ENHANCED EXTRUSION WITH
INTERNAL COOLING DIE,

A Thesis Presented to
The Faculty of the College of Engineering and Technology
Ohio University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science

by
Chadalavada Bhaskar Rao
August, 1980

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ACKNOWLEDGEMENTS

The author is most grateful to Professor John R. Collier for his guidance and counsel during the time of this study. Special thanks to Professors C. H. Baloun and C. A. Sperati for their help and valuable suggestions. The author acknowledges the National Science Foundation for supporting this study.
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CHAPTER I
INTRODUCTION

The goal of achieving the high level of mechanical properties inherent to the covalent bonds of linear polymers, first documented in 1932 (1), has received increased attention in recent years with the reduction to practice of a variety of methods for producing fibers with extraordinarily high modulus and tensile strength. It has been known for some time (2) that an ideal oriented polymer with all its molecules in the fully extended state would exhibit mechanical properties similar to those of metals or inorganic materials.

In order to produce high modulus polymers, continuity must be present along with the orientation axis, either as extended chain crystals or as stressed tie chains. But in reality, semi-crystalline polymers rarely attain even one tenth of their theoretical modulus because of dislocations such as chain folding, trapped entanglements, chain ends and twists and lack of crystalline c-axis alignment.

In practice, the polymers are not considered for load bearing material due to their relatively low modulus which is two orders of magnitude lower than steels which have modulus of around 30 X 10^6 Psi (2 X 10^{11} Dynes/Cm^2). The ultimate theoretical modulus of many crystalline polymers is on the order of 10^6 Psi (10^{11} Dynes/Cm^2), comparable to that of steel (3). Recently, P.S. Hope et al. (4) has shown that, with high modulus polymers, tubular and non-circular sections can be prepared successfully.

The studies on "Polymer Orientation" are as follows:
Pressure Bomb Crystallization (5-8)

It has been reported that extended chain crystal domains occur above a critical pressure which have higher densities and higher melting points than exhibited by the same material processed below the critical pressure.

Super Drawn Filament Process (9-10)

In this process, the polymers were drawn in two stages of drawing. The first stage involves rapid free boundary drawing of an unoriented cylindrical billet to a draw ratio of 7. In the second stage, the sample is slowly drawn at 50 percent/minute to a draw ratio of 20 which resulted to obtain very high modulus and highly oriented samples.

Radial Compression Method (11)

In this method the solid polymer cylinder is extended uniaxially under intense transverse squeezing stress. An increase of orientation and melting point was reported.

Flow Induced Crystallization (12-24)

The oriented morphologies produced by flow induced crystallization (FIC) is a fibrous structure, where both chain folded and extended chain crystals are present and are parallel to the stress direction. The crystallization time under flow is much shorter than that in quiescent melt crystallization.

Solid-State Extrusion (25-36)

Highly crystalline polymer was extruded under very high pressure near but below the melting point of the polymer. The result was high modulus, transparent and highly oriented extrudates which contained extended chain crystals.

Southern and Porter (27) obtained highly oriented samples with
high tensile strength and modulus by solid-state extrusion using pressures near 2000 atmospheres (0.2 G Pa). Though it attracted the attention of many researchers for adoption this to polymer processing, the process is not economically feasible due to its slow rate of extrusion and high pressures.

A faster extrusion technique through a conical die, so called solid-state coextrusion, has been illustrated by Griswold et al. (30) to obtain high orientation and modulus by using less pressure than solid-state extrusion.

Collier and coworkers (37-42) developed a process to obtain highly oriented and ultra-high modulus fibers by using a single screw extruder and specially designed dies. They were also able to obtain highly oriented, transparent and high modulus ribbons of Polyethylene and Polypropylene at moderate pressures. Fiber and ribbon extrudates have high degrees of orientation and elevated melting point. The above work is limited to downward extrusion into a water bath and the temperatures in the land of the die are limited. Surface defects (41) were noticed in some samples which are possibly due to bending the rigid extrudate around a sharp corner in the water bath.

Therefore, the primary goal of this work was to design a new die, with which extrusion can be done horizontally, allowing control of the temperature in the land and improving the operating conditions. The new die is designed to be used with a melt conditioner being developed by another student, but may be used without it. With the melt conditioner, 

\[ 1 \text{ G Pa} = 10^9 \text{ N/M}^2 = 10^