very short) die; 2) stick-slip extrusion which is common to hydrostatic extrusion (the magnitude was too small to be
observed visually); and, 3) decrease in the ductility of the solid plug because of annealing and pressure packing coupled with an extreme draw ratio of 350. Hare and Cuculo warn other researchers of the difficulties of working with oriented viscoelastic liquids. They stated, "It is extremely difficult to take advantage of the molecular orientation developed by converging flows because of rapid molecular relaxation at the capillary exit."

Crater, Cuculo and Bordeaux [21] attempted to use a temperature gradient in the die as a method to produce high modulus poly(ethylene terephthalate) (PET) filaments directly from the melt. The authors' desired objective was to use converging geometry with the related elongational flow, to orient and extend the macromolecules prior to crystallizing the structure. PET was selected for this study as it has a slower crystallization rate than polyethylene. Crater et al felt that this property gave greater control over the location at which the phase transformation occurred in the capillary. If the crystallization could be induced at the end of the capillary, then lower extrusion pressures would be required. Lower extrusion pressure would permit higher production rates. The extrusion apparatus was an Instron capillary rheometer utilizing type 316 stainless steel dies with internal angles of 20, 30 and 40°. The temperature gradient in the die land was established by passing liquid nitrogen through a cooling chamber fastened to the exterior face of the die. The extrusion operation was started by loading the rheometer barrel with PET chips and heating to 285 °C for five minutes under low pressure. After loading and heating, the barrel was set to the desired temperature of 255, 260, 265 or 270 °C. The plunger speed was fixed at a rate between 2.5 and 25 mm/min (0.1 and 1.0
inch/min). The temperature gradient was adjusted by metering the flow of liquid nitrogen through the cooling chamber on the die face. Once polymer flow was initiated, the die pressure would increase until polymer flow ceased. In some experiments post-die tension was applied to the extrudate. The die swell was virtually the same for all barrel temperatures. The inception of extrudate distortion occurred at flow rates between 0.003 cm$^3$ s$^{-1}$ and 0.03 cm$^3$ s$^{-1}$ for a given temperature. An increase of pressure of about 15% was observed at the point of extrudate distortion. The die angle affected the pressure for both the onset of extrudate distortion and the maximum die swell. Crater et al found that the pressure at the beginning of distortion and the pressure for maximum die swell, increased with the die angle. Melt fracture was found to occur at about 8 MPa (1100 psi) for the 40° die and 13 MPa (1900 psi) for the 20° die. The principal conclusions of Crater, Cuculo and Boudreaux in this very useful paper were:

1) The temperature gradient must be large enough to keep the oriented material in the oriented state, yet not so great as to promote melt fracture or flow stoppage.

2) Faster flow rates do not allow sufficient time for heat exchange and as a result the temperature gradient is less effective.

3) Wide angle dies promote greater elongational velocity gradients which lead to greater degree of orientation, and greater probability of melt fracture and distortion.

4) Longer convergence lengths allow the temperature gradient to be more effective.
5) The application of external post-die tension to the extrudate reduces the extrusion pressure and permits longer extrudates prior to flow cessation.

6) Post-die tension inhibits die swell which resulted from relaxation.

7) External tension and after-quench should be utilized to freeze in the orientation and prevent relaxation.

Cuculo and Crouse [22] attempted to explain the pressure oscillations that were observed in the extrusion of PET (Crater, Cuculo and Boudreux 1980). They found that the pressure oscillations were associated with the formation of a previously unknown fibrous toroidal crystal in the entry region to the capillary and were associated with extrudate distortion. The fibrous crystals were initiated in the extensional flow field and migrated laterally into the secondary flow fields. The authors felt that the pressure oscillations were a result of repeated formation and breakdown of the polymer network which also resulted in extrudate distortion.

Crater and Cuculo [23] found that elongational velocity gradients (ie. stretching rates) and time in the stretching field were both important to net orientation of the polymer. They stated that a minimum effective stretching rate must be sustained for as long a time as possible. Crater et al found that higher degrees of orientation occurred when the minimum effective velocity gradients were imposed on the polymer chains for the maximum period of time. They suggested that a hyperbolic nozzle may be the ideal die contour. A
temperature gradient for the lower portion of the die and extrudate tension were also recommended. Crater and Cuculo believed that extrudate tension coupled with rapid quenching was required to affect molecular order and resist relaxation of the polymer.

Ledbetter, Cuculo and Tucker [24] used converging flow and high pressure quenching to prepare oriented PET extrudates. The stated objectives were to analyze the morphology of the extrudate using SEM and transmission electron microscopy (TEM) techniques and correlate the modulus and orientation with the structure. Ledbetter et al believed that the orientation induced in the PET extrudates by the single step process approached the highly drawn commercial fibers. Ledbetter, Cuculo and Tucker found that the converging flow achieved a high degree of orientation in the melt. The crystallization of the oriented melt was enhanced which resulted in a stoppage of flow and an increase of pressure. The high pressure acted as a quench to stabilize the oriented structure. This structure was described as relatively highly oriented with both crystalline and amorphous regions. The extrudate had high dimensional stability, high modulus and low optical density. Ledbetter, Cuculo and Tucker concluded that the converging flow can be used to produce highly oriented, high modulus PET extrudates. The pressure quench was found to limit the available modulus since the degree of supercooling reduced the crystallite size to about 10 nm. As a result, pressure quenching should be restricted and instead extrudate tension should be used to prevent relaxation of the chains.
2.3 Research Objectives

The essential concepts of extrusion-orientation are known. Previous workers have understood the importance of the elongational velocity gradient in the melt, of the relaxation process and the induction of oriented crystallization. Some of the authors are aware of the consequences of a pressure quench, the potential of tension on the melt, the use of linear higher molecular weight resins and the reduction of friction in the die. The literature review has established that relaxation and remelting, prior to full crystallization of the extrudate, were the principle difficulties in extrusion-orientation.

The specific objectives of this work are:

1. To establish if flow orientation in a streamlined die, at an appropriate temperature and elongational velocity gradient, could produce stable chain extended crystals from conventional low molecular weight polypropylene. It was hypothesized that the entropy of the oriented chains would be low enough to induce oriented crystallization at a higher temperature than for normal chain folded crystals.

2. To test if low temperature extrusion through a streamline die could be used to extrusion-orient conventional (ie. lower molecular weight) polypropylene. It was hypothesized that lower extrusion temperatures resulted in longer relaxation times.

3. To develop a methodology to achieve continuous screw extrusion of higher molecular weight polyethylenes.
4. To prove that VHMWPE and UHMWPE, with relaxation times much longer than conventional resins, have the potential to be extrusion-oriented. It was hypothesized that the longer relaxation times of higher molecular weight resins, will allow sufficient time for crystallization to occur before the orientation is lost by relaxation.
3 Streamlined Die Experiments

3.1 Introduction

The preliminary work, conducted in section 3, was an introduction to the difficulties of extrusion-orientation. This work led to a more profitable approach which involved the lubricated extrusion of higher molecular weight polyethylenes.

Streamlined dies were believed to be superior to conventional shear dies for the extrusion of polymers [25]. It was hypothesized that the streamlined die would allow higher throughput and consequently higher elongational velocity gradients to orient the polymer chains during extrusion. This initial section of the thesis compared the effectiveness of a shear die to that of a streamlined die in extrusion-orientation potential.

The literature search had revealed that it was possible to orient melts at elongational velocity gradients (EVG) that were achievable in the extrusion die, but it was difficult to crystallize the extrudate without losing the orientation to conformational relaxation. Two hypotheses, based upon increasing the relaxation time of the melt, were tested in this section.

1. During the flow of a melt through a converging nozzle, the polymer chains are extended parallel to one another. This leads to lower entropy, because of the increase of chain order, and reduced resistance to crystallization. If the melt is near the crystallization temperature and the EVG is large enough to stretch and keep the chains extended, then crystallization of the longer oriented chains would occur.
at higher than normal temperatures. These extended chain crystals would have greater resistance to relaxation and would stabilize some of the orientation in the melt, allowing oriented crystallization.

2. If the melt were cooled as it passed through the converging nozzle, the oriented melt would have a longer relaxation time. The longer relaxation time would allow oriented crystallization to occur.

3.2 Streamlined Die Design for Polypropylene

3.2.1 Rationale for a Streamlined Die

Sigmoidal dies, later referred to as streamlined dies, were known to reduce the stresses and power requirements for the forming of metals [26][27]. These type of dies were also found to reduce the structural damage during drawing [28]. Gunasekera and Hoshino, in an analysis of streamlined metal extrusion dies, concluded that streamlined dies were superior to converging dies for the reasons cited above [29].

Collier, Gunasekera and Sargand [30] have stated that the principles developed for streamlined metal extrusion dies were appropriate for the design of streamlined dies for polymers. They emphasized that smooth entry and exit into passages of changing cross-section were fundamental to the streamlined technique. Substantial flow velocities perpendicular to the extrusion direction resulted in a reduction of extrudate dimensional control and excessive residual stresses. If the exit from the converging
section was not smooth, then significant transverse velocity may occur in the die. Collier, Gunasekera and Sargand believed that properly designed streamlined extrusion dies minimize the transverse velocity component, provide an equal supply of polymer to each section of the die, and reduce the rotational flow of polymer which leads to vortices and unstable flow.

### 3.2.2 Design Criteria

Marrucci [31] in an analysis of elongational flow presented a number of limiting conditions that must be satisfied for flow orientation and crystallization of stable oriented macromolecules. Marrucci stated that the product of the velocity gradient and time in the flow field must be greater than 4, or \( Gt > 4 \). The numerical value of this product allows an estimation of the minimum draw ratio, \( S \), which was given by

\[
S = \exp (Gt)
\]

Based upon this simplistic analysis, the extrusion ratio \(^1\) (ie. draw ratio) should be approximately 55 for \( Gt \) equal to 4. Marrucci also indicated that \( G > 0.5/\tau \) was required to orient the macromolecules. Since the die was to be operated near the self-blocking temperature, the relaxation times were expected to be very long.

The nozzle entry diameter was 9.906 mm (0.390"). This diameter was chosen to fit a cylindrical tube fashioned from a rifle barrel blank. The exit diameter of the nozzle

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\(^1\) Extrusion ratio is the ratio of the entry area of the die to the exit area of the die.

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was 1.016 mm (0.040"). The extrusion ratio based upon these entry and exit diameters was 95.1:1. This extrusion ratio was greater than minimum of 55 suggested above, but considerably less than 350:1 used by Hare and Cuculo [32]. Hare et al found that an extrusion ratio of 350:1 was extreme and resulted in a loss of extrudate ductility.

Work carried out by Mackley and Keller [33] indicated that an elongational velocity gradient of approximately 50 s⁻¹ was sufficient to produce oriented fibrous crystals. This paper would seem to indicate that relaxation of polymer melts were sufficiently slow as to allow extrusion of oriented fibrils.

3.2.3 Estimation of Power-Law Constants for Polypropylene

The die was designed to use an extrusion grade of polypropylene with a melt flow index of 1 at melt temperature of 170 °C. The empirical equation used for flow modelling was the Ostwald-de Waele model which requires two constants, the consistency index, \( K \), and power-law index, \( n \). The shear viscosity was estimated from \( \eta = K \gamma^{n-1} \). This equation had several flaws as it is only valid at higher shear rates and the units of \( K \) depend upon the value of \( n \) [34].

Shenoy et al [35][36][37] discussed the theory and the method of estimating the power-law constants based upon the Melt Flow Index and how temperature affected the power-law constants. In a later paper[38], A.V. Shenoy and U.V. Shenoy introduced a simple microcomputer spreadsheet 'program' to generate rheograms for var-
ious polymers. The spreadsheet program was used to estimate the power-law constants. The estimated value of $K$ was $22\,000\,\text{Pa}\cdot\text{s}^n$ and $n$ was 0.34 for an extrusion grade of polypropylene with melt flow index of 1.

3.2.4 Design Method for the Approach Region of Nozzle

Collier et al [39] have experimentally shown that forced polymer streamlines do not always follow the contours of the die. In converging dies with semi-cone angles of $10^\circ$ to $20^\circ$, the streamlines defined by the polymer melt deviated from the die wall. As a result, the authors indicated that the non-Newtonian and viscoelastic nature of the polymer melt must be taken into consideration when designing the flow path of the die. Collier et al used the finite element method (FEM) to predict the flow path of non-Newtonian fluids in the die. The authors stated, "It may be necessary to predict the streamline shape that the fluid would describe, if it were to change its shape in a shear free environment, ie. without the influence of constraining walls, and then to machine the dies to that shape." At the same time Collier et al also reported that the shearing flow near the walls would not be limited to the skin layer, which may invalidate the first prediction of the die contour. As a result, the authors proposed using a succession of iterations using progressively altered die shapes in order to determine the ideal contour.\(^2\)

\(^2\) It would appear that Collier was essentially using an iteration method to determine the "natural approach angles" for a particular inlet and outlet geometry.
A commercial general purpose finite element fluid mechanics program\textsuperscript{3} was used to streamline the approach section of the nozzle in the manner proposed by Collier et al. The flow field region was made up of 520 axisymmetric quadrilateral elements (52 elements along the principle axis and 10 elements along the radial axis). The power-law constants required for the finite element analysis were estimated in section 3.2.3. A no-slip boundary condition was hypothesized for the die walls. This required that the radial and axial velocity must be set to zero for the nodes which fell upon the loci of the die wall. The radial velocity of nodes located on the centre-line of the finite element model (ie. the axial nodes) were constrained to zero.

The streamlining process was carried out in 6 iterations. The first iteration was conducted on a rectangular array of elements as schematically illustrated in Figure 3-1. The streamline with a stream function value of approximately zero \((< 0.01)\) was then found using the post-processor. This streamline was then used as the wall for the next iteration. Remeshing between iterations was conducted using a computer program which remapped the nodal points to the new contour such that the elements aspect ratio was limited to approximately 2. The second through sixth iterations were required to find a die wall position which did not alter appreciably from one iteration to the next.

\textsuperscript{3} NISA/3D-FLUID was the finite element program used for this research. The program was purchased from Engineering Mechanics Research Corporation, PO Box 696, Troy, Michigan 48099, USA. The personal computer version of the program (rel. 88.0) was capable of modelling fluid flow for 2D and axisymmetric steady lamellar flow. The possible constitutive equations for this program were Newtonian and power-law Non-Newtonian.
Figure 3-1  Schematic illustration of the first iteration of the streamlining procedure. The 'wall' streamline was shown for streamline with stream function value of approximately zero.

The streamlined nozzle designed for direct extrusion-orientation of polypropylene is shown in Figure 3-2. The approach angle for the nozzle was found to be approximately 20°.
Figure 3-2  Axisymmetric streamlined extrusion die. All linear dimensions are in mm. The nozzle is sigmoidal in shape with zero degree entry and exit angles.

A numerical model was written to calculate the elongational velocity gradient along the centre-line of the die and the pressure drop, which resulted from telescopic shear flow. The model was based upon tracing a control-volume of polymer as it passed through the converging nozzle. The numerical model was tested for the pressure drop for shear using data reported by Cogswell [40]. Figure 3-3 shows the elongational velocity gradient, along the die centre-line, as a function of position along the center-line in the converging section of the nozzle. The numerical prediction was
made for a power-law fluid with $K$ of 22 000 Pa·s$^n$ and $n$ of 0.34 assuming no-slip at the polymer-die wall. The volume flow rate was $6.0 \times 10^{-8}$ m$^3$ s$^{-1}$ which corresponded to the output of the extruder running at 2 rpm.

Figure 3-3 The calculated elongational velocity gradient in the converging section of streamlined nozzle versus the displacement along the centre-line. The centre-line EVG was calculated using a control volume model for a volumetric flow rate of about $6.0 \times 10^{-8}$ m$^3$ s$^{-1}$.

The product of the elongational velocity gradient, $G$, and the time, $t$, was calculated by numerically integrating the curve shown in Figure 3-3, using the trapezoidal rule.
The calculated product was approximately 4.5 for the die operated with a flow rate of 6.0 x 10^{-8} \text{ m}^3 \text{ s}^{-1} (\text{i.e. extruder operating at 2 rpm}). This product exceeds the minimum of 4 suggested by Marrucci [41]. The peak velocity gradient was 153 s^{-1}. The time weighted average velocity gradient, for the region around the peak, was calculated from

\[ \frac{\sum(EVG_i \delta t_i)}{\sum \delta t_i} \]

where $E1 \cdot G_i$ was the instantaneous EVG and $\delta t_i$ was the time interval that the instantaneous velocity gradient was valid. The time weighted elongational velocity gradient was found to be about 52.5 s^{-1}. These data indicated that it should be possible to orient the polymer chains with the extruder operating at 2 rpm.

### 3.3 Experimental Procedure

Two dies, with identical extrusion ratios, were constructed from aluminum. The die fabrication consisted of rough boring with a forming tool to the approximate dimensions, followed by electrodischarge machining to the final dimensions. The streamlined die is shown in Figure 3-2; the shear die, which acted as a control, is shown in Figure 3-4. Both dies had the same extrusion ratio of 95.1:1 and the same capillary L/D ratio of about 10:1.
Figure 3-4  Axisymmetric shear die. All linear dimensions are in mm.

The extrusion apparatus for the polypropylene is shown in Figure 3-5. The melt pump was a Brabender 19 mm diameter, smooth barrel extruder with a L/D ratio of 25:1. A shear or streamlined die was fitted to the extruder using a die adapter. Electric resistance heaters and controllers were used to govern the temperature of the 3 extruder zones, the die adapter zone and the die zone. Cooling of the extrudate, when used, was accomplished by water spray or by refrigerated air supplied by a "Cold Gun" manufactured by the Exair Corporation.

The resins chosen for these experiments were extrusion grades of polypropylene with melt flow indices of about 0.1 to 2. The melting point was taken to be 168 °C and the glass transition temperature assumed to be -13 °C.
Polypropylene pellets (MFI < 1)

19 mm smooth barrel extruder

Entry Mid Exit Extruder Heat Zones

Die Adapter

Streamlined or shear die

Water or refrigerated air cooling

7.5 HP computer controlled variable speed drive

Extrudate

Figure 3-5  Schematic diagram of the extrusion apparatus for polypropylene.

Conventional extrusion of polypropylene is normally carried out at 204 to 260 °C (400 to 500 °F) [42]. For this thesis, the experiments were conducted with the extrusion die temperature in two broad temperature regions; near conventional temperature extrusion at 200 to 250 °C and sub-normal extrusion at 170 to 200 °C. Most experiments were conducted with the three extruder zones set to 200 °C.
A typical extrusion experiment consisted of setting the temperature zones and allowing the extruder to heat for approximately an hour to the set points. The hopper was then loaded with polypropylene chips. Extrusion was commenced and the extruder speed was adjusted to the desired rpm. Once stable extrusion began, samples of the extrudate were collected for analysis. The preliminary analysis consisted of birefringence and shrinkage measurements to detect orientation, coupled with tensile tests to determine if any of the mechanical properties had improved.

3.4 Results and Discussion

3.4.1 Near Conventional Extrusion Temperatures

The streamlined die formed smooth, sound, macroscopically defect free extrudates at screw circumferential speeds of less than 2 rpm and die temperatures between 200 and 250 °C. The shear die produced extrudates which could not be distinguished from the extrudates created by the streamlined die under these conditions. (Neither die was capable of producing smooth distortion free extrudates at 3 rpm or greater.) The approximate volumetric flow rate at 2 rpm was about 2.7 g min⁻¹.

Birefringence, if it existed in an extrudate, can be visually detected when viewed through crossed polarized sheets. Birefringence was observed in the melt at the exit of the capillary and for about 1 to 2 cm along the spinline (die temperature of 225 °C)

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4 A shrinkage test consists of heating the extruded specimen to a temperature greater than the melting point and holding the specimen at this temperature for approximately 10 minutes. If any orientation is present in the specimen, entropic relaxation will cause the specimen to shrink in the extrusion direction and dilate in the transverse direction.
and an extruder rate of 2 rpm). This birefringence disappeared prior to the polymer crystallization. A useful estimate of the relaxation time was derived from the length of the zone in which birefringence can be observed through crossed polarized sheets. If the approximate length was 2 cm, the time for the birefringence to have disappeared was approximately 0.9 s for a typical extrusion speed of 1.4 m min⁻¹.

For the die temperature region of 200 to 250 °C, no orientation, as measured by shrinkage tests, could be trapped in the melt by crystallization. The extrudates were observed to swell in the region immediately after the die exit. This extrudate swell was a result of the chains retracting from the elongated oriented conformation and returning to the coiled disoriented conformation [43]. Tension was applied to the extrudate to prevent die swell and concomitant relaxation, but this only resulted in extrudate fracture. All of the polypropylene melts, even those with melt flow index less than 1, had insufficient melt strength to support the tensile forces required to prevent extrudate swell (ie. relaxation). A combination of tension and rapid quenching, to hasten crystallization, was found to be unsuccessful in the attempt to trap the orientation. Severe quenching frequently resulted in the filament severing, even if only a small amount of tension was applied. In brief, all cooling and tensions regimes were found to fail in an endeavor to solidify an oriented extrudate for die temperatures of 200 to 250 °C.

**Heat Transfer Model**

The region along the longitudinal center-line of the extrudate was believed to contain
the highest degree of orientation due to the greater elongational velocity gradient experienced in this region. It was hypothesized that the slow heat transfer maintained temperatures greater than the melting point of the polypropylene in the central longitudinal core region of the extrudate for significant periods of time. This condition allowed the extended chain crystals, if they existed, to remelt and the oriented chains to disorient by relaxation. A one-dimensional finite difference model (FDM) was written to predict the radial temperature distribution of a polypropylene extrudate as a function of cooling time. The purpose of this model was to give a first order approximation of the time to cool the extrudate core from the temperature of extrusion to the solidification temperature. If the core cooling time was on the order of a second, then extrusion-orientation should be feasible for these resins. If the time required to solidify the centre of the extrudate was greater than about a second, then extrusion-orientation under these conditions would probably be impossible.

The finite difference model required the numerical solution of the one-dimensional transient conduction equation which in the reduced polar coordinates was given by

$$\frac{\delta T}{\delta t} = \alpha \frac{1}{r} \frac{\delta}{\delta r} \left( r \frac{\delta T}{\delta r} \right)$$

where \( T \) was the temperature of a node, \( t \) was time and \( r \) was the radial distance of the differential element to the axis of symmetry. The term thermal diffusivity, \( \alpha = \frac{k}{\rho C_p} \), gave the rate of response of the volume surrounding a node in which \( k \) was the thermal conductivity, \( \rho \) was the density and \( C_p \) was the specific heat of the
polypropylene. The rate of heat removal from the surface of the extrudate was given by \( h \cdot A (T_s - T_f) \) where \( h \) was the heat transfer coefficient, \( A \) was the area of the element exposed to the cooling fluid, \( T_s \) was the temperature of the polypropylene and \( T_f \) was the temperature of the circulating cooling fluid. The grid size in the radial direction contained up to 21 nodes. Although each volume that surrounded a node had constant thermal properties, the thermal properties for individual nodes could be different since these properties were influenced by temperature. The one-dimensional analysis for a moving filament during extrusion was conceived using the following assumptions.

1) Axial conduction has been considered negligible in comparison to radial conduction for a 2 mm diameter UHMWPE fiber cooled during fiber spinning [44]. For a fiber with diameter of 1.6 mm this assumption would have greater applicability.

2) The heat transfer coefficient at the polymer-water interface was 1000 W/m²K. This value was given as a realistic upper limit for forced convection of water by Croft and Lilley [45].

3) The specific volume, specific heat and thermal conductivity of the polypropylene have been shown to vary significantly with temperature [46]. For this analysis, the data from each of the temperature dependent properties were fitted to one or more linear equations. From these equations a better prediction of the
temperature dependent property was estimated. The values of the specific volume were in the region of 1.15 to 1.35 cm$^3$ g$^{-1}$. The specific heat had values of 3.0-5.5 x 10$^5$ J kg$^{-1}$. The value of the thermal conductivity varied from 0.13 to 0.18 J/m$^2$K.

4) The fibre diameter was 1.2 mm at the instant of emergence from the die. Extrudate swell was about 33% during quenching which resulted in a fibre dimension of 1.6 mm for this analysis. This diameter was constant during the cooling cycle.

5) The velocity gradient in the fiber rapidly diminished to zero at the exit to the die. The extrudate element moved as a plug (ie. no shearing in the extrudate melt after exiting the die.) for this analysis.

6) To simplify the model, the heat of fusion of the polypropylene was ignored. This omission resulted in predictions that were biased to more rapid cooling than would be experimentally observed.

Figure 3-6 shows the cooling curves, derived using the finite difference method, for a polypropylene fiber that was quenched in circulating water at 0 °C. The fibre was extruded through a die and capillary at 225 °C. The time required to cool a 0.4 mm diameter longitudinal core of the polypropylene extrudate to the solidification temperature of 168 °C was at least 5 s. Since the relaxation times were at best in the
order of a second for these fibers, it would appear that orientation was impossible to achieve by severe quenching, if the diameter of the extrudate was more than 1 to 2 mm.

This analysis showed that simple thermal quenching of polypropylene extrudates with melt flow index of 0.1 to 1.0 probably cannot be used for extrusion-orientation for melts at temperatures near 200 to 250 °C. The slow cooling of the longitudinal core of the extrudate probably permitted the remelting of any oriented crystals present and relaxation of any oriented chains in the melt.
Figure 3-6 Cooling curves of 1.2 mm diameter polypropylene extrudate, initially at 225 °C, quenched in rapidly circulating ice water. The extrudate was assumed to swell approximately 33% to a diameter of 1.6 mm. Five curves are shown for this analysis. The top curve shows the centre temperature while the bottom curve shows the surface temperature of the extrudate. The 3 remaining curves reflect the temperatures at 1/4, 1/2 and 3/4 of the radius. The true solidification times would be longer, as heat of fusion was ignored and heat transfer coefficient was at the high end of the range for forced convection of water.

3.4.2 Sub-Normal Extrusion Temperatures

Extrusion was attempted at die temperatures of around 175 °C which was near the melting point of the polypropylene resins. This type of extrusion proved to be impos-
sible for either the streamlined or shear die. The profiles always exhibited extreme melt distortion and in most cases were too weak to support the weight of the hanging extrudate. In some cases, fragments of the extrudate were ejected from the die and travelled up to a meter. The fragments ejected were around 2 mm in length. At die temperatures less than 175 °C, the extrusion pressure exceeded the maximum of 70 MPa (10 000 psi) which forced the immediate shut-down of the extruder.

The poor quality extrudates were thought to be a result of either stick-slip at the die wall or elongational stresses greater than the melt's ability to support them. These hypotheses were tested by extrusion through a lubricated streamlined die. Lubrication of the die channel allowed the polymer to slip along the wall which eliminated the potential for stick-slip. The lubrication of the die was accomplished by first removing the die from the extruder, then coating the interior walls of the die with a lubricant. After the die was refitted, extrusion was commenced. Evidence of the lubricant persisted for up to a minute of extrusion. A number of lubricants were tested which included silicone oils, glycol and commercial high temperature spray lubricants.

Little difference was seen between the lubricated and non-lubricated extrudates. This indicated that the melt fracture was most likely because of the excessive elongational gradients which resulted in correspondingly high elongational stresses. When the extensional stresses in the converging section of the die exceeded the melt strength, the extrudate was pulled into about 2 mm long pieces. The elastic energy, imparted
by the deformation in the die, was recovered by irregular extrudate swell or on occasion by fragments of the extrudate springing from the die. The low melt strength of conventional resins and high elongational stresses allowed the melt to fracture.

Shaw [47] showed a similar, although less severe, type of melt fracture for polyethylene extruded through greased dies. Shaw's extrusion was carried out at normal rheometer temperature of 190 °C. He found that grease applied to the internal walls of a conical die decreased the pressure drop during extrusion and increased the extrudate distortion. Shaw concluded that the grease had eliminated the shear stresses, but had favoured extensional stresses which resulted in deep, transverse cuts in the extrudate. Shaw's conclusion appeared to be in agreement with this work.

3.5 Conclusions

The outcome of this preliminary work was summarized as follows:

1) Severe cooling regimes and tension were insufficient to maintain orientation of conventional extrusion grades of polypropylene when extruded through a die at a temperature of 200 to 250 °C.

2) Melt strength of the conventional extrusion grade resins, at temperature high enough for smooth extrusion, were too low to support the tensile forces which may be essential to conserve orientation.
3) Entropic relaxation of conventional extrusion grade of polypropylene, extruded at 200 to 250 °C, occurred too rapidly to be arrested by crystallization, at least for extrudates with diameter greater than about 1 mm.

4) At die temperatures of about 175 °C (just above the melting point of 168 °C), the tensile forces generated by elongational flow exceeded the strength of the resin for the shear and streamlined dies. This indicated that these die designs imposed too large an elongational velocity gradient for the extrudate to support during low temperature processing.

5) The extrudates formed by the shear and streamlined dies were macroscopically indistinguishable for all temperature regimes. Streamlined dies appeared to offer few advantages in the extrusion of conventional grades of polypropylene under the conditions of these experiments.
The preliminary conclusions suggested that:

1) Resins with longer relaxation times were required to allow sufficient time for oriented crystallization to occur.

2) Systematic study of extrusion die design, lubrication and extensional flow behaviour was required. It was apparent that high elongational stresses resulted in the fracture of the cold melts.

3) Resins with higher melt strengths were required for extrusion-orientation. This would have allowed greater elongational forces in the die to orient the chains and greater tension on the extrudate to have perpetuated the orientation.
4 Extrusion of Higher Molecular Weight Polyethylenes

4.1 Introduction to the Study

Although the principal objectives of the thesis were to develop extrusion-orientation methodologies, the purpose of this section was to derive a screw extrusion procedure for higher molecular weight polyethylenes. The rationale for this decision was that higher molecular weight polymers had longer relaxation times [48], since the relaxation time, \( \tau \), depended upon molecular weight, \( M \), as

\[ \tau \propto M^3. \]

The relaxation times for polymer melts have been found in the order of \( 10^{-2} \) to \( 10^2 \) s [49]. Relaxation times at the higher end of this range would allow sufficient time for oriented crystallization during processing.

Bashir et al [50] had found that the high molecular weight fraction of the melt formed the oriented extended chain crystals which greatly strengthened the extrudate. The molecular weight distribution of VHMWPE and UHMWPE resins had extensive high molecular weight tails which may make these types of resins ideal for extrusion-orientation experiments. In addition, Bashir et al also discovered that resins with high molecular weight tails and limited low molecular weight tails had high melt strength which permitted large wind-up stresses. This discovery indicated that it may be possible to select higher molecular weight melts with the potential to support higher tensile forces which would be advantageous for extrusion-orientation.
The extrusion of higher molecular weight polyethylenes has been considered a difficult problem to solve. Rauwendaal [51] stated that UHMWPE is not melt processable and is normally ram extruded. Narh and Keller [52] disclosed that UHMWPE is known to be unextrudable for conventional capillary extrusion. In the same paper, Narh and Keller presented evidence that a "temperature window" between 150-152 °C enabled reduced pressure extrusion for Hizex MIL145M powder (MW of about 0.95 Mg mol⁻¹) at shear rates of 0.83 s⁻¹. Smoluk [53], in a feature article discussing UHMWPE processing, conveyed that the Allied-Signal Corporation had announced a new resin additive which permitted the injection moulding and screw extrusion of UHMWPE without significant loss of properties. Subsequent discussion with Koller [54] of Allied-Signal corporation indicated that extrusion rates, using this new resin additive, were not significantly greater than ram extrusion. Screw extrusion of higher molecular weight polyethylene resins was probably possible, but poorly understood.

The objective for this section was to form unoriented extrudates from higher molecular weight resins. The extrudates must be visually smooth with the absence of macroscopic defects (ie. melt fracture) which limited the cohesiveness and integrity of the extrudate. The specific objectives were:

1) Determine the lubrication conditions required to extrude VHMWPE and UHMWPE resins. Lubricated flow of the melt was hypothesized to reduce or prevent stick-slip melt fracture.
2) Determine the elongational velocity gradient which would permit lubricated extrusion of higher molecular weight polyethylenes. It was hypothesized that a range of EVG may exist that would result in sufficient tensile stresses to draw out the polymer chains without provoking elongational melt fracture and defects which limit the cohesiveness of the melt. This work would involve experiments with different die semiangles and extrusion ratios.

4.2 Initial Work

4.2.1 Introduction

The purpose of this initial work was to determine if the extrusion of the higher molecular weight resins was feasible. The first specific objective was to determine if a low viscosity fluid could be used to act as an external lubricant\(^1\), in the manner devised by Shaw [55], and prevent stick-slip melt fracture at the melt-die interface. The second specific objective was to determine if low speed extrusion, with the accompanying low deformation rates, would permit the smooth extrusion of the higher molecular weight resins.

4.2.2 Experimental

Material

The resin selected for this trial was Hizex MIL145M supplied by the Mitsui Petro-
chemical Industries Ltd. This resin was selected for the ability to form oriented chain extended crystals during melt-drawing operations [56]. The processing aids used for this experiment were Dow Corning DC 200 silicone oil and high temperature grease.

Apparatus
The tooling used for this experiment was an aluminum, streamlined die, with an extrusion ratio of about 7:1. A Brabender smooth barrel extruder with L/D ratio of 25:1 was employed for these trials. A fixed pitch 1:1 compression ratio screw was utilized.

Method
The extruder and die were allowed to heat at the set points, shown in Table 4-1, for approximately an hour prior to extrusion. Extrusion was attempted at circumferential speeds of 2 to 10 rpm. For the lubricated die experiments, the die was removed for the adapter and the melt channel was liberally coated with grease or silicone oil. Extrusion was again attempted after the die was refitted.
Table 4-1 Extrusion Temperature Profile

<table>
<thead>
<tr>
<th>Heated Zone (Refer to Fig. 3-5)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Feed Zone</td>
<td>130</td>
</tr>
<tr>
<td>Extruder Mid Section</td>
<td>170</td>
</tr>
<tr>
<td>Extruder Exit Zone</td>
<td>200</td>
</tr>
<tr>
<td>Die Adapter</td>
<td>160</td>
</tr>
<tr>
<td>Die</td>
<td>160-180</td>
</tr>
</tbody>
</table>

4.2.3 Results

Three broad regimes were observed for the extrusion of Hizex MIL145M without a processing aid. The first region involved extrusion of a chaotic extrudate under conditions of high elongational velocity gradient and stick-slip at the die wall. The second regime consisted of extrusion, with a low elongational velocity gradient and pronounced stick-slip, which resulted in extrudates with regular repeating defects. The last regime was observed only at shutdown. After the extruder was stopped,
pressure which remained in the extruder would continue to force a smooth apparently defect free extrudate to slowly emerge from the die. The conditions after shut off were probably slow slip at the die wall and extremely low elongational velocity gradients in the die.

**Non-Lubricated Extrusion**

Figure 4-1 illustrates one possible type of regular repeating extrudate defect observed for HIZEX MIL145M when extruded without a processing aid. (The appendix shows a variety of cyclic melt fracture observed for non-lubricated extrusion.) The maximum elongational velocity gradient of the die was about 1.4 s\(^{-1}\) (ie. fairly low in comparison to the next section). The velocity gradient was calculated based upon steady flow, but because of stick-slip at the die walls and surging flow when slip occurred, this estimate may be slightly in error. The extrudate was prepared with a die temperature of 170 °C. A number of different and interesting melt fracture variations were extruded depending upon temperature and extrusion ratio. The stick-slip cycle for HIZEX MIL145M occurred over a fairly long period of time (ie. in the order of a second or more). The stick-slip cycles and the pressure variations were approximately periodic with the same frequency. The regular pressure variation had a magnitude of 2 to 6 MPa (300 - 900 psi) with a base pressure of 4 to 6 MPa (600 - 900 psi).
Figure 4-1  Regular repeating extrudate defects observed during the extrusion of HIZEX MIL145M from streamlined aluminum die at 170 °C. The die had a capillary diameter of 3.75 mm and an extrusion ratio of 7.0.

Three steps occurred in the stick-slip cycle. These were:

1) The cycle began with a sharp and rapid surge of the extrudate. The pressure dropped rapidly to the base value. The extrudate had a relatively smooth surface and uniform diameter.

2) The extrudate speed gradually decreased until the extrusion was blocked. Simultaneously, the polymeric melt contracted in length and dilated in diameter.
It should be noted in Figure 4-1 that the length of the extrudate segment formed in step 1 and 2 was rather long compared to the final length. The pressure was starting to increase in this part of the cycle.

3) Extrusion was blocked. The pressure builds up to the peak more rapidly than in the second step. The extrudate from the cycle continued to swell. A cut between the die-land and the newly formed segment was visible on some occasions.

The length of the slipped region was approximately the same length as the length of the die-land immediately after extrusion.

The stick-slip frequency was a strong function of temperature. Figure 4-2 illustrates that as temperature increased the stick-slip frequency decreased. The data has been fitted to straight line with goodness of fit (ie. \( R^2 \)) of 0.95 for both the 1 and 2 rpm lines.
Figure 4-2  Stick-slip frequency as a function of the die temperature. The streamlined aluminum die had a capillary diameter of 3.75 mm and an extrusion ratio of 7.0. Extruder circumferential speeds were 1 and 2 rpm.

Figure 4-3 shows that the stick-slip frequency was not a strong function of extruder throughput for extruder circumferential speeds greater that 4 rpm. Although the stick-slip cycle was still periodic, gross melt fracture was observed at higher circumferential speeds.
Figure 4-3 Stick-slip frequency as a function of the extruder circumferential speed. The die temperature was 160 °C. The streamlined aluminum die had a capillary diameter of 3.75 mm and an extrusion ratio of 7.0.

Figure 4-4 shows the irregular chaotic extrudate observed for HIZEX MIL145M when extruded without a processing aid at maximum elongational velocity gradient of approximately 8.0 s⁻¹ or greater. (again assuming steady flow). Stick-slip at the die walls and surging were observed along with a segmented extrudate. Four of the joints between segments are pointed out by arrows on Figure 4-4. The extrudate was prepared with a die temperature of 180 °C.
Figure 4-4  Chaotic extrudate defects observed during the extrusion of HIZEX MIL145M at temperature of 180 °C. The streamlined aluminum die had a capillary diameter of 3.75 mm and an extrusion ratio of 7.0. Extruder circumferential speed was 10 rpm.

**After Shutdown - Without Lubricant**

Melt was observed to slowly discharge from the die after extrusion was stopped and the apparatus maintained at the operating temperature. Over a period of about 0.5 h, a 5 to 10 mm length extrudate with smooth surfaces would be formed at the exit to the die. This extrudate was formed at very low deformation rates.
**Lubricated Extrusion**

Extrusion of a smooth coherent melt was possible for two experimental practices. The first method required a well lubricated die operated at low extrusion speeds. The second instance of smooth extrusion occurred after the extruder was shutdown and the melt was observed to seep from the die.

**Lubricated Dies at Extruder Speed of 1-2 RPM**

The extruder was operated for several minutes; the die was removed and the melt channel was coated with silicone oil or grease. After the die was replaced, extrusion was commenced. At an extruder circumferential speed of 1 or 2 rpm, smooth extrusion was possible for a period of about 15 to 30 s. Die temperatures between 160 and 180 °C had no apparent effect upon the extrudate surface. After the lubricant had been swept from the nozzle, the regular repeating defects shown in Figure 4-1 were observed.

**Lubricated Die at Extruder Speed of 10 RPM**

At extruder circumferential speed of around 10 rpm and with lubricated dies, rough uneven extrudates were observed. The extrudates would initially exhibit an uneven continuous surface. After the lubricant was swept from the die, the extrude would revert to that shown in Figure 4-4.
4.2.4 Discussion

Extrusion distortions are normally classified as gross melt fracture or sharkskin melt fracture. Rauwendaal [57] stated that melt fracture is a gross distortion of the extrudate and is associated with the whole extrudate and not just the surface. Rauwendaal recounted that the causes of melt fracture were: 1) critical elastic deformation in the entry zone, 2) critical elastic strain, 3) slip-stick flow in the die. Cogswell [58] believed that extrusion distortion is a result of tensile stresses exceeding the maximum strength of the material in the converging zone of the die. Kurtz [59] described sharkskin melt fracture as a surface pattern formed during steady state extrusion. Kurtz characterized the extrudate as having an undisturbed central core and that the extrusion process exhibited no significant pressure fluctuations upstream of the die. Kurtz found that the frequency of the sharkskin could be related to the molecular weight (in terms of MFI) and temperature. The frequency of sharkskin was commonly between 10 and 500 s⁻¹. The depth of sharkskin was linearly related to the shear stress above a critical value. Kurtz also believed that continuous slip, near the die exit, reduced sharkskin. Rauwendaal defines sharkskin as a regular rigid surface distortion, with the ridges running perpendicular to the extrusion direction. Less severe sharkskin produced a matte finish. Sharkskin was caused by the rapid change in velocity of the melt as it left the die. Near the surface of the capillary, the melt was assumed to have a very small velocity. When the melt exited the die, the whole melt had a uniform velocity and the surface was stretched. If this stretching was severe, the
stresses were sufficient to cause the surface to rip.

**Non-Lubricated Die Experiments**

Cyclic (ie. stick-slip) melt fracture, with accompanying large pressure variations, was observed for all non-lubricated extrusion experiments. At low extruder speeds, the extrudate had coherent regions interrupted by deep radial cuts which appeared at the same frequency as the stick-slip. The radial cuts were formed at the capillary exit by small cracks which propagated towards the center. The cracks became less evident by extrudate swell (ie. appeared to close), but were still present. At higher extruder speeds (ie. 10 rpm), uneven chaotic melt distortion regions were separated by stick-slip.

The extrudate formed at 1 to 2 rpm exhibited many of the features of sharkskin melt fracture. This extrudate had the characteristic regular rigid surface distortions with an apparently undisturbed core. The melt distortion disappeared when continuous slip was initiated by lubrication. Several differences were apparent in comparison to Kurtz's work [60]. The surface cuts were very deep and the undisturbed core very small when compared to normal sharkskin melt fracture of low molecular weight linear polyethylene. The frequency was about an order of magnitude lower than previous observations. A large pressure variation was found to exist for the stick-slip cycle which was also dissimilar to Kurtz's work. These differences were probably a result of the much higher molecular weight of the Hizex MIL145M resin. The length of the slipped region was about the same length as the die-land. The slipped region
would rapidly exit from the die which indicated almost complete detachment from the die walls. The slip process would stop when new material filled the die-land. Slip was a result of rapid failure of adhesion at the polymer/die interface which occurred at higher pressure. Fresh material would re-adhere to the die-land at the lower pressure until the cycle was repeated. Kalika and Denn [61], in similar experiments with linear low density polyethylene, have stated that a free energy change occurred at the interface as a result of desorption. They believed that convective flow is the only replacement mechanism since diffusion was too slow to modify the interface for re-adhesion.

At an extruder speed of 10 rpm, gross melt fracture regions were found to be superimposed upon stick-slip. It seemed that either shear rate or more likely stretch rate had the ability to cause the gross melt fracture in these experiments. A good explanation for the gross melt fracture at higher extrusion speeds and corresponding stretch rates seems to be Cogswell’s theory that stated the tensile stresses can be high enough to fracture the melt in the converging section of the die [62]. Once the polymer emerges from the die, each elongated fragment of the melt recovers individually in a very disorganized manner to form the chaotic melt fracture. The extrudates produced after shutdown were formed with an extremely low velocity gradient and consequently low tensile stresses. These high quality extrudates formed after shutdown would tend to support the stretch rate hypothesis.
Several authors have attributed stick-slip or cyclic melt fracture to melt-die adhesion failure [63][64]. Rudin et al [65] have stated that the adhesive bond strength is a function of temperature. Figure 4-2 shows that the cyclic melt fracture frequency was a function of die temperature. An increase in the die temperature was accompanied by a decrease in the cyclic melt fracture frequency and an increase in the time (ie. period) required for slip. The longer time between slip indicated an increase of adhesion at the die wall for higher temperatures. Conversely, lower die temperatures resulted in weaker adhesion. The decrease of adhesion at lower temperatures may have resulted from the separation of impurities and lower molecular weight materials, to the polymer/die interface, because of decreased solubility. These impurities may have acted as a lubricant.

**Lubricated Die Experiments**

At low extruder speeds of 1 to 2 rpm, when grease or silicone oils were applied to the die channels, no visual melt fracture was observed until the lubricant was expelled from the die. A film formed by the lubricant probably prevented adhesion of the melt to the die wall and allowed continuous slip of the melt. Since the melt did not accelerate at the exit of the die, shear stresses were too low to result in tearing of the surface.

For lubricated extrusion, the principal form of melt deformation in the die was most likely elongation rather than shear. No melt fracture was observed when the elongational velocity gradient was about 1.4 s⁻¹. Melt fracture was observed under the same
lubrication conditions, but when the elongational velocity gradients was around $8 \text{s}^{-1}$. It appeared that the elongational velocity gradient contributed to the gross melt distortion.

Clearly two types of melt distortions were possible for the HIZEX MIL145M and possibly other VHMW polyethylenes. The first and most pronounced melt distortion was the stick-slip melt fracture which was eliminated by lubrication. The second type of melt distortion occurred at higher rates of melt flow (and corresponding melt deformation) and was reduced or eliminated at low flow rates.

### 4.2.5 Specific Conclusions from the Initial Work

1) The principal conclusion is that lubricated extrusion of higher molecular weight resins, such as Hizex MIL145M, are possible at low flow rates.

2) Cyclic (ie. stick-slip) melt fracture of Hizex MIL145M can be prevented or reduced using a lubricating film to prevent the cyclic slip and re-adhesion at the die wall.

3) The rate at which the Hizex MIL145M melt is deformed is another important parameter which determines whether gross melt fracture will appear for either lubricated on non-lubricated extrusion. Low rates of deformation achieved at low extruder speeds (ie. 2 rpm) resulted in little chaotic melt fracture. High melt deformation rates were accompanied by gross melt distortion.
4) Extrusion of lubricated and non-lubricated VHMW polymers may provide a model system for the study of sharkskin melt fracture. The advantages of VHMW polymer as a model system in comparison to conventional low molecular weight resins are: 1) exaggerated response, 2) much longer response time and 3) probably almost pure elongational flow when externally lubricated.

4.3 Lubrication Study

4.3.1 Introduction to Lubrication Study

The previous work has shown that it was feasible to screw extrude Hizex MIL145M resin using a lubricant to prevent stick-slip melt distortion at a low flow rate.

This unit investigated the use of lubricants and processing aids to prevent melt distortion. The elimination of stick-slip melt distortion was an important step towards the extrusion of higher molecular weight resins and the overall objectives of developing extrusion-orientation methodologies. In order to achieve lubricated extrusion the following objectives were formulated.

1) Evaluate lubrication methods for Hizex MIL145M resin.

2) Determine the type of flow which occurs in the capillary and die when using a lubricant or processing aid.

3) Develop a model to calculate the pressure requirements for lubricated flow in a capillary.
4) Clarify the mechanism by which lubrication reduces the melt distortion of Hizex MIL145M during screw extrusion.

4.3.2 Lubrication Injection of Silicone Oil

4.3.2.1 Introduction to Lubrication Injection

The first method considered to lubricate the melt-die wall interface and hopefully promote smooth extrusion, was lubrication injection. Lubrication injection involved pumping of a lubricant through a porous ring or injector ports which were located between the extruder exit and the die. The injected lubricant was intended to coat the external surface of the polymer melt and promote continuous slip of the polymer along the die wall. A similar technique, which used a porous ring as a "lubrication insertion device", was disclosed for the extrusion of UHMWPE [66]. Everage and Ballman [67] constructed an extensional flow capillary rheometer using the principal of lubricant injection. Very thick layers of lubricant were used for this device as the ratio of sheathing lubricant to the core polymer was 0.7.

4.3.2.2 Lubrication Injection Experimental

Materials

The resin used for these experiments was Hizex MIL145M manufactured by Mitsui Petrochemical Industries Ltd. The principal lubricant used for these experiments was Dow Corning 200 silicone oil with a viscosity of 10 000 cp at 20 °C.
**Apparatus**

Two types of lubricant injection devices were constructed. The first type was a porous metal ring with inner diameter exactly the same as the inlet diameter of the die. The second type is shown in Figure 4-5. Lubricant was pumped from an Isco LC-2600 syringe pump (maximum pressure of 50 MPa) into the porous ring or the cylindrical injector assembly. The flow rate of the lubricant could be adjusted and was independent of back-pressure. In the case of the cylindrical injector port, the lubricant passed through 8 radial drillings (ie. injector ports) in the cylindrical sleeve. The drillings were located adjacent to a cylindrical step that projected about 0.05mm into the melt path. As the melt traversed the step, the lubricant flowed in a circumferential manner to coat the melt surface.

The die used for these experiments was the aluminum, streamlined die with an extrusion ratio of about 92:1. The smooth barrel extruder setup from section 4.2 was employed for most of this work. A few lubrication experiments were conducted with a 19 mm fully grooved extruder, which had an L/D ratio of 25:1.
Figure 4-5  Cross-sectional schematic of lubrication injection port.

Method

The extruder and die were allowed to heat at the set points, shown in Table 4-2, for approximately one hour prior to extrusion. The lubricant pump was set to 0.01 mL h\(^{-1}\) to prevent melt seepage from blocking the lubricant injector during warm-up or temporary halts. Extrusion was carried out at circumferential speeds of 10 rpm.
Table 4-2 Extrusion Temperature Profile

<table>
<thead>
<tr>
<th>Heated Zone</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Entry Zone</td>
<td>135</td>
</tr>
<tr>
<td>Extruder Mid Section</td>
<td>205</td>
</tr>
<tr>
<td>Extruder Exit Zone</td>
<td>205</td>
</tr>
<tr>
<td>Lubrication Injector</td>
<td>160</td>
</tr>
<tr>
<td>Die Adapter</td>
<td>160</td>
</tr>
<tr>
<td>Die</td>
<td>160</td>
</tr>
</tbody>
</table>

4.3.2.3 Results and Discussion

The initial lubrication injection experiments were conducted using a porous metal ring to distribute the lubricant to the melt surface. This methodology was quickly abandoned because 1) the porous ring would fracture and deform during extrusion, 2) the porosity of the ring was infiltrated with polymer which could not be removed for subsequent experiments.

The lubrication injector design, shown in Figure 4-5, was found to be a compromise for these experiments. Poor lubrication distribution was suspected using this design. After disassembly of the injector apparatus for cleaning, 7 of the 8 injector ports were frequently found to be plugged with plastic. The uneven injection of
lubricant had the potential for dry regions in the die. Excess lubricant was required to wet the dry regions, which resulted in uneven distribution, seepage and spattering. Smooth extrudates were generally accompanied by silicone oil dripping from the die exit. Although the design was durable and easy to disassemble for cleaning, it required excessive lubricant and spattering.

Figure 4-6 shows the die pressure as a function of silicone oil flow rate. The pressure dropped rapidly, with increased lubricant flow rates, in the region of 0.01 mL h\(^{-1}\) to approximately 20 mL h\(^{-1}\). Above 20 mL h\(^{-1}\), the lubricant flow rate did not have a great effect on pressure. The minimum die pressure was about 9.5 MPa which probably cannot be reduced much further even with an ideal lubricant. The 9.5 MPa pressure was largely attributed to deformation that occurred in the die. Since the elongational viscosity and the stretch rate of the Hizex MIL145M was elevated in the high extrusion ratio die, considerable pressure was probably required to deform the polymer.
Figure 4-6 Extrusion die pressure as a function of silicone oil flow rate for HIZEX MIL145M.

The use of Silicone oil had a large effect on extruder throughput for a constant screw speed of 10 rpm. The throughput of non-lubricated resin was about 5.7 g min\(^{-1}\). The throughput for resin extruded with lubricant flow rate of 80 ml h\(^{-1}\) was 7.8 g min\(^{-1}\). Lubrication increased the output by approximately 37%.

Injection of Dow Corning Silicone (10 000 cp) lubricant was found to be effective in suppressing the stick-slip melt defects. Smooth surfaces could be produced for
lubricant flow rates of about 10 to 80 mL/h at very low extrusion rates (screw speed of 1 to 2 rpm). Gross melt fracture was again observed at greater extrusion rates. Spattering was observed during extrusion experiments.

**Fully Grooved Extruder Barrel**

At start up, shut down and occasionally during extrusion, it was possible to have the lubricant leak back into the extruder. This would cause the molten polymer to slide on the smooth barrel. Once this condition occurred, the extruder torque decreased to zero and polymer flow ceased. Lubricant leakage required that the extruder be disassembled and the barrel and screw cleaned.

Grooved feed sections, of length 3 to 5 barrel diameters, benefit extrusion by 1) enhanced output, 2) improved extrusion stability and 3) lowered pressure sensitivity of the output [68]. The feed grooves increase the solids conveying [69]. C.W. Brabender Instruments Inc. markets a fully grooved extruder barrel to the food industry. In this extruder, the grooves are parallel to the length and extend from the feed section to the exit. The fully grooved extruder is used for sausage manufacturing and the extrusion of clay because of the excellent ability to convey solids.

A fully grooved extruder was thought to be suitable for the extrusion of lubricated resins, as the grooves would allow the lubricated melt to slide forward in the extruder, but not to rotate with the screw. A fully grooved extruder was purchased
from C.W. Brabender. With this barrel arrangement, it was possible to extrude lubricated melts. After installing the fully grooved barrel, no extrusion experiments were halted as a result of lubrication leakages.

4.3.3 A Commercial Processing Aid

4.3.3.1 Introduction

The principal difficulties with lubrication injection were over lubrication, as evidenced by spattering, and the problem of gripping the slippery extrudate for further processing. At about this time, a commercial processing aid for UHMWPE extrusion and injection moulding was introduced [70]. Since this new processing aid, ACuflow\(^2\), appeared to be ideal for the extrusion of higher molecular weight resins and the manufacturer had limited knowledge of this product, extrusion experiments were initiated using this processing aid.

ACuflow was described as an internal and external\(^3\) lubricant [71]. It is a white powder compound which was blended with the VHMWPE or UHMWPE resin prior to extrusion. Acuflow is a compound of:

1) Ultra high molecular weight olefin polymer. The preferable material was UHMWPE with molecular weight of 2 to 6 Mg mol\(^{-1}\).

\(^2\) ACuflow is trademark of Allied Signal, A-C Polyethylene, Morristown, NJ, USA.

\(^3\) Internal lubricants increase the ease with which polymer molecules slip past one another. External lubricants reduce the friction between the polymer melt and equipment surfaces.
2) Polymeric material containing more than one acid group. The preferred copolymer was that of ethylene and acrylic acid with an acid number of 40 to 120. The preferred number average molecular weight was 1000 to 3500 g mol$^{-1}$.

3) Polyfunctional carboxylic acid salt. Aluminum stearate or zinc stearate were found to be successful.

The mechanism by which these ingredients lubricated polymer flow involved diffusion to the die walls and a chemical reaction at that site. During melt processing, the low molecular weight acid copolymer migrated to the surface of the UHMW melt where it was continuously neutralized by the acid salt. The product of this reaction was believed to be an ionic crosslinked material (i.e., an ionomer) which acted as an internal and external lubricant. The lubricant was continually formed at the surface during extrusion.

The objectives for this work were to: 1) evaluate the suitability of using ACuflow to prevent stick-slip melt fracture, 2) establish the general method of how ACuflow allowed extrusion of UHMWPE and 3) determine the processing conditions required to produce smooth surfaced, coherent extrudates.

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4 Acid number is the number of mg of potassium hydroxide needed to neutralize one gram of acid.
4.3.3.2 Experimental

Materials
The resin used for these experiments was Hizex MIL145M. The processing aid used was ACuflow supplied by AC Polyethylene of Morristown New Jersey. The concentration of the lubricant investigated was 1 to 7.5% ACuflow by weight, although 2.5% ACuflow was most frequently employed.

Apparatus
ACuflow lubricant and polymer were blended using a high intensity Werner and Pfleiderer kinetic mixer (ie. K Mixer). Extrusion was carried out with a 19 mm fully grooved extruder with an L/D ratio of 25:1. The die used for this work was conical with semiangle of 5°.

Method
Mixing of the ACuflow and resin was carried out in a K Mixer at a temperature just above the melting point of the acid (90 to 100 °C) for about 1 to 4 minutes. The extruder and die were allowed to heat at the set points, shown in Table 4-3, for approximately an hour prior to extrusion. Extrusion was carried out at circumferential speeds of 2-6 rpm.
Table 4-3  Extrusion Temperature Profile

<table>
<thead>
<tr>
<th>Heated Zone</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Entry Zone</td>
<td>135</td>
</tr>
<tr>
<td>Extruder Mid Section</td>
<td>190</td>
</tr>
<tr>
<td>Extruder Exit Zone</td>
<td>200</td>
</tr>
<tr>
<td>Die Adapter</td>
<td>170</td>
</tr>
<tr>
<td>Die</td>
<td>150-160</td>
</tr>
</tbody>
</table>

4.3.3.3 Effects of ACuflow On Dynamic Viscosity

The purpose of these experiments was to investigate in what manner ACuflow changed the rheological properties of the Hizex MIL145M resin.

The rheological properties of VHMWPE and UHMWPE resins cannot be determined using traditional capillary rheometry, because of the high viscosities and severe stick-slip problems. Consequently, the rheological properties were determined by dynamic means \(^5\). Dynamic testing incorporated cyclic straining of a suspended specimen which allowed detection of changes resulting from internal lubrication.

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\(^5\) Dynamic viscosity is defined as viscosity measured under sinusoidal deformation. It denotes the viscous part of the complex viscosity.

Figure 4-7 shows the dynamic viscosity of Hizex MIL145M as a neat (ie. non-lubricated) resin compared to the resins blended with 3.75% and 5.0% ACuflow. The curves are all similar in shape with a minor shift to lower viscosity when the lubricant was present. During the dynamic viscosity measurement of the ACuflow specimens, it was surprising to see that the 3.75 % ACuflow appeared to have a greater effect than the 5.0 % ACuflow.

The logarithm of the dynamic viscosity versus the logarithm of frequency for HIZEX MIL145M at a test temperature of 190 °C 6. The three curves are for neat resin (0% AF), resin blended with 3.75% ACuflow (3.75% AF) and 5.0 % ACuflow (5.0% AF) by weight.

6 Data provided by Dr. H. Mavridis, Quantum-USI Division, USA, Sept. 1990.
The dynamic viscosity was reduced by a maximum of 32 % when using the ACuflow. This reduction in viscosity, with the addition of ACuflow, indicated that ACuflow had some ability to act as an internal lubricant. This work was unable to give any information concerning the external lubricating properties of ACuflow.

4.3.3.4 Effect of Processing Conditions

The objectives of this sub-section were to determine the processing conditions required to extrude Hizex MIL145M resin and to deduce the lubrication mechanism of ACuflow. Successful extrusion, of higher molecular weight resins, was a requisite for the continued work in extrusion-orientation.

The processing experiments were carried out using HIZEX MIL145M blended with ACuflow. The concentration of the ACuflow was 2.5 % for most of the tests, but it was varied from 1 to 7.5 % for the concentration experiments. The extruder speed was normally limited to 2 or 4 rpm so that chaotic melt fracture was not observed, but screw speeds of 2 to 10 rpm were also attempted. Table 4-3 contains the equipment temperatures that were used for these experiments.

4.3.3.4.1 Temperatures of the Extrusion Tooling

Introduction

The temperature of the extrusion tooling was considered an important factor for the extrusion of higher molecular weight polyethylenes and was the first parameter to be investigated.
Experimental

The temperature of the die and reservoir were found to be crucial in the extrusion of smooth sound profiles. If the die temperature was greater than 180 °C, the extrudate would exhibit the periodic stick-slip defects as described earlier. This regular extrudate defect was found to disappear when the die temperature was reduced. This was initially considered unusual, since extrusion defects are normally reduced by increasing the die temperature.

The melt temperature was determined by an immersion thermocouple located in an adapter upstream to the die entry. Melt temperatures for most of these experiments were 170 to 177 °C depending upon screw speed.

The optimum die temperature was generally determined by starting extrusion at 180 °C and gradually cooling the die to the temperature at which blockage occurred. At higher temperatures, stick-slip was always exhibited and would become less intense as the die temperature was decreased. At a die temperature of 155 °C to 165 °C, the regular extrudate defects would normally vanish and smooth extrudates were formed.

The temperature at which the regular defects vanished was somewhat imprecise, but appeared to be some function of the die capillary diameter and not the die semiangle. For a die diameter of 1.17 mm, the temperature at which smooth extrudates were produced was about 165 °C. For the same die, drilled
to 3.26 mm, the temperature at which smooth extrudates were formed was about 155 °C. The die temperature at which the stick-slip defect was eliminated was always less than the melt temperature determined by the immersion melt thermocouple.

**Discussion**

The precise lubrication behaviour of ACuflow was not fully understood. Brotz[72] stated that lubricant molecules were squeezed out of the compound by high pressures and covered the surface to act as a lubricant between the thermoplastic and the walls. This proposition appeared to be faulty for ACuflow. At low temperatures ACuflow was more effective than at higher temperatures. If the lubricant were only squeezed from the melt, then higher temperatures would have allowed faster transport and better lubrication. It was hypothesized that ACuflow components were soluble in the melt. When the melt was chilled at the cooler walls, the melt adjacent to the walls becomes saturated and the excess lubricant components were deposited. Larger diameter extrudates had a smaller area to volume ratio than smaller diameter extrudates. This means that small diameter specimens cooled more rapidly than large diameter specimens and released the ACuflow more rapidly. In this manner, the fact that small diameter extrudates were smooth whereas large diameter extrudates were rough for the same die temperature, can be rationalized.
In summary, ACuflow has the ability to eliminate stick-slip melt distortions. Experiments have established that the temperature of the die must be cooler than the polymer melt for ACuflow lubrication to occur. This suggests that the lubricant components are soluble in the melt and cooling is required to deposit them upon the die wall. Smooth extrusion requires that larger diameter extrudates require cooler die temperatures than smaller diameter extrudates. For capillaries of 1.17 mm to 3.26 mm, die temperatures of 155 °C to 165 °C provides satisfactory lubrication action for Hizex MIL145M treated with ACuflow.

4.3.3.4.2 ACuflow Concentration

Introduction
The primary objective of this sub-section was to determine the optimal concentration of ACuflow required for smooth extrusion of Hizex MIL145M. The secondary objectives of this sub-section were to determine the effect of ACuflow concentration upon extruder torque, extruder throughput and pressure gradient for capillary flow.

Experimental
The ACuflow concentration was varied from 1.0 to 7.5 % by weight while all of the other variables were maintained constant. An aluminum conical die with a semiangle of 5° was chosen for these experiments. The die temperature was 155 °C and die-land temperature was 139 °C. The die-land diameter was fixed
at 3.26 mm, although the die-land length was varied from 18.9 mm to 143.5 mm in equal four steps. The extruder circumferential speed was 4 rpm. The extruder barrel was fully grooved and the screw had a compression ratio of 1.7:1.

Results and Discussion
Extrusion was possible for all concentrations between 2.0 and 7.5 % ACuflow in the Hizex MIL145M resin. A concentration of 1.0 % ACuflow was unsatisfactory because of stick-slip motion of the extrudate and non-uniform diameter of the extruded profile.

Figure 4-8 shows the effect of ACuflow concentration upon the extruder torque. As the concentration of ACuflow was increased, the torque decreased. The relationship appeared to be linear and was fitted to a straight line with goodness of fit of 0.976.

Several possible explanations existed for this reduction in torque with increased concentration of ACuflow. The first hypothesis was that the reduction in torque was due to a reduction of friction in the die and extruder at higher ACuflow loading. Another hypothesis was that the lubricant promotes faster consolidation and melting which resulted in lower torque.
Figure 4-8 Extruder torque versus ACuflow concentration.

Figure 4-9 illustrates the effect of ACuflow concentration upon the extrusion mass flow rate. As the concentration of ACuflow was increased, the mass flow rate decreased linearly with a goodness of fit of 0.952. A hypothesis to explain this trend was that slip was occurring in the extruder which limited the output. As the lubricant concentration increased in the melt, the greater the slip in the extruder, and the lower the output. Melt leakage was known to occur in the clearances between the extruder barrel and the screw flight [73] and this suggested the possibility of leakage in the barrel grooves. Since the internal vis-
cosity was previously shown to be reduced by ACuflow, the lower viscosity melt may recirculate in the grooves rather than flow axially as a plug. This lower viscosity melt would in this manner, have reduced the pumping efficiency of the extruder.

![Graph showing extruder mass flow rate as a function of ACuflow concentration.](image)

Figure 4-9 Extruder mass flow rate as a function of ACuflow concentration.

The pressure gradient in the die-land (ie. capillary) as a function of ACuflow concentration is shown in Figure 4-10. This figure exhibits that the pressure
drop across the die-land increased in proportion to the ACuflow concentration. The goodness of fit was 0.839. The increase in pressure gradient with the increase of ACuflow concentration was completely unexpected. A workable justification for this unusual relationship was that the higher concentration of the reactants (acid copolymer and the polyfunctional acid salt) produced a more highly crosslinked ionomer. If the crosslink density was increased, it followed that the viscosity of the lubricant layer would be increased thus requiring greater pressure. This hypothesis can also explain the decrease in mass flow rate with increased ACuflow concentration. However, it appears to contradict one of the hypotheses expounded for the torque versus concentration relationship observed earlier.

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7 The dynamic viscosity tests are in agreement with this data. At the time that the dynamic viscosity tests were first conducted, there was some discussion that the 5.0% and 3.75% specimens were mislabelled as the effect of the 3.75% was greater than the 5.0%.
Smooth coherent extrudates were processed with 2 to 7.5 % ACuflow. The minimal concentration for acceptable surfaces was about 2 to 2.5 % ACuflow. Experimentation has established that increasing the concentration of the ACuflow within limits of 1 to 7.5 % will 1) decrease the extruder torque, 2) decrease the mass flow rate, 3) increase the pressure gradient of the melt in the die-land.

Figure 4-10  Pressure gradient in the capillary (ie. die-land) versus ACuflow concentration.
4.3.3.4.3 ACuflow Blending Time

Introduction

The manufacturer of ACuflow recommended that it be mixed with the UHMWPE resin for 4 minutes in a high intensity mixer at 100 °C. The purpose of this mixing operation was to coat the grains of resin with the lubricant. The ACuflow-resin mixture could only be maintained at temperatures of 90 to 100 °C for period of about 1 minute prior to overheating because of the intensity of the K Mixer located at the University of Toronto. Early work with ACuflow established that overheating during mixing would result in stick-slip extrusion. In order to prevent overheating, discontinuous mixing with a long cycle time of about 8-10 minutes was required. In an attempt to ascertain if the mixing time could be reduced, a blending-time study was carried out.

The objectives of this sub-section of work was to determine if the blending time of the ACuflow had any influence on the effectiveness of ACuflow as a lubricant.

Experimental

Initial work had established that 15 s and 30 s blending times would not allow defect free extrusion of the Hizex MIL145M resin. Four batches of resin were blended at 95-100 °C for 1, 2, 3 and 4 minutes respectively. The resins were then extruded through an aluminum conical die with a 5° semiangle. The
extrusion temperatures are stated in Table 4-3 while the die temperatures utilized were either 151, 153, 155, 157 or 159 °C. The extruder was operated at 4 rpm.

Results and Discussion
All of the extrudates formed during these experiments had smooth surfaces and uniform diameters.

The experiments showed that the amount of time that the ACuflow and resin were mixed had an effect on the pressure required for extrusion as is shown by Figure 4-11. The lowest extrusion temperature (151 °C) exhibited the largest slope and the highest extrusion temperature (159 °C) exhibited the smallest slope. The least extrusion pressure, for a given extrusion temperature, was achieved with a blending time of 1 minute. Longer mixing times probably resulted in greater amounts of crosslinking in the ionomer lubricant which may have led to a more viscous film.
Figure 4-11  Pressure drop across the extrusion die versus the resin mixing time for extrusion die temperatures of 151, 155 and 159 °C. The resin was HIZEX MIL-145M blended with 2.5% ACuflow by weight.

Figure 4-11 also shows that the extrusion die temperature had a greater and more complicated effect than mixing time upon the die pressure. For the sake of clarity only curves for die temperatures of 151, 155 and 159 °C are shown. Figure 4-12 plots die pressure versus die temperature for a constant blending time of 1 minute. The least extrusion pressure for this range of temperatures occurred at around 155 °C.
Figure 4-12 Pressure drop across the die versus the die temperature. The resin and 2.5 % ACuflow were blended for 1 minute. Screw speed was 4 rpm. Confidence interval of one standard deviation.

Two competing processes were invoked to explain Figures 4-11 and 4-12. As the temperature of the die was reduced, the shear viscosity of the lubricant layer and viscosity of the Hizex MIL145M resin were increased. These viscosity increases required higher driving pressures. At the same time, a decrease in temperature resulted in reduced solubility of the lubricant in the resin.
Consequently, lubricant separated from the melt and reduced the pressure. When these two processes were summed, a local pressure minimum occurred between 153 and 157 °C.

Pressure variations, within the extrusion process, signified a variation in the polymer flow rate [74]. Oscillations in the extruder output were clearly undesirable as oscillations were accompanied by nonuniform extrudates. In this light, the standard deviation of the extrusion pressure may give a measure of the extrusion stability. The standard deviation was calculated from 10 pressure values, sampled once per minute.

As shown by Figure 4-12, extrusion temperature appears to have the greatest effect upon the standard deviation of the extrusion pressure. The minimum standard deviation for all blend times was found at a die temperature of about 155 °C. Blending time does not seem to have much effect upon the standard deviation.

This work has found that blending time and extrusion temperature are important parameters. Blending time of approximately 1 minute and extrusion temperatures of 155 °C provided smooth uniform extrudates. The smallest standard deviation for pressure and the most stable operating conditions were observed at 155 °C.
4.3.4 Extrusion of Resin-Lubricant Blend

4.3.4.1 Introduction

Silicone oil was found to lubricate the flow of Hizex MIL145M melt during extrusion, but the difficulties of uneven distribution, injector blockage and spattering were the reasons that lubrication injection was abandoned. Over lubrication with a smooth barrel extruder proved to be a major problem. An example was the leakage of lubricant into the extruder which caused the complete cessation of pumping during injection experiments. De Smedt and Nam [75] stated that an appropriate balance of incompatibility and diffusion rate were required to ensure that the processing aid coated the die, but did not allow slip at the inner wall of the extruder to reduce the pumping efficiency. Previously in this thesis, a fully grooved extruder was found to allow the extrusion of lubricated resins without significant concern for lubricant diffusion and compatibility. The experiments described in this sub-section were designed to exploit the pumping efficiency of the fully grooved extruder.

The primary objective of this section was to determine if a lubricant, such as silicone oil, can be dry blended with a higher molecular weight resin and then screw extruded with a fully grooved extruder. If this concept was successful, this lubrication technique can probably be adapted to other resin-lubricant systems.
4.3.4.2 Experimental

Materials
The resins used for these experiments were Hizex MIL145M and Himont LF 00459 (Molecular weight of 5.25 to 5.75 Mg mol$^{-1}$). The lubricant was Dow Corning 200 silicone oil with a viscosity of 12 500 cp at 20 °C.

Apparatus
A steel, essentially constant elongational velocity gradient die with an extrusion ratio of 5:1 was attached to a 19 mm fully grooved extruder which had an L/D ratio of 25:1.

Method
Approximately 250 mL of resin was blended with 4 % silicone oil by weight. Mixing of the resin and silicone oil was carried out in a kitchen blender for approximately 15 s at room temperature. The resin was then transferred to the extruder hopper. The extruder and adapter were allowed to heat at the set points, shown in Table 4-3, for approximately an hour prior to extrusion. The die temperature was 140 °C for the Hizex MIL145M resin and 120 °C for the Himont LF 00459. Extrusion was carried out at a circumferential speed of 4 rpm. No attempt was made to optimize the blending or extrusion conditions as these experiments were meant to only demonstrate the possibility of the concept.
4.3.4.3 Results

Smooth coherent extrudates were produced using the silicone oil lubricated Hizex MIL145M resin. The surface of the extrudates was not tacky and could be marked with an alcohol ink pen. There was no evidence of stick-slip melt fracture. The extrusion pressure over a period of 5 measurements, at 1 minute intervals, was 10.5 MPa with a standard deviation of 0.6 MPa. The extrusion speed was about 0.4 m min⁻¹.

In a similar manner, smooth coherent Himont LF 00459 extrudates were produced with the adapter temperature at 190 °C and the die at 120 °C. Extrusion speeds of approximately 1.5 m min⁻¹ were found to be possible when the extrudates were drawn from the die with a belt puller.

A fully grooved extruder was capable of extruding silicone oil lubricated, higher molecular weight polyethylene resins and producing macroscopically defect free extrudates. The results indicated that a fully grooved extruder can be successfully used to extrude lubricated resins without any significant worry about slip in the extruder. This allowed extrusion of a wide range of linear higher molecular weight resins.
4.3.5 Analysis of Lubricated Polymer Flow

4.3.5.1 Introduction

Since experimentation has found that the extrusion of Hizex MIL145M was impossible without utilizing a lubricant, the principal objective of this section was to determine the manner in which lubricant altered the flow of Hizex MIL145M to improve the extrudability.

4.3.5.2 Experimental

Materials

The resin used for these experiments was Hizex MIL145M. ACuflow was used as a processing aid at a concentration of 2.5 % by weight. The Acuflow was blended for 4 minutes at 90 to 100 °C in a K Mixer.

Apparatus

Extrusion was carried out with a 19 mm fully grooved extruder with an L/D ratio of 25:1. The die used for this work was conical with semiangle of 23°. The capillary (ie. die-land) had a diameter of 1.61 mm and the length to diameter ratio was varied from 2 to 37.2 in four equal steps.

Method

The extruder and adapter were set to the temperatures contained in Table 4-3 while the die and die-land temperatures were adjusted to 160 °C. The apparatus was allowed to heat at the set points for approximately an hour prior to extrusion.
Extrusion was carried out at a screw speed of 4 rpm. The pressure and melt flow rates were determined for each of the four die-lands of different length and for the die without a die-land.

4.3.5.3 Results

Figure 4-13 shows the pressure drop in the die and capillary as a function of length/diameter ratio (ie. dimensionless length) of the capillary. The relationship between pressure and length was linear with an $R^2$ of 0.9989. Two points of interest can be determined from Figure 4-13. First, the slope of the graph is proportional to the pressure gradient in the capillary. The pressure gradient was calculated and found to be -228 MPa m$^{-1}$. The second point of interest was the point where the curve intersects the pressure drop axis (ie. where $L/D$ was 0). This intercept showed the entry loss for the die and can be interpreted as an approximate measure of the pressure required for elongational deformation of the polymer [76]. The entry pressure drop was about 9.5 MPa.

---

8 The pressure gradient in the capillary is $dP/dL$ measured in MPa m$^{-1}$. The slope of Figure 4-13 is measured in MPa per dimensionless length and can be converted to MPa m$^{-1}$ by multiplying the dimensionless length by the numerical value of diameter.
Figure 4-13  Plot of pressure drop versus dimensionless capillary length for HIZEX MIL145M resin blended with 2.5 % ACuflow.

The average mass flow rate was 4.4 g min⁻¹.

4.3.5.4 Discussion of Lubricated Polymer Flow

4.3.5.4.1 Slip

Smooth polymer flow of Hizex MIL145M probably occurred by continuous slip of the polymer over a layer of lubricant at the capillary walls. If the pressure gradient calculated from the shear viscosity data, determined by the Cox-Merz rule, was greater than the pressure gradient calculated from the
experimental data, then wall slip must have occurred.

**Pressure Gradient from the Dynamic Viscosity Data**

The Cox-Merz rule allows the determination of the steady-state viscosity from the dynamic data [77]. The Cox-Merz rule is given by

\[ \eta_{app} (\dot{\gamma}) = \eta^* (\omega) \mid \omega = \dot{\gamma} \]

where \( \eta_{app} \) is the apparent viscosity at the apparent strain rate of \( \dot{\gamma} \) in \( s^{-1} \), and \( \eta^* \) is the complex viscosity with the rotation frequency, \( \omega \) in radians \( s^{-1} \).

The apparent viscosity can be represented by the power-law expression

\[ \eta(\gamma) = K | \gamma |^{n-1} \]

where \( K \) is the consistency and \( n \) is the power-law index [78]. Using the Cox-Merz rule on the data provided for the non-lubricated resin in Figure 4-7, the consistency at 190 °C was 2.6 MPa•s\(^n\) and the power-law index was 0.30. This was a good agreement with Kwag [79] who found a consistency of 2.672 MPa•s\(^n\) and a power-law index of 0.301.

The viscosity given by the Cox-Merz rule was obtained at 190 °C and must be corrected for the extrusion temperature of 160 °C. A widespread empirical relationship to calculate the consistency [80] is given by

\[ K = K_r \exp(\beta(T_r - T)) \]
where \( K_r \) is the reference consistency at the reference temperature \( T_r \), \( T \) is the corrected temperature and \( \beta \) is a constant for polyethylene of 0.015. The corrected consistency was 4.1 MPa \( \cdot \) s\(^n\).

McCrum et al. [81] presented a relationship

\[
Q = \frac{n\pi}{(3n + 1)} R^{(3 - 1/n)} \left( \frac{1}{2K} \frac{\Delta P}{\Delta L} \right)^{1/n}
\]

where \( Q \) was the volumetric flow rate, \( R \) was the capillary radius, and \( \Delta P/\Delta L \) was the pressure gradient. This analytic relationship was based upon shear flow of the power-law fluid with no slip at the capillary wall. The pressure gradient calculated from this relationship was \(-5.79 \times 10^4\) MPa m\(^{-1}\) for a flow rate of \(8.63 \times 10^{-8}\) m\(^3\) s\(^{-1}\) (ie. 4.4 g min\(^{-1}\)) using the power-flow data derived for Hizex MIL145M.

The pressure gradient, found by experiment (ie. calculated from the pressure versus L/D plot), was \(-228\) MPa m\(^{-1}\). The pressure gradient determined from the analytic relationship, which assumes no slip, was \(-5.78 \times 10^4\) MPa m\(^{-1}\) which was approximately 253 times greater. Based upon these pressure gradients, slip between the capillary wall and the polymer must have occurred.
Wall Shear Stress

The shear stress at the wall $\tau_w$, can be calculated from the relationship

$$\tau_w = -\frac{R}{2} \frac{\Delta P}{\Delta L}$$

where $R$ is the radius of the capillary [82].

The shear stress predicted from the dynamic data was 24.3 MPa. In a comprehensive study of the wall slip phenomena of rubber compounds [83], the wall shear stress at the start of wall slip (ie. critical shear stress) was always less than 2 bar (0.2 MPa). Agassant [84] found that the critical shear stress for slip was 0.52 MPa for calendering of PVC. Ramamurthy [85] discovered that at a shear stress of about 0.10 to 0.145 MPa that melt fracture, which resulted from slip, occurred for high density polyethylenes. The predicted wall shear stress from the dynamic data was several orders of magnitude greater than the maximum normally observed without wall slip. This argued that slip must occur at the capillary wall for the non-lubricated Hizex MIL145M.

The shear stress, for the ACuflow treated resin, determined from the pressure versus L/D plot was 0.092 MPa which was in the region of no wall slip. This probably indicated that a lubricant layer was present at the capillary wall which eased the extrudate flow.
4.3.5.4.2 Slip Velocity

When a lubricant was present, the shear stress at the wall was only a very small fraction of shear stress predicted from the dynamic shear viscosity data. This indicated that some fraction of the polymer flow took place by slip at the tooling surfaces. Since the experimental shear stress was very small in comparison to shear stress predicted for shear flow, a substantial slip velocity was expected.

Kalika and Denn [86] showed a relationship to calculate the slip velocity $V_s$, of a power-law fluid.

$$\frac{8V}{D} = \frac{8V_s}{D} + \frac{4n}{3n+1} \left( \frac{\sigma_w}{K} \right)^{1/n}$$

This relationship can be rewritten in the form

$$\frac{4V_s}{R} = \frac{4Q}{\pi R^3} - \left( \frac{4n}{3n+1} \right) \left( \frac{\sigma_w}{K} \right)^{1/n}$$

from which the slip velocity may be calculated. For the values given in the previous section and a wall shear stress of 0.092 MPa, the slip velocity was found to be 0.042 m s$^{-1}$. The average extrudate velocity under these condition was also 0.042 m s$^{-1}$ which indicated that the polymer flow occurred by slip rather than by shear. Since the average and slip velocities appeared to be identical, the transverse velocity gradient must be zero (ie. flat). All calculations of the slip velocity for ACuflow and silicone oil experiments have found
that plug flow occurred for lubricated extrusion.

Two definite conclusions can be drawn from these calculations concerning the lubricated extrusion of Hizex MIL145M:

1. Flow of the polymer melt occurred by sliding along the capillary wall rather than by shearing.

2. The velocity profile of the polymer in the capillary must be nearly flat. Plug flow occurs during the lubricated extrusion of Hizex MIL145M.

Venkatraman et al [87] stated that the Cox-Merz rule required verification for HDPE. These authors found that the corrected steady-state viscosity was always greater than the dynamic viscosity regardless of the molecular weight distribution. Since little is known concerning Hizex MIL145M, the slip calculations were conducted using a consistency which was 2 orders of magnitude lower than that found from the Cox-Merz law. Under these conditions the ratio of the slip velocity to average velocity was 0.96. Even if the consistency was as much as 2 orders of magnitude in error, the conclusions of continuous slip and plug flow are still essentially valid for extrusion of Hizex MIL145M through a capillary.
4.3.5.4.3 External Lubrication

The dynamic viscosity tests of the ACuflow treated Hizex MIL145M resin (Figure 4-7) shows that the internal viscosity was reduced by less than one third which was much too small to account for the observed pressure decrement. The pressure gradient was reduced by a factor of about 250 times when the lubricated extrusion experiments were compared to the pressures calculated for shear flow from the dynamic viscosity data. It can be concluded that the principle effect of ACuflow was that of an external lubricant. Kalika and Denn [88] in a study of linear low density polyethylene found that the transition to stick-slip melt fracture was by catastrophic failure of adhesion in the die-land which allowed almost complete slip of the capillary contents. They found that the new material would adhere until the stresses again built to the point of catastrophic failure. A lubricant, such as ACuflow or silicone oil, prevented the polymer from adhering to die walls. This leads to continuous slip of the polymer over the die walls.

Cogswell [89], in a paper which included work on constrained converging flow, stated that, for lubricated walls, no shear flow of the polymer occurred for conical dies (unfortunately no die angles were given). As such, the insight concerning plug flow and lubricated slip, should also be applicable to low angle converging geometries when the elongational properties are taken into
consideration. Deformation by elongation, in the converging channel, would be the primary means of deformation for Hizex MIL145M resin rather than shear, during lubricated extrusion.

4.3.6 Model to Calculate Pressure for Lubricated Polymer Flow

4.3.6.1 Introduction

A simple lubrication film model was devised to test the concept of continuous slip of the Hizex MIL145M on the tooling wall and to predict the pressure requirements for this type of flow.

Figure 4-14 shows a schematic diagram of the lubricated flow of Hizex MIL145M through a capillary. The molten VHMWPE which flowed through the center of the capillary was supported by a thin film of lubricant. The lubricant film was sheared, while the polymer melt exhibits essentially plug flow. Only the viscosity to thickness ratio of the lubricant layer was determined by the model, but this is sufficient information to calculate the pressure required for flow through a capillary.
4.3.6.2 Pressure Model Experiments

Over a period of about a year, extrusion experiments were conducted with 6 conical dies of semi-angle 5, 10, 15, 23, 45 and 90°. The capillary diameter for each of these dies was drilled, polished and extrusion tested at 1.17, 1.61, 2.36 and 3.26 mm. For each die, the capillary length to diameter ratio was varied from about 2:1 to about 40:1 at each capillary diameter. This allowed pressure versus L/D plots (ie. Figure 4-13) to be drawn for each die at each capillary diameter. The temperature of the die was maintained at 160 °C for all of the experiments. The tempera-

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Figure 4-14  Schematic diagram of lubricated flow of VHMWPE through a capillary.
ture of the die-lands was initially 160 °C. Unfortunately, the temperature of the die-lands had to be decreased to maintain smooth, spurt free extrusion with the 2.36 and 3.26 mm capillary diameters.

The slope of the pressure versus L/D plot allowed the calculation of the pressure gradient for the capillary region. For each of the four capillary diameters, the average pressure gradient and the related standard deviation were calculated from the slope of the pressure versus L/D plot from each of the 6 different dies and are contained in Table 4-4.
4.3.6.3 The Lubrication Film Model

Requirements and Assumptions for Model

1. Previous work has established that the Hizex MIL145M melt flowed by slip along the wall of the capillary and the slip velocity of the melt was almost identical to the average velocity. This established that plug flow occurs for the VHMWPE core.

2. The ratio of the viscosity of the polymer melt to that of the lubricant was very large. This was inferred from the large decrease of pressure gradient with lubricated flow.

3. The lubricant layer was a relatively low molecular weight ionomer or a fluid such as silicone oil. The lubricant layer probably behaved as a Newtonian fluid and was characterized by the relationship, \( \eta = \frac{\tau}{\gamma} \).

4. The lubricant layer was very thin film and could not be detected by direct optical examination of the extrudates. A thin dark coating was observed on the extrudate after heating in air. Annealing of an extrudate for 30 minutes at 180 °C probably caused thickening of the lubricant layer by seepage and discoloration by oxidation.
5. The lubricant film did not slip at the capillary wall. The shear stress for the lubricant film at the capillary wall was previously found to be 0.092 MPa. This was less than the critical shear stress for slip at the wall as presented in section 4.3.5.4.1.

6. The lubricant film at the boundary with the Hizex MIL145M core had the same velocity as the core.

7. The viscosity of the lubricant film was probably a complicated function of temperature. The film thickness depended upon the rate of reaction of the acid and acid salt supplied by the ACuflow, the rate of transport through the polymer melt to the surface and the degree of saturation of lubricant. All of these factors were dependent upon the temperature.

**Derivation of the Model**

The shear velocity gradient in the lubricant film was given by

\[ \gamma = \frac{dV}{dr} = \frac{1}{t} \frac{dV_p}{dr} \]

where \( V_p \) was the plug velocity of the VHMWPE core and \( t \) was the thickness of the lubricant film. It follows that the shear stress was

\[ \tau = \eta \gamma = \eta \frac{1}{t} \frac{dV_p}{dr} \]

in which \( \eta \), was the shear viscosity of the lubricant.
The force that acts, over the cross-sectional area, to propel the extrudate through the capillary was

\[ F = P(2\pi R^2) \]

where \( P \) was the pressure. The sheared area was \( A = 2\pi R L \), and \( L \) was the length of the cylindrical shear surface. The shear stress after simplification was then

\[ \tau = \frac{F}{A} = \frac{PR}{2L} . \]

Equating the two shear stress formulae resulted in

\[ \frac{PR}{2L} = \eta \frac{V_p}{t} . \]

Dividing pressure with the respect to \( L \) and simplifying, yields

\[ \frac{P}{L} = \left( 2\eta \frac{t}{\nu_p} \right) \frac{V_p}{R} . \]

Examination of the previous relationship revealed that \( \eta/t \) should be a constant for constant temperature. Rewriting the equation resulted in

\[ 2\frac{\eta}{t} = \frac{\left( \frac{\nu_p}{\nu} \right)}{\frac{\nu}{R}} . \]

Table 4-4 shows values of \( 2\eta/t \), obtained from experimentation.
Data Supporting the Model

Table 4-4  Values of $2\eta/t$ and related experimental conditions.

<table>
<thead>
<tr>
<th>Capillary Diameter (mm)</th>
<th>Die Temperature (°C)</th>
<th>Capillary Temperature (°C)</th>
<th>$2\eta/t$ (MPa·s/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.17</td>
<td>160</td>
<td>160</td>
<td>4.0 ± 0.3</td>
</tr>
<tr>
<td>1.61</td>
<td>160</td>
<td>160</td>
<td>3.8 ± 0.6</td>
</tr>
<tr>
<td>2.36</td>
<td>160</td>
<td>138</td>
<td>4.2 ± 0.7</td>
</tr>
<tr>
<td>3.26</td>
<td>160</td>
<td>139</td>
<td>6.7 ± 1.0</td>
</tr>
</tbody>
</table>

4.3.6.4 Discussion of the Pressure Model

Lubricated extrusion was possible with identical die and capillary temperatures (160 °C) for the two smallest capillary diameters. In the case of the two larger diameter capillaries, the capillary temperature had to be reduced by about 20 °C from the die temperature to prevent stick-slip. If it had been experimentally possible, the die and capillary temperatures would have been fixed at the same temperature for all capillary diameters.
Examination of Table 4-4 shows that the average $2\eta/t$ ratio was approximately equal for the two smallest capillary diameters when the die and capillary were at the same temperature. The $2\eta/t$ ratio, for the next larger capillary, was about the same as the two smallest, when the standard deviations were taken into consideration. The average ratio for the 3 smallest capillaries was 4.01 MPa·s m$^{-1}$. The $2\eta/t$ ratio of the largest capillary was about 66% greater than the average ratio.

The difference in value of the $2\eta/t$ ratio for the largest capillary in comparison to the three smaller capillaries may be a result of the sluggish cooling of the largest diameter extrudate while in the capillary. The slower cooling may have kept the lubricant in the melt rather than at the interface. This would result in a velocity greater viscosity or thinner film, both of which dictate a larger $2\eta/t$ ratio. In general, isothermal extrusion tooling would deliver easier to interpret experimental results, but, may not permit smooth extrudates.

The model can be easily rewritten to determine the pressure drop along a capillary in the form

$$\Delta P = \frac{C_s V_p}{R} \Delta L$$

where $C_s = 2\eta/t$ is a lubricated slip constant which can be experimentally determined for a given resin and lubricant. A value of $C_s$ in the domain of 4 to 7
MPa s m\(^{-1}\) seemed to be adequate for 2.5 % ACuflow lubricant blended with Hizex MIL145M. For die and capillary temperatures near 160 °C, the 2\(\eta/\rho\) ratio of about 4 MPa s m\(^{-1}\) would give reasonable results. This model should be sufficiently accurate to predict the approximate pressure requirements for simple reservoir-die designs to ensure the pressure capacity of the equipment will not be exceeded. Insufficient isothermal data is available to make predictions for other temperatures.

The data collected for the lubrication film model supports, but does not prove, the concept of a viscous central polymer core continuously shearing a thin lubricant film. The ratio of 2\(\eta/\rho\) for the film appeared to be relatively constant for the three smaller diameter capillaries.

4.3.7 Lubrication and Melt Fracture

The melt disturbance commonly observed for non-lubricated extrusion of Hizex MIL145M is shown in Figure 4-15 (a). This type of melt distortion had many of the characteristics of sharkskin melt fracture as defined by several authors [90][91]. Surface cuts were transverse to the direction of flow and had a relatively constant spacing which implied a constant frequency. Cogswell [92] suggested that rapid stretching at the surface, as the melt accelerated from rest at the die exit to the uniform extrudate velocity, resulted in stresses large enough to tear the skin.
Normally, sharkskin melt flaws produce an uneven "matt" surface formed by closely spaced ridges. The disturbances observed for the non-lubricated Hizex MIL145M extrudates were much deeper, possibly because of the high melt elasticity of HMWPE melts. External lubrication was found to eliminate these melt disturbances. Figure 4-15 (b) shows the velocity profiles of a lubricated extrudate. The velocity
profile of the extrudates does not change appreciably at the exit of the die. Since no change in velocity was required for the surface, no additional surface stresses were generated to split the skin.

External lubrication prevents the sharkskin type of melt fracture by permitting continuous slip of the extrudate. Since the surface moves at the same velocity as the bulk extrudate, no acceleration of the skin layer occurs to produce skin fracture.
4.4 First Study of Elongational Velocity Gradient

4.4.1 Introduction

The initial work carried out in section 4.2 had established that a lubricating film and slow rates of deformation permitted the screw extrusion of higher molecular weight polyethylene. In the lubrication study of section 4.3, it was well established that a lubrication film prevented cyclic melt fracture and that the melt flowed as a plug. Higher rates of deformation of the melt, had been shown to be detrimental to extrusion, yet the limits have not been investigated for higher molecular weight resins.

Polymer flow can occur without disturbance as long as the rate of deformation is sufficiently low that Brownian motion can return the molecules to their equilibrium state at approximately the same rate as the deformation occurs. Lower molecular weight resins, with rapid relaxation, can be deformed rapidly, whereas higher molecular weight resins can probably undergo only limited deformation rates. The mode of deformation for lubricated flow of higher molecular weight polyethylene is chiefly elongation and the rate of deformation is related to the elongational velocity gradient (EVG). A range of EVG may exist that would result in sufficient tensile stresses to draw out the polymer chains without provoking elongational melt fracture and defects which limit the cohesiveness of the melt.
The objectives of this section were to:

1. Determine the effect of EVG (i.e., deformation rate) and other processing conditions upon extrudate properties and structure.

2. Establish the range of elongational velocity gradients that permitted the extrusion of substantially unoriented higher molecular weight polyethylenes.

3. Ascertain the extrusion conditions which allow the production of ductile extrudates that can be melt-drawn to high strength and modulus. The room temperature elongation to break was used as one method of screening the extrudates prior to melt-drawing experiments. (Melt drawing has great commercial importance. The extrusion of higher molecular weight polyethylenes that can be melt drawn was a driving force for this research.)

4.4.2 Calculation of Elongational Velocity Gradients

Previous work has shown that the polymer slides along the capillary wall by shearing the lubricant film. Lubricated slip furnishes little or no shear deformation to the polymer. Consequently, in a low angle converging die, little shear deformation will occur and the primary mode of deformation will be elongational. The elongational velocity gradient is a method of determining the rate of deformation during lubricated extrusion. The elongational velocity gradient can be calculated from the relationship
\[
\frac{dv}{dx} = \frac{-2mQ}{\pi (R_0 + mx)^3}
\]

where \( m = -\tan(\alpha) \), \( Q \) is the volume flow rate, \( R_0 \) is the entry radius and \( x \) is illustrated in Figure 4-16. The formula required that lubricated plug flow occur in the converging section of the die.

![Diagram of a conical converging die](image)

**Figure 4-16** The coordinate system to describe conical converging dies.

The elongational velocity gradient can be calculated from the die dimensions and the volume flow rate assuming slip along the wall and plug flow. Figure 4-17 shows the elongational velocity gradient imposed upon the polymer melt as it passed through a conical die with a semi-angle of 5°. The flow rate for this simulation was 5.38 g/min.
Figure 4-17  The elongational velocity gradient (EVG) as a function of the x coordinate. The EVG ascends from a small value at the entrance to the die, to a maximum at the exit of a conical die. Note that the EVG is zero for regions of constant radius. The die radius is shown on the secondary axis of the figure.

4.4.3 Experimental

Materials

Two higher molecular weight resins were chosen for these experiments. The first resin, donated by the Mitsui Corporation, was HIZEX MIL145M with molecular weight of 0.95 Mg mol$^{-1}$. The alternate resin was Hoechst GX-573-L with molecular weight of 0.8 Mg mol$^{-1}$. Both of these resins were selected for their ability to be melt-
drawn to high draw ratios and their high strength and modulus [93]. ACuflow was blended at a concentration of 2.5 % by weight to prevent cyclic melt fracture during extrusion.

**Apparatus**
The apparatus required for the higher molecular weight polyethylene extrusion is shown in Figure 4-18.
VHMWPE or UHMWPE
Powder

Conical die with variable length die-land

Screw type hopper feed

19 mm smooth or fully grooved barrel extruder

7.5 HP computer controlled variable speed drive

Extrudate

Figure 4-18 Schematic diagram of the extrusion apparatus for VHMWPE and UHMWPE.

Six conical dies were constructed. Figure 4-19 shows the important parameters, die semi-angle, $\alpha$, capillary length, $L$, and capillary diameter, $D$, which were investigated in this section. The die semi-angles used for these experiments were 5, 10, 15, 23, 45 and 90°.
Since the length to diameter ratio of the capillary (ie. die-land) was known to have a great effect on extrudate swell [94] and subsequent relaxation, this ratio was investigated by constructing a variable length capillary which could be fitted to each of the six dies. The capillary assembly is shown in Figure 4-20. The length of the capillary was changed by inserting or removing capillary inserts into the support tube. Each of the four capillary insert was machined to a length to diameter ratio of about 10:1. The capillary support tube had the potential to contain 0 to 4 capillary inserts which allowed the length to diameter ratio to be varied from approximately 2 to 40.

The six dies was initially constructed with the smallest capillary entrance of 1.17 mm. Each die was tested with one capillary insert through four capillary inserts which took approximately six to eight hours. After these experiments were completed, the dies were drilled and polished to the next largest diameter. New capillary inserts, with the
larger diameter, were machined to fit the capillary support. This procedure of testing then machining to the next larger diameter was repeated for the four capillary diameters. A summary of the experimental conditions is shown in Table 4-5.

Figure 4-20  Schematic diagram of the die and capillary assembly.
### Table 4-5 Extrusion Die and Die-Land Details

<table>
<thead>
<tr>
<th>Die Semi-angles (°)</th>
<th>5, 10, 15, 23, 45, 90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Die-Land Diameter (mm)</td>
<td>1.17, 1.61, 2.26, 3.26</td>
</tr>
<tr>
<td>Capillary L/D Ratios⁹</td>
<td>2.. 40 approximately (in 4 steps)</td>
</tr>
<tr>
<td>Extrusion Ratio</td>
<td>72, 39, 18, 9.2</td>
</tr>
</tbody>
</table>

**Typical Procedure**

The extrusion experiments generally required setting the temperature zones of the extruder, die adapter and die, to the values shown in Table 4-3. After warming the apparatus for about an hour, the hopper was loaded with the polyethylene powder. The hopper feeder was set to 3 rpm and extrusion was started at the desired extruder rpm. Once stable extrusion had commenced, samples of the extrudate were collected for analysis. The prime extrudate analysis consisted of tensile tests to determine the strength and elongation to fracture. The elongation to fracture of fibres was known to be adversely affected by defects trapped during the extrusion process [95]. The tensile tests were conducted at room temperature using an Instron test machine with crosshead speed set to 10% of the fiber gauge-length per minute as

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⁹ Each semi-angle and die-land diameter was tested at 4 different L/D ratios. The L/D ratios varied from about 2 to approximately 40 in 4 steps.
specified by ASTM D638. DSC tests were conducted, to investigate the whether the structure contained oriented material, using a Du Pont model 2000 differential scanning calorimeter. The heating rate was 10 °C min⁻¹.

4.4.4 Results

Die Semi-angle and Elongational Velocity Gradient

Figure 4-21 shows the average elongation to fracture of Hizex MIL145M versus the extrusion die semi-angle for 3 capillary diameters. At first sight, very little regularity was found in the data.

Some of the lack of apparent regularity may have been a result of extrusion at different die-land temperatures. Extrusion of smooth extrudates required a unique die-land temperature for each capillary diameter. Another difficulty was that smaller diameter filaments, with a lower surface area, were less likely to contain critical surface flaws, and thus fail in tension. This makes comparison of tensile properties, between filaments with different diameter, somewhat difficult.

Altering the volumetric flow rate was considered an alternate method of varying the EVG for a constant extrudate diameter. This idea had a severe drawback, as altering the extruder speed, also altered the melt temperature.
Figure 4-21  Average elongation to fracture of Hizex MIL145M versus die semi-angle for capillary diameters of 1.61 mm, 2.26 mm and 3.26 mm. Data was collected for dies with capillary length of about 30 to 35 L/D ratios and screw speed of 4 rpm. Error bars were not shown because of the crowding of the data. A 300% elongation was the approximate limit of the tensile machine for the standard 254 mm long specimen suggested by ASTM D638.
The elongational velocity gradient was calculated from relationship given in section 4.4.2. After the data was replotted, in terms of elongational velocity gradient rather than die semi-angles, a more coherent picture was observed. Figure 4-22 shows the average elongation to fracture versus the maximum elongational velocity gradient.

![Graph showing elongation to fracture versus maximum elongational velocity gradient.](image)

Figure 4-22 The average elongation to fracture versus the maximum elongational velocity gradient for Hizex MIL145M. Data was collected for dies with capillary length of about 30 to 35 L/D ratios and screw speed of 4 rpm. Capillary diameters ranged from 1.61 mm to 3.26 mm.
Figure 4-23, which contains data for a single capillary diameter of 3.26mm, shows a clearer picture of the relationship between elongation to break and EVG with no distraction due to extrudate diameter differences.

![Graph](image)

**Figure 4-23** Elongation to fracture versus the maximum EVG for Hizex MIL145M. Extrusion was carried out at 4 rpm with the die at 160 °C and the capillary at 139 °C. The capillary diameter was 3.26 mm with a L/D ratio of about 30 to 35 for all dies.

It appeared that low EVG (i.e. shallow die semi-angles) promoted ductile extrudates, but a single data point was not convincing evidence. The experiments were then con-
ducted for a second VHMWPE resin - Hoechst GX-573-L with molecular weight of 0.8 Mg mol⁻¹. Figure 4-24 shows the effect of EVG upon the elongation to fracture of the Hoechst GX-573-L resin. The elongation to fracture of the Hoechst GX-573-L extrudates had the same pattern as the Hizex resin. For both resins, an abrupt transition between extreme ductile behaviour (approximately 300 % elongation) and normal ductility of about 100 % elongation occurred at EVG of less than 5 s⁻¹.

Figure 4-24  Elongation to fracture versus the EVG for Hoechst GX-573-L. Extrusion was carried out at 6 rpm with the die at 160 °C and the capillary at 139 °C. The capillary diameter was 3.26 mm with a L/D ratio of about 40 for the dies.
The Effect of Die Temperature on Extrudate Ductility

Figure 4-25 shows the relationship between elongation to fracture and die temperature for the extrusion of Hizex MIL145M. It was apparent that ductility of the polymer increased with increased die temperature.

Figure 4-25  Elongation to fracture versus the die temperature for Hizex MIL145M. Extrusion was carried out at 4 rpm with the 10° semi-angle die. The capillary diameter was 2.26 mm with a L/D ratio of 42.5.
Capillary Length and In-Line Annealing

Figure 4-26 shows the effect of capillary length on elongation to break (i.e. ductility) for extrudates that have not been annealed. For these experiments, a die with a semi-angle of 5° was employed. The capillary length to diameter ratio (L/D) was varied from about 6 to 44, with a capillary diameter of 3.26 mm. Even without annealing, the elongation to break was large for L/D ratio of approximately 16.

In-line annealing consisted of passing the extrudate through a short heated tube immediately after exiting the die. The temperature of the tube was 139 °C with a length of 15 cm. The traverse time in the heated tube was 10.4 s. Examination of the top left corner of Figure 4-26 shows that in-line annealing substantially increased the elongation to break for specimens prepared with a 5° semi-angle die and L/D of 6. In-line annealing increased the elongation to break from 240 % to 740 % (740 % was the maximum extension for the tensile test machine). In-line annealing appeared to be a very effective technique to increase the ductility of VHMWPE extrudates.
Figure 4-26  The set of data points joined by the straight lines show the effect of capillary length to diameter ratio on elongation to break for extrudates that have not been annealed. The single point on the top left corner of this figure shows the effect of in-line annealing on a specimen extruded through a capillary with an L/D of 6.

The Effect of EVG on Extrudate Structure

Hoogsten, ten Brinke and Pennings [96] have shown that differential scanning Calorimetry (DSC) is an excellent technique to study the morphological differences in
fibres and allowed these authors to distinguish between lamellar and shish-kebab structures. Although the work of Hoogsten et al was concerned only with solution spinning, it was reasonable to expect similar types of structures for this thesis.

DSC analysis was carried out using a Du Pont model 2000 differential scanning calorimeter with a heating rate of 10 °C min⁻¹. Figure 4-27 shows the DSC trace for a ductile extrudate which was formed at a low EVG and was in-line annealed for 10 s after exiting the die. The maximum EVG was approximately 1.3 s⁻¹. The curve was smooth with a single endotherm at 136.6 °C. A closer examination of the curve in the temperature range of 150-158 °C is presented in Figure 4-28. Figure 4-27 shows no evidence of a secondary endotherm. This specimen was found to be very ductile and could be cold drawn to limits of the tensile test machine (approximately 740 % elongation) without breaking. The evidence from the DSC analysis indicates a structure composed of lamellar chain folded crystals.
Figure 4-27  DSC trace for ductile profile extruded with a maximum EVG of 1.3 s\(^{-1}\). Q is a measure of heat absorbed by the specimen. The die had a 5° semi-angle. Extrusion was carried out at 4 rpm. The die temperature was 160°C and the capillary temperature was 139°C.
Figure 4-28 Magnified DSC trace for ductile extrudate in the temperature range of 150-158 °C. The die had a 5° semi-angle. Extrusion was carried out at 4 rpm. The die temperature was 160 °C and the capillary temperature was 139 °C.

A different picture is shown in Figure 4-29 for a specimen prepared with a maximum EVG of about 15 s\(^{-1}\). In the temperature region near 152 °C a small endotherm indicating chain extended microfibril material was detected. Figure 4-30 shows a
closer view of the region from 144-160 °C. In Figure 4-30 the secondary endotherm is shown unquestionably. This is clear evidence that a small amount of chain extended material was present in the more rapidly deformed extrudate. The presence of chain extended material was accompanied by a reduction of elongation to break. The elongation to break for this sample was only 90.5 ± 23.3 %, in comparison to 740 % for extrudate deformed with an EVG of 1.3 s⁻¹. The structure of this specimen was essentially lamellar with a small amount of chain extended (ie. oriented) crystals.
Figure 4-29  DSC trace for non-ductile profile extruded with a maximum EVG of about 15 s⁻¹. The die had a 45° semi-angle. Extrusion was carried out at 4 rpm. The die temperature was 160 °C and the capillary temperature was 139 °C.
Figure 4-30 Magnified DSC trace for non-ductile extrudate in the temperature range of 147-155 °C. The die had a 45° semi-angle. Extrusion was carried out at 4 rpm. The die temperature was 160 °C and the capillary temperature was 139 °C.

As a general observation, any specimen that exhibited a second endotherm, at a temperature greater than 133 °C, was not found to be extendible. The maximum draw ratio, for these specimens, was always less than 2.
4.4.5 Discussion

The EVG at which a sharp change in ductility is observed, can be considered a critical EVG. In Figures 4-23 and 4-24 a rapid change in elongation to fracture is observed at values EVG less than 5 s\(^{-1}\). The critical EVG for HIZEX MIL145M (MW 0.95 Mg mol\(^{-1}\)) was in the region of 1.3 to 2.6 s\(^{-1}\). The critical EVG for Hoechst GX-573-L with a MW of 0.8 Mg mol\(^{-1}\), was found to be approximately 4 to 5 s\(^{-1}\). The resin with the higher molecular weight had the lower critical EVG. An EVG, during extrusion, less than the critical EVG resulted in ductile extrudates, which could be cold drawn up to 740 % without fracture. These extrudates showed no evidence of chain extended crystallization when subjected to DSC analysis. An EVG that was greater than the critical EVG, produced extrudates with an elongation to fracture which was always less than 100 %. Specimens produced at an EVG greater than the critical value contained chain extended material, as evidenced by a second endotherm at about 152 °C.

The ductility of the extrudates was improved by raising the die temperature during extrusion. The limits of the die temperatures were constrained to approximately 140-160 °C. At the lower end of the temperature range, self blocking occurred; at the upper end of the temperature range, cyclic melt fracture and poor surfaces were observed.
W. Hoogsteen, R.J. Van der Hooft, A.R. Postema, G. Ten Brinke and A.J. Pennings [97] found that high deformation rates during spinning introduced defects into the gel-spun polyethylene fibres. These spinning defects limited the tensile properties after hot drawing of the gel-spun fibres. If the spinning conditions were severe enough to induce a shish-kebab structure, the elongational stresses were high enough to introduce defects into the gel. Lower deformation rates and higher spinning temperatures permitted the transient entanglement networks, formed during spinning, to slip. Potential defects, such as chain scission and tight knots, were reduced by the entanglement slip process.

In the case of VHMWPE melt extrusion, deformation rates greater than the critical EVG, and low temperature extrusion, did not permit sufficient relaxation to occur for defect removal. Once cooled, the extrudate contained trapped defects. These defects permitted extrudate rupture at small strains. For extrusion carried out at higher temperatures and at a sub-critical EVG, fewer defects were trapped, which consequently allowed much higher strains before rupture. The molecular weight of the resin would be expected to be important. Lower molecular weight resins relaxed at a more rapid rate than higher molecular weight resins. Faster relaxation resulted in a greater rate of defect removal. This was evident in comparison of the critical EVG of the VHMWPE resins tested. The higher molecular weight, Hizex MIL145M resin, had a critical EVG of less than 1.3 s\(^{-1}\), while Hoechst GX-573-L resin, with a lower molecular weight, had a critical EVG of less than 5 s\(^{-1}\).
It was shown experimentally that the capillary length was an important factor to be considered when designing dies to produce ductile extrudates. If the capillary was short, relaxation would start to occur at the exit to the capillary, but the extrudate exhibited mild melt fracture and poor dimensional control (i.e. surface flaws). These surface flaws may have propagated during the tensile tests and limited the ductility of the extrudate. When the die land was long, some of the structure and the defects introduced by elongational stresses in the converging zone of the die were trapped during the passage through the cool capillary. This left defects in the extrudate which imparted reduced drawing ability. It was apparent that the die-land length must be optimized for each polymer being extruded.

In-line annealing of the extrudate, immediately after exiting the die, had also been found effective for removing undesirable extrudate structure and defects. Although the annealing did not increase the temperature of the extrudate, it allowed an additional 10s before cooling started. This period of time at a temperature above the melting point coupled with the lack of constraint upon the extrudate, enhanced the relaxation and defect removal. In-line annealing has shown the potential for ductile VHMWPE extrudates when used with a properly designed and operated die.

4.4.6 Conclusions

Elongational Velocity Gradient and Processing Conditions

The magnitude of the EVG, along with die temperature, determined the structure and properties of the VHMWPE extrudates. The study established that a critical
EVG appeared to exist for the extrusion of ductile VHMW polyethylenes. If severe extrusion conditions (ie. large die semi-angle, high extrusion ratio or extensive throughput) imposed an EVG greater than the critical EVG, then the extrudates formed were not ductile in tension. The morphology of these extrudates was mostly lamellar crystals with a small amount of chain extended material. In the case of an EVG less than the critical EVG, the extrudates were found to be highly ductile and exhibited large elongations at break. Ductile extrudates were characterized by a lamellar structure with the absence of oriented crystals. This critical EVG was different for each of the different resins and higher molecular weight probably correlated with lower critical EVG. An EVG peak of less than about 1 s⁻¹ to 4 s⁻¹ seemed to permit ductile VHMWPE extrudates.

The temperature of the die affected the ductility of extrudate. High die temperatures (ie. 160 °C) resulted in more ductile extrudates. The breakdown of lubricated flow at higher temperatures limited the upper temperature range. The length of the capillary was also found to be important for the extrusion of ductile VHMWPE. If the capillary was too short or too long, then the ductility would be reduced. The optimal capillary length must be determined by experimentation. Post extrusion annealing was found to enhance the ductility of extrudates.

**Relaxation**

Processing conditions which permitted polymer relaxation to occur during extrusion, aided in the production of ductile extrudates. The conditions required for ductile
extrudates were low EVG, high extrudate temperature, post extrusion annealing and lower molecular weight. All of these conditions promoted more rapid relaxation of the polymer chains and consequently more rapid defect removal. These ductile extrudates could be melt-drawn to higher strength and modulus in a secondary processing step.

4.5 Second Study of Elongational Velocity Gradient

4.5.1 Introduction

Conventional conical dies were relatively easy to construct, but the elongational velocity gradient varied greatly in the passage from entrance to the exit of the nozzle as was presented in 4.4.2. The previous work had also shown that the ductility of VHMWPE extrudates appeared to greatly increase at low values of maximum EVG. Due to the limited evidence which suggested a link between EVG and ductility, it was felt that more work was required to establish whether this relationship was valid.

An extrusion nozzle was designed to maintain the EVG at a low approximately constant value in the converging region of the die. In addition, a larger extrudate diameter than the previous dies was required for subsequent melt-drawing experiments\textsuperscript{10}. The constant EVG die was designed to operate at a low EVG of about 0.1 s\textsuperscript{-1} with

\textsuperscript{10} Melt-drawing is not discussed in this thesis.
the extruder operating at 4 rpm. Figure 4-31 illustrates a schematic diagram of a constant EVG nozzle. The EVG in this type of die was only a function of the flow rate, Q, in the nozzle.

![Schematic diagram of a constant elongational velocity die.](image)

Dies in which the EVG remains constant during the flow through the nozzle are not new and are not just of interest to polymer processors. LaNieve [98] patented a constant elongational strain rate nozzle for the extrusion of polymers with a constant maximum strain rate. Everage and Ballman [99] constructed an extensional flow capillary rheometer in which the flow channel was machined to provide a constant EVG when a lubricant was present in the nozzle. Ihm and Cuculo [100] designed a "psuedohyperbolic" nozzle. In this design, the EVG was initially large at the entrance to the nozzle and maintained at a minimum near the exit. This die was designed for
maximum chain ordering potential during extrusion. Gunasekera et al [101] presented a theory and FEM justification for metal extrusion through controlled-strain-rate dies. James [102] used a constant EVG nozzle in a program to measure the elasticity of non-Newtonian fluids in extensional flow. No literature and patents discussed the use of these dies for the extrusion of higher molecular weight polyethylenes.

The objectives for this section were to:

1. confirm if low values of EVG (ie. EVG of about 0.1 s\(^{-1}\)) enabled the extrusion of ductile extrudates which could be melt drawn.

2. determine the effect of low constant EVG upon extrudate melt-drawing properties of Hizex MIL145M.

4.5.2 Experimental

4.5.2.1 Constant EVG Die Design

The nozzle design was based upon lubricated plug flow of the polymer. Surface friction did not cause appreciable shear of the melt since:

1. the maximum semi-angle at the entry of the nozzle was less than 10° and most of the die length had considerably smaller converging semi-angles.

2. the melt was extremely viscous and slid on a well lubricated converging nozzle wall rather than undergo shear.
Figure 4-32 shows the ideal average velocity of the melt as it passed through the nozzle. The slope of the curve is the EVG, $dV_x / dx$, and is constant.

![Figure 4-32 Plug velocity of the melt in the die.](image)

Die Equation

It can be seen by examining Figure 4-32 that $dV_x = G dx$. After integration and applying the boundary condition that at $x = 0$, $V_x = V_{in}$ the equations is now

$$V_x = Gx + V_{in}.$$

The volumetric flow rate, $Q$, is defined as $Q = V_x \cdot A_x$ where $A_x$ is the cross-sectional area at die coordinate $x$. Then $V_x$ is given by
Substituting \( \frac{Q}{\pi R_v^2} \) for \( V_x \) into the integrated expression results in

\[
\frac{Q}{\pi R_v^2} = G x + V_{in}.
\]

After simplification, the expression for the nozzle radius as a function of the \( x \) coordinate is

\[
R_v = \left[ \frac{Q}{\pi (G x + \dot{V}_{in})} \right]^\frac{1}{2}.
\]

The die was designed to operate at a EVG of 0.1 s\(^{-1}\) at a volumetric flow rate of 1.1 \( \times 10^{-7} \) m\(^3\) s\(^{-1}\). The extrusion ratio was approximately 5 with exit radius of 2.22 mm. The nozzle length was 57.2 mm. The constant EVG die contour and EVG are shown as functions of the \( x \) coordinate in Figure 4-33. The figure shows that the EVG is zero in the pre-nozzle region. When the melt enters the nozzle, the EVG rapidly attains a value of 0.1 s\(^{-1}\). After exiting the nozzle the EVG drops to zero.
Die Construction

The die was fabricated by Flamborough Tool and Mould from D2 tool steel. The die-blank was rough formed then heat treated and tempered to HRC 58-62. The electrodes used for the electrodischarge machining were turned and polished on a screw-machine lathe to the dimensions shown in Figure 4-33. The internal channel of the die was electrodischarge machined and electropolished.

Figure 4-33  The die radius and EVG as functions of the x coordinate.
4.5.2.2 Die Experiments

Materials

The resin used for these experiments was Hizex MIL145M blended with ACuflow at a concentration of 2.5% by weight.

Apparatus

A 19 mm fully grooved extruder with an L/D ratio of 25:1 was used for the extrusion experiments. The die used for this work was the approximately constant EVG with a 5:1 extrusion ratio.

Method

Extrusion was carried in the same manner as the previous experiments. The equipment temperatures are given in Table 4-3, but the die was set to 160 °C. The screw speed was 4 rpm. The resulting extrudates were examined for melt fracture. Mechanical testing of the extrudates consisted of elongation to fracture and melt-drawing.

4.5.3 Discussion and Results

It was immediately apparent that high quality Hizex MIL145M extrudates could be formed without difficulty at a die temperature of 160 °C. Extrudates formed with the constant EVG nozzle had smooth surfaces and uniform diameters with the general absence of visual flaws, as is shown in Figure A-2 of the appendix.
The elongation to fracture for these specimens was approximately 500 % when tested to the ASTM D638 specification. This was less than expected when compared to some of the specimens prepared with the conical dies, but the larger diameter is known to reduce strength of a fibre [103] and subsequently the elongation to fracture. Melt-drawing experiments found that these extrudates could be drawn to very high draw ratios at a temperature of 135 ºC. In a series of melt drawing experiments conducted at constant wind-up speed, the draw ratio varied from 35 for a draw speed of 2.4 m min\(^{-1}\) to 235 for a draw speed of 0.3 m min\(^{-1}\).

Direct comparison of extrudate properties prepared with the constant EVG die and with the smaller diameter conical dies are difficult. The conical dies had served their purpose in elucidating the role of EVG on ductility and were subsequently abandoned. Since the conical dies were not drilled to the same diameter and extrusion ratio as the constant EVG die, clear comparisons were not possible. Table 4-6 shows a comparison of elongation to fracture for the two types of die.
<table>
<thead>
<tr>
<th>Die Type</th>
<th>Constant EVG</th>
<th>Conical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Converging Semi-angle (°)</td>
<td>Continuously varying from 10° to less than 1°</td>
<td>Fixed at 5°</td>
</tr>
<tr>
<td>Exit Diameter (mm)</td>
<td>4.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Extrusion Ratio</td>
<td>4.7</td>
<td>9.2</td>
</tr>
<tr>
<td>Capillary L/D Ratios</td>
<td>0</td>
<td>6</td>
</tr>
<tr>
<td>Die Temperature (°C)</td>
<td>160</td>
<td>155</td>
</tr>
<tr>
<td>Room Temperature</td>
<td>Approx. 500</td>
<td>Approx. 300</td>
</tr>
<tr>
<td>Elongation to Fracture (%)</td>
<td>From 35 to 235 depending upon draw speed</td>
<td>Hand drawn to 30 after annealing</td>
</tr>
</tbody>
</table>

Table 4-6 Comparison of Elongation to Fracture for Constant EVG Die and Conical Die
4.5.4 Conclusions

A low elongational velocity gradient (ie. in the region of 0.1 s⁻¹) imposed upon the polymer during processing enabled the extrusion of very ductile Hizex MIL145M extrudates which can be readily melt-drawn. These extrudates could be cold drawn to draw ratios of about 6 (ie. 500 % elongation) and melt-drawn to draw ratios of up to 235.
5 Extrusion-Orientation of Higher Molecular Weight Polyethylene

5.1 Introduction

It is now possible to consistently extrude higher molecular weight polyethylenes. These resins, with greater relaxation times, were considered prime candidates for extrusion-orientation. The objective of this section was to develop a methodology to extrusion-orient higher molecular weight polyethylenes and thus increase the strength and modulus of the extruded profiles. The extrusion-orientation was to be achieved in a unified process; the melt was to be oriented and crystallized during the passage through the die. This method was in contrast to the extrusion of an unoriented extrudate which was oriented by drawing in a subsequent process. The amount of orientation imparted to the extrudate would be determined by the extrusion ratio of the die and the amount of orientation lost during cooling by relaxation of the polymer chains.

Extrusion-orientation was thought to be achievable by controlling the flow conditions using a controlled elongational velocity gradient nozzle. The nozzle would be operated at lower than normal temperatures to induce crystallization while the polymer passed through the die. The amount of orientation, as measured by the molecular draw ratio, would be primarily determined by the extrusion ratio of the die (the extrusion ratio of the die for these experiments was 5.0) and relaxation. The elongational velocity gradient, established by the die contour and volumetric flow rate, must be large enough to extend the polymer chains, yet small enough to prevent elongational melt fracture. Plug flow, of the melt in the die, would be promoted using external lubrication of the molten polymer.
Stick-slip melt fracture, generally a problem in a cold die, would be prevented by this external lubrication. Lower extrusion pressures and reduced conformational relaxation of the polymer chains would be realized by extracting the crystallized profile using a haul-off device. Although the removal of the crystallized extrudate from the die would require large tensile forces, little or no draw-down was desired in this step.

5.2 Experimental

Polyethylene Resins

The polyethylene resins used in these experiments ranged in molecular weight from 0.5 Mg mol\(^{-1}\) (high molecular weight) to 5.75 Mg mol\(^{-1}\) (ultra high molecular weight). Table 5-1 lists the resins extruded successfully.
Table 5-1 Polyethylene resins utilized for unified extrusion-orientation.

<table>
<thead>
<tr>
<th>Manufacturer</th>
<th>Identification</th>
<th>Approximate MW (Mg mol⁻¹)</th>
<th>Method of estimating MW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dow</td>
<td>62013</td>
<td>0.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Hoechst</td>
<td>GM 6255</td>
<td>0.5</td>
<td>N/A</td>
</tr>
<tr>
<td>Mitsui</td>
<td>HIZEX MIL145M</td>
<td>1.0</td>
<td>N/A</td>
</tr>
<tr>
<td>DSM</td>
<td>Stamylan UH210</td>
<td>1.7</td>
<td>Flow value of 0.23 N/mm²</td>
</tr>
<tr>
<td>DSM</td>
<td>Stamylan UH410</td>
<td>2.5</td>
<td>Flow value of 0.36 N/mm²</td>
</tr>
<tr>
<td>Himont</td>
<td>LF00459</td>
<td>5.25-5.75</td>
<td>Intrinsic viscosity of 29</td>
</tr>
</tbody>
</table>

**Lubricants**

Acuflow and Dow Corning silicone fluids were used as lubricants for these experiments. The concentration of ACuflow was 2.5 % by weight. Dow Corning 200 silicone lubricant was used at 2 to 4 % concentration by volume.

**Extrusion Line**

The apparatus used for the experimental extrusion line is shown in Figure 5-1. The extruder and the controlled EVG nozzle have been described previously. A Killion 12/2 belt puller was used as the haul off device for these experiments. The purpose of this device was to withdraw the oriented crystallized extrudates from the die and to maintain tension on the extrudate.
Figure 5-1 Unified extrusion-orientation apparatus.

Processing Procedure

The resin and a lubricant were blended and placed into the extruder hopper. The mixture was metered by a screw feeder, from the hopper, into the feed section of the extruder. The die zone temperature was set to 160 °C for start-up and then after 5 minutes of operation was reset to the lower operating temperature. The temperature of the apparatus is given in Table 5-2. The extruder was generally operated at 4 rpm although some experiments were conducted at 1 to 20 rpm. The lubricated polymer melt was pumped from the extruder into the cooler die. The crystallized extrudate was pulled
from the die by the Killion belt puller. Draw forces were not measured in this study.

<table>
<thead>
<tr>
<th>Zone</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extruder Feed-Zone</td>
<td>135</td>
</tr>
<tr>
<td>Extruder Mid-section</td>
<td>190</td>
</tr>
<tr>
<td>Extruder Exit</td>
<td>200</td>
</tr>
<tr>
<td>Die Adapter</td>
<td>200</td>
</tr>
<tr>
<td>Die</td>
<td>160-110</td>
</tr>
</tbody>
</table>

Analysis of the extrudates consisted of 1) shrinkage tests to determine the molecular draw ratio imparted during extrusion-orientation, 2) tensile tests to evaluate changes in strength, stiffness and ductility as a result of processing and 3) differential scanning calorimetry to establish the structural changes that occurred during extrusion-orientation.

5.3 Results and Discussion

5.3.1 General

Extrusion at die temperatures low enough to solidify the melt was impractical without drawing since the pressure in the extruder would rapidly increase to the shutdown limit of 70 MPa (10,000 psi). The tensile strength of the extrudate limited the amount
of pull used to extract the extrudate from the die.

Figure A-3 of the appendix shows a typical extrusion-oriented specimen. The specimen had a smooth surface, uniform diameter and was free of visible defects. The specimen was not opaque, but showed some translucence.

The extrudate had a thick crystallized surface layer or was crystallized throughout at die temperatures about 140 °C or less. Very little draw-down of the solidified extrudate occurred between the die exit and the belt puller. Typical draw ratios for this zone were less than 1.2:1 for Hizex MIL145M at a die temperature of 155 °C or as little as 1.03:1 for Stamylin UH210 at a die temperature of 120 °C.

Experiments established that it was possible to extrude with drawing all of the resins contained in Table 5-1 using ACuflow and Dow Corning 200 silicone fluid as lubricants. It was further possible to extrude Himont LF00459 resin at a screw speed of 20 rpm (EVG of about 0.5 s\(^{-1}\)) and draw speed of 1.8 m min\(^{-1}\) when Dow Corning 200 silicone fluid was employed.

Figure 5-2 shows that the die pressure for the extrusion-orientation of Hizex MIL145M increased with die temperatures less than 150 °C, for a constant draw rate of 0.43 m min\(^{-1}\). The EVG was about 0.1 s\(^{-1}\). Temperatures lower than 120 °C proved to be impossible at a draw speed of 0.43 m min\(^{-1}\) because of extrudate fracture.
Figure 5-2 Extrusion die pressure versus the extrusion die temperature for Hizex MIL145M resin. The die had an approximately constant EVG and an extrusion ratio of about 5:1. The screw speed was 4 rpm with a puller draw speed of 0.43 m min⁻¹.

Figure 5-3 illustrates the effect of the draw speed upon extrusion die pressure for a constant screw speed of 4 rpm. The EVG was about 0.1 s⁻¹. As the draw speed (and draw stress) was increased, the extrusion pressure was reduced for Himont LF00459. For draw speeds greater than 0.41 m min⁻¹, it was possible to reduce the die pressure to near zero, just prior to the extrudate fracture.
Figure 5-3 Extrusion die pressure versus the draw speed for Himont LF00459 resin. The die had an extrusion ratio of about 5:1. The screw speed was 4 rpm with a die temperature of 155 °C.

Experimentation has established that die temperature, screw speed and puller speed were the principle variables for extrusion-orientation with the constant EVG die employed in this study. The contours of the die dictated the magnitude of deformation that arose during extrusion-orientation. The extrusion pressure and draw stress worked together to determine the rate at which deformation occurred. If the
extrudate was not drawn from the die (temperatures less than 140 °C), the pressure climbed to 70 MP which forced immediate shutdown. At draw rates greater than about 0.4 m min⁻¹ and low screw speeds of 4 rpm, die pressure dropped to near zero. The draw rate, extruder screw speed and die temperature must be coordinated for higher throughput.

5.3.2 Molecular Draw Ratio

The molecular draw ratio (MDR) was used to determine the orientation efficiency of the extrusion-orientation process. The MDR provided a quantitative measure of the amount of molecular extension produced and retained during processing. For example, if a specimen was homogeneously deformed to a draw ratio of 5, then the ideal molecular draw would be also be 5. In reality, the molecular draw ratio was less than the geometric draw ratio because of disorientation (ie. relaxation) which occurred during processing and cooling.

The MDR was experimentally determined by shrinkage tests, which involved heating the unconstrained extrudate to 160 °C for 15 minutes. Once an oriented extrudate was molten, the entropic forces would cause the oriented chains to return to the unoriented state. This transition was manifested by contraction along the machine direction and dilation in the transverse direction. The specimens were cut to 200 mm. The MDR was calculated from the relationship lo/l where lo was the machine direction length of the extrudate before heating and l was this length after heating. Surface
energy did not appear to have a significant role in the shrinkage experiments. This was evidenced by the specimens remaining cylindrical and not becoming spherical as would be demanded by significant surface tensions.

The molecular draw ratio was found to be a strong function of the die temperature during the unified extrusion-orientation process. Figure 5-4 shows that the MDR decreases in a linear manner with increasing extrusion die temperature. The goodness of fit (ie. $R^2$) was 0.976.

The geometric draw ratio and the MDR were almost identical for the Hizex MIL145M at low die temperatures. For example, extrusion at a die temperature of 115 °C produced an extrudate that was drawn about 1.14 times while in the region between the die and the puller. The total draw ratio of the polymer, both in the die and the post die region, was approximately 5.7 (ie. 5 x 1.14). The experimental MDR, established by shrinkage tests, was about 5.4. As can be seen, the MDR from shrinkage tests and the geometric draw ratio for extrusion-orientation process were more or less equivalent at low die temperatures.
The effect of extrusion die temperature upon the MDR of HIZEX MIL145M. The extruder circumferential speed was 4 rpm with EVG was about 0.1 s\(^{-1}\). The draw speed was 0.43 m/min. The die had an extrusion ratio of approximately 5. The draw ratio between the die exit and the puller was in the order of 1.1 - 1.2. Under these conditions the maximum possible draw ratio was about 5.5 - 6.0.
The MDR-die temperature relationship established for Hizex MIL145 holds for the DSM UH210 and 410 resins. Figure 5-5 shows that the MDR of the extrudates prepared by extrusion-orientation of the DSM resins was comparable in magnitude to the geometric draw ratio. These resins were deformed very little by drawing between the die and the puller since the local draw ratio was only 1.03. For an extrusion temperature of 125 °C, the MDR was 5.2 compared to a maximum possible geometric draw ratio of approximately 5.2. This indicates that orientation generated in the die was conserved during the cooling of this resin. It is interesting to note that these higher molecular weight resins exhibited less draw-down in the region between the die and the puller than the Hizex MIL145M.
The effect of extrusion die temperature upon the MDR of DSM UH210 and UH410 resins. The draw speed was 0.43 m/min. The extruder circumferential speed was 4 rpm. The die had an extrusion ratio of approximately 5. The draw ratio between the die exit and the puller was about 1.03. Under these conditions the maximum possible draw ratio was about 5.2.
Extrusion-orientation experiments conducted with Himont LF00459 have found a MDR of 5.1 for a geometry in which the theoretical draw ratio was 5.2. This experiment was conducted at 130 °C. Similar results were found for the Dow 62013 and GM6255 resins. These resins were extrusion-oriented at die temperatures of 115 to 130 °C and were found to have MDR of 5.0 for geometric draw ratio of approximately 5.2.

The results of these experiments have shown that the MDR, found by shrinkage tests, and the theoretical draw ratio, determined from die geometry, were almost equivalent. It was reasonable to presume that molecular orientation was imparted to the extrudates by the processing operation, although DSC analysis and tensile properties of the extrudate must first be used to confirm this assumption.

It appears that extrusion-orientation of thicker sections was possible with higher molecular weight resins. Disorientation occurs more rapidly in the melt for conventional lower molecular weight resins. As a consequence, it was more difficult to maintain orientation for these conventional resins during conventional processing. On the other hand, the disorientation of the higher molecular weight resins appeared to be slow enough that orientation can be trapped by crystallization. The consequence of slow relaxation of higher molecular weight resin has shown the possibility of a new polymer processing technology involving commercial extrusion-orientation.
5.3.3 Tensile Properties

The unified extrusion-orientation process was found to increase the tensile strength and tensile modulus of the extrudates. The amount of improvement in the tensile properties was a strong function of extrusion die temperature. Figure 5-6 shows the effect of die temperature on the ultimate tensile strength (UTS) of HIZEX MIL145M. The tensile strength was seen to increase with decreasing die temperature. The data has been fitted to straight line with a goodness of fit of 0.960.
Figure 5-6. The effect of extrusion die temperature upon the tensile strength of HIZEX MIL145M. The draw speed was 0.43 m/min. The extruder circumferential speed was 4 rpm. The die had an extrusion ratio of approximately 5. The draw ratio between the die exit and the puller was in the order of 1.1 - 1.2. Under these conditions the maximum possible draw ratio was about 5.5 - 6.0.
Figure 5-7 displays the relationship between the extrusion die temperature and Young's modulus of HIZEX MIL145M. The figure clearly established that the tensile modulus of the polymer was improved with decreasing die temperature. Linear least square regression analysis showed a goodness of fit of 0.784. The scatter of this data may be a result of the difficulty of gripping the heavy, 4.6 mm diameter, extrudates in the flat tensile testing machine jaws. (Rod grips were unavailable and adapters were found to be ineffective.)
Figure 5-7. The effect of extrusion die temperature upon the Young's modulus of HIZEX MIL145M. The draw speed was 0.43 m/min. The extruder circumferential speed was 4 rpm. The die had an extrusion ratio of approximately 5. The draw ratio between the die exit and the puller was in the order of 1.1 - 1.2. Under these conditions the maximum possible draw ratio was about 5.5 - 6.0.

Figure 5-8 exhibits the relationship between the elongation to break and the extrusion die temperature. At the low end of the temperature range (ie. less than 140 °C) the ductility was limited; the elongation to fracture of the extrudates was about 5 - 13 percent. The ductility at the high end of the range (ie. 160 °C) was greater than 150
percent. No fracture was observed for the extrudates at 160 °C as the specimens were pulled to the maximum available extension of the tensile test machine at room temperature.

Figure 5-8. The effect of extrusion die temperature upon the elongation to fracture of HIZEX MIL145M for specimens tested at 23 °C. The extruder circumferential speed was 4 rpm. The draw speed was 0.43 m/min. The die had an extrusion ratio of approximately 5. The draw ratio between the die exit and the puller was in the order of 1.1 - 1.2. Under these conditions the maximum possible draw ratio was about 5.5 - 6.0.
The increase in strength and modulus, coupled to the decrease in ductility with lower
die temperatures, was probably a result of flow induced chain orientation that was
more effectively arrested by cooler dies. Strengths and modulus were increased by
about 3.5 times using the extrusion-orientation process.

5.3.4 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was used to detect the presence of oriented
crystals in the extrudate. Oriented extended chain specimens have been found to
melt at higher than normal melting points [104] (ie. superheat). The DSC analysis
was carried out on a Du Pont model 2000 differential scanning calorimeter. The heating rate for all tests was 10 °C/min. The specimens were placed into aluminum DSC pans and the lids were fitted and crimped into place. No attempt was made to
restrain the polymers using excessive clamping force or epoxy encapsulation.

Table 5-3 shows that the extrusion-oriented polymers have the ability to be super-
heated. The heat of fusion was also increased by extrusion-orientation. These results
indicate that chain extended crystals were formed in this process.
Table 5-3  DSC data collected for DSM UH210 resin both in the annealed state and after extrusion at various temperatures.

<table>
<thead>
<tr>
<th>Extrusion Temperature (°C)</th>
<th>Melting Point (°C)</th>
<th>Superheat (°C)</th>
<th>Heat of Fusion (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed</td>
<td>132.4</td>
<td>0.0</td>
<td>92.2</td>
</tr>
<tr>
<td>150</td>
<td>133.6</td>
<td>1.2</td>
<td>95.3</td>
</tr>
<tr>
<td>140</td>
<td>134.3</td>
<td>1.9</td>
<td>156.6</td>
</tr>
<tr>
<td>130</td>
<td>133.9</td>
<td>1.5</td>
<td>141.1</td>
</tr>
<tr>
<td>125</td>
<td>133.2</td>
<td>0.8</td>
<td>142.8</td>
</tr>
<tr>
<td>120</td>
<td>135.7</td>
<td>3.3</td>
<td>130.8</td>
</tr>
</tbody>
</table>

Some of the thermal data, from the DSC study, shown in Table 5-3 may be inexact because of the nature of the oriented specimens. The oriented specimens were found to relax and shift in the DSC pans during heating. On many occasions, the lid of the pan was lifted by the entropic retraction forces. If the specimens do not remain in contact with the pan walls, heat transfer between the specimen and the apparatus was altered which resulted in less accurate data. However, the data clearly showed that the extrudates could be superheated and required more heat energy to melt.
It was unquestionably shown that the specimens produced by the unified extrusion-orientation experiments could be superheated from 1 to 3 °C and had a higher heat of fusion. This indicated the presence of oriented crystals in the extrusion-oriented specimens.

5.4 Conclusions

1. Higher molecular weight polyethylenes (0.5 - 5.75 Mg mol⁻¹) can be extrusion-oriented to near the full extent of the die geometry. The MDR of the extrusion-oriented extrudates was virtually the same as the geometric draw ratio for the die and puller combination. Molecular draw ratios of approximately 5 were achieved for extrusion-oriented profiles using a constant EVG die with an extrusion ratio of 5. DSC analysis of the extrusion-oriented extrudates established a 1 to 3 °C superheat and a higher heat of fusion. These data indicated that oriented extended chain crystals were present in the extrudate.

2. Low elongational velocity gradients (0.05 to 0.5 s⁻¹) and externally lubricated melts prevented stick-slip and gross melt fracture for the extrusion-orientation of the higher molecular weight polyethylene resins. Extrudates formed by the unified process, were smooth and sound without any obvious melt fracture.

3. The tensile strength and tensile modulus can be significantly improved by unified extrusion-orientation.
4. Most of the orientation was achieved in the die, since the draw ratio in region between the puller and die was in the region of 1.03 to 1.14 at low die temperatures.
6 Discussion

6.1 Introduction

Rauwendaal [105] stated that ultra high molecular weight polyethylene is not considered to be melt processable by conventional melt processing machines. Waddon and Keller [106] expressed the view that high molecular weight polyethylenes (> 0.4 Mg mol⁻¹) are unprocessable at conventional temperatures (> 160 °C) and at practical extrusion rates (> 1 cm min⁻¹). Waddon et Keller further stated that a narrow temperature window (150-152 °C) exists with minimal flow viscosity which is relevant to the process of melt extrusion. Narh and Keller [107] reiterated that ultra high molecular weight polyethylene is known to be unextrudable for conventional capillary extrusion. Narh and Keller found that UHMWPE dissolved in a solvent to form a gel and then dried could be profitably employed in studies of the newly discovered temperature window for melt processing. In their paper Narh et al attributed pressure oscillations, above the temperature window, not to stick-slip, but to elastic turbulence.

In this thesis, it has been shown that melt extrusion of higher molecular weight polyethylenes (0.5 Mg mol⁻¹ to 6 Mg mol⁻¹) was indeed possible in the temperature range of 120 to 160 °C at rates as high as 180 cm min⁻¹ using conventional melt processing apparatus. The ability to melt process higher molecular weight polyethylenes with conventional equipment depends upon the prevention of melt fracture. Cyclic melt fracture was eliminated using lubricated extrusion techniques and gross melt fracture was eliminated by controlling the elongational velocity gradient (i.e. the strain rate).
6.2 A Strain-Rate Window for Extrudability of Higher Molecular Weight Polyethylene

The magnitude of the strain rate (ie. elongational velocity gradient) determined the presence of gross melt fracture. This thesis found that constant strain rates in the region of 0.05 s$^{-1}$ to 0.5 s$^{-1}$ permitted smooth extrusion without gross melt fracture, at temperatures of 120 °C to 160 °C, for resins with molecular weight of 0.5 Mg mol$^{-1}$ to 6.0 Mg mol$^{-1}$, assuming lubrication was present to overcome cyclic melt fracture.

The magnitude of the strain rate is divisible into three broad ranges. 1) The relaxation strain rate, $\epsilon_r$, is a strain rate for which the rate of relaxation is greater than or equal to the rate of orientation. These slow strain rates allow sufficient time for entanglements to slip rather than form temporary crosslinks. The stresses required for the low strain rates are small enough that defects are not introduced into the polymer during extrusion. 2) The fracture strain rate, $\dot{\epsilon}_f$, is a strain rate which induces stresses large enough to fracture the specimen or cause elastic flow instabilities. 3) The orientation strain rate, $\epsilon_o$, can be considered any strain rate which lies between the fracture strain rate and the relaxation strain rate. A characteristic of this strain rate is that the rate of orientation is greater than the rate of disorientation and orientation of the extrudate will increase with strain.
Dealy and Wissbrun [108] stated the conditions necessary to ensure that tensile stresses do not build up during flow of a viscoelastic fluid through a converging nozzle are given by

\[ \tau \frac{dV}{dz} \ll 1 \]

where \( \tau \) is the relaxation time of the fluid and \( \frac{dV}{dz} \) the average axial velocity gradient.\(^1\)

In a similar manner, the relaxation strain rate and the relaxation time can also be related by

\[ \epsilon_r \ll \frac{1}{\tau}. \]

Figure 6-1 schematically depicts the relationship between the fracture strain rate and the relaxation strain rate for a small temperature region. At an arbitrary temperature \( T_1 \), any point on the vertical line, between the fracture strain rate and the relaxation strain rate, permits the polymer to orient. Two opposing processes occur during straining. Hydrodynamic orientation occurs at some rate proportional to strain rate. The opposing disorientation is a function of temperature and will occur at approximately the same rate for all straining rates. For a strain rate which is just greater than the relaxation strain rate, the maximum orientation of the polymer requires very large strains. At a strain rate

\(^1\) The product of the velocity gradient and the relaxation time is a dimensionless Deborah number. The Deborah number gives a measure of the extent to which elasticity plays a role in the motion of the fluid.
just less than the fracture strain rate, the maximum orientation of the polymer will be accumulated at a relatively low strain. Strain hardening effects (ie. strain crystallization) are ignored in this figure.

Figure 6-1 A schematic graph which shows the fracture strain rate and the relaxation strain rates as a function of polymer temperature. The graph depicts a temperature region in which the polymer can be oriented by elongational flow.
Figure 6-2 introduces the complication of strain hardening. The figure shows two surfaces contained in space bounded by the temperature, strain rate and strain axes. The relaxation surface, $\varepsilon$, in Figure 6-2 is essentially parallel to the strain axis and indicates that strain has no effect on the relaxation process. The underlying reason is that if the relaxation strain rate is slow enough, any structure developed from straining has sufficient time to disorient. As a result, no new structure is developed. Figure 6-2 also shows the fracture strain rate surface, $\dot{\varepsilon}_f$. This surface is not parallel to the strain axis and shows a decrease in strain rate with increasing strain. As the polymer is strained, orientation is developed. This oriented material is more structurally perfect and crystallizes in the fluid. Consequently the fluid stiffens (i.e. strain hardening occurs). The new oriented structure that is developing has less ability to be deformed rapidly and as such, the fracture strain rate is reduced with strain.
Figure 6-2 A schematic graph which depicts the fracture strain rate surface and the relaxation strain rate surface as functions of polymer temperature and strain. The graph illustrates a temperature region in which the polymer can be oriented by elongational flow.

A constant orientation strain rate of about 0.05 s\(^{-1}\) to 0.5 s\(^{-1}\) seemed to apply to the polyethylene resins with molecular weight of 0.5 Mg mol\(^{-1}\) to 6 Mg mol\(^{-1}\) at die temperatures of about 120 to 160 °C. The relaxation strain rate for higher molecular weight polyethylenes appeared to be too small for realization at practical extrusion rates and temperatures. All experiments with these resins attained some orientation as demonstrated by the molecular draw ratio of the extrudates. The molecular draw ratio of Hizex
MIL145M was about 3 for free extrusion into still room temperature air at an EVG of 0.1 s\(^{-1}\) and a die temperature of 160 °C. The ductility of the extrudate was observed to drop at instantaneous strain rates 2 s\(^{-1}\) to 5 s\(^{-1}\). Strain rates greater than about 5 s\(^{-1}\) resulted in gross melt fracture.

Figure 6-2 shows that a constant strain rate may not be ideal to orient a polymer if a large extrusion ratio is desired. If the fracture surface is known, then it would be advantageous to control the die contours, such that, the polymer is subjected to strain rates slightly less than the fracture strain rate at all strains.
7 Summary

The primary objective of this work was to develop a better understanding of the extrusion-orientation of polymers. The literature search had revealed that extrusion-orientation was frequently unsuccessful because of remelting and relaxation of the extrudate during processing. This first attempt at solving this problem was to elevate the melting point by ordering the chains of a polypropylene melt by elongational flow and then cooling. The second attempt involved the use of higher molecular weight polyethylene resins, with longer relaxation times, which ultimately proved to be successful.

A streamlined die, with extrusion ratio of 92:1, was designed for polypropylene, using the finite element method, to determine the natural streamline for flow. This die was found to be unsuitable for extrusion-orientation as the elongational velocity gradient was too severe for the melt and severe melt fracture resulted. This preliminary work suggested that resins with longer relaxation times may permit extrusion-orientation. This first study also established that systematic research of die design, lubrication and extensional flow behaviour were required to meet the primary objective of developing extrusion-orientation process.

Higher molecular weight polyethylenes, with the potential for longer relaxation times, were chosen for the extrusion-orientation experiments. Cyclic and gross melt fracture proved to be the problems that needed resolution during the extrusion of these less tractable resins. External lubrication was found to reduce or eliminate the cyclic melt fracture. Gross melt
fracture was forestalled by limiting the magnitude of the elongational velocity gradient during passage of the melt through the die convergence. Once the role of lubricant and elongational velocity gradient were understood, the extrusion of higher molecular weight polyethylene resins was easily accomplished.

Successful extrusion-orientation experiments were now possible with the higher molecular weight resins. A unified process in which the melt was oriented and crystallized in the die was developed. This procedure was found to increase the molecular draw ratio in the extrudate to near the geometric maximum for the die-puller combination. The tensile strength, tensile modulus and the DSC melting point of the polyethylene were increased by this process.
8 Conclusions

Extrusion of Higher Molecular Weight Resins

This thesis has proven, contrary to conventional wisdom, that higher molecular weight polyethylene resins, in the range of 0.5 Mg mol\(^{-1}\) to 6 Mg mol\(^{-1}\), can be readily screw extruded with commercial extrusion equipment. The solution of the extrusion problem was the prevention of melt fractures and this was accomplished in two ways. 1) External lubrication was used as a barrier to inhibit periodic attachment and detachment of the melt to the die walls which resulted in cyclic pressure variations and cyclic melt fracture. 2) Controlling the elongational strain rate to constant values less than 0.5 s\(^{-1}\) suppressed gross melt fracture in the converging zone of the die.

External lubrication of the higher molecular weight polyethylene resins resulted in plug flow in the capillary and probably in low angle converging dies.

Extrusion of smooth, sound extrudates, at rates as great as 1.8 m min\(^{-1}\), were successfully extruded through an approximately constant EVG nozzle. This die was designed to operate at a constant EVG of 0.1 s\(^{-1}\) for a flow rate of 1.1 \(\times\) 10\(^{-7}\) m\(^3\) s\(^{-1}\).

Lubricated melts were difficult to screw process, because of slippage in a smooth barrel extruder. Slippage in the extruder barrel resulted in a reduction of melting and pumping efficiency. Commercial lubricants have been formulated to partially overcome this problem, but are expensive and difficult to synthesize. This thesis found that full grooving of the barrel permitted easy melting and pumping of higher molecular weight resins that have been mixed
with an incompatible lubricant.

**Extrusion of Ductile Extrudates**

Hizex MIL145M, when extruded at a constant EVG of about 0.1 s⁻¹ and at a die temperature of 160 °C, was found to be highly ductile. These extrudates could be drawn at room temperature to draw ratios of approximately 6. Melt drawing at 135 °C resulted in draw ratios of as high as 235. These extrudates could be cold or warm drawn to higher strengths and modulus in secondary processing.

Ductile extrudates had a single endotherm when subjected to DSC analysis and are believed to be essentially lamellar crystals. Evidence of a second endotherm, at about 152 °C, indicated the presence of oriented chain extended crystals which substantially reduced the cold drawability.

**Extrusion-Orientation of Higher Molecular Weight Resins**

Higher molecular weight polyethylenes (0.5 - 5.75 Mg mol⁻¹) can be extrusion-oriented to near the full extent of the die geometry. The molecular draw ratio of the extrusion-oriented extrudates was virtually identical to the geometric draw ratio for the die and puller combination. Molecular draw ratios of approximately 5 were achieved for extrusion-oriented profiles using an approximately constant EVG die with an extrusion ratio of 5. DSC analysis of the extrusion-oriented profiles established a 1 to 3 °C superheat and a higher heat of fusion. These data indicated that oriented extended chain crystals were present in the extrudate.
The tensile strength and modulus were increased by a factor of about 3.5 times by the extrusion-orientation process.
9 References


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Appendix

Photographs of Specimens Prepared from Hizex MIL145M

Figure A-1 shows four specimens exhibiting extreme cyclic melt fracture. All specimens were prepared at an extruder speed of 4 rpm which corresponds to volumetric flow rate of about 1.1 x 10^-7 m^3 s^-1. The extrusion direction for these specimens is from bottom to top in the photograph.

Figure A-1. Specimens exhibiting extreme cyclic melt fracture. Figure has magnification of 1.4.
Description of Specimens in Figure A-1

The specimens are discussed in order from left to right. The first specimen was prepared with the constant EVG die (extrusion ratio of 5:1). The remainder of the specimens were prepared with the streamlined die having an extrusion ratio of 6.9:1.

1. Extrusion was carried out at a die temperature of 180 °C. The lubricant used for this specimen was ACuflow. At this higher than normal die temperature, the lubricant was largely ineffective in preventing cyclic melt fracture.

2. Extrusion took place at a die temperature of 180 °C with out using lubricant.

3. The die temperature for extrusion was 160 °C. No lubricant was used.

4. This specimen was prepared without lubricant. Extrusion was started at 180 °C. After resetting the die to 160 °C and allowing the die to cool to an intermediate temperature, this mixed type of cyclic melt fracture was observed.
Figure A-2 shows a specimen extruded with the constant EVG die at a die temperature of 160 °C. At this temperature the ACuflow is effective in preventing cyclic melt fracture. The flow rate for this specimen was $1.1 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$ which corresponded to an EVG of about 0.1 s⁻¹. The lubricant was ACuflow. This specimen had good ductility and could be melt drawn up to an extension ratio of 235.
Figure A-3 shows an extrusion-oriented specimen. The specimen was extruded at a die temperature of 120 °C using Dow Corning 200 silicone fluid as a lubricant. The constant EVG die (extrusion ratio of 5:1) was used to prepare this specimen. The molecular draw ratio was about 5.4.

Figure A-3. Extrusion-oriented extrudate. Figure has magnification of 1.4.
### Notations and Confidence Intervals

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>A</td>
<td>area</td>
</tr>
<tr>
<td>Cs</td>
<td>lubricated slip constant</td>
</tr>
<tr>
<td>D</td>
<td>diameter</td>
</tr>
<tr>
<td>DSC</td>
<td>differential scanning calorimetry</td>
</tr>
<tr>
<td>EVG</td>
<td>elongational velocity gradient</td>
</tr>
<tr>
<td>G</td>
<td>velocity gradient, free energy</td>
</tr>
<tr>
<td>h</td>
<td>heat transfer coefficient</td>
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<tr>
<td>H</td>
<td>enthalpy</td>
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<td>K</td>
<td>consistency index</td>
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<tr>
<td>L</td>
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<tr>
<td>M, MW</td>
<td>molecular weight</td>
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<tr>
<td>MDR</td>
<td>molecular draw ratio</td>
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<tr>
<td>n</td>
<td>power-law index</td>
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<tr>
<td>P, Pc</td>
<td>pressure, static pressure</td>
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<tr>
<td>Q</td>
<td>volumetric flow rate</td>
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<tr>
<td>r</td>
<td>radius</td>
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<tr>
<td>R</td>
<td>ideal gas constant</td>
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<tr>
<td>R²R₀</td>
<td>capillary radius, radius at entry to converging zone</td>
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<tr>
<td>R²</td>
<td>goodness of fit</td>
</tr>
<tr>
<td>S</td>
<td>entropy, minimum draw ratio</td>
</tr>
<tr>
<td>t</td>
<td>time, thickness of a lubricant film</td>
</tr>
<tr>
<td>T</td>
<td>temperature</td>
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<tr>
<td>Tc, Tₘ, TM</td>
<td>temperature of crystallization, effective melting point, equilibrium melting point</td>
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<tr>
<td>Tₚ, Tᵣ, Tₛ</td>
<td>temperature of fluid, reference temperature, temperature of surface</td>
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<tr>
<td>UTS</td>
<td>ultimate tensile strength</td>
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<tr>
<td>V</td>
<td>velocity</td>
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<tr>
<td>Vₐn, Vₚ, Vₛ</td>
<td>average velocity into the converging zone, plug velocity, slip velocity</td>
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#### Greek Letters

<table>
<thead>
<tr>
<th>Symbol</th>
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<tbody>
<tr>
<td>α</td>
<td>thermal diffusivity, die semi-angle</td>
</tr>
<tr>
<td>β</td>
<td>constant</td>
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<tr>
<td>ε</td>
<td>strain</td>
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<tr>
<td>ε₉, εᵣ</td>
<td>fracture strain rate, relaxation strain rate</td>
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<td>η, ηₑₐₗ₉</td>
<td>shear viscosity, elongational viscosity</td>
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<td>γ, γₑₐₗ₉</td>
<td>shear strain, rate of shear strain</td>
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<tr>
<td>ω</td>
<td>rotational frequency</td>
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</table>
Density

\( \rho \)  

\( \sigma, \sigma_u \)  
stress, wall shear stress

\( \tau \)  
relaxation time

Confidence Intervals

Error bars (confidence intervals), when included in a figure, represent limits of one standard deviation from the mean of the measurement.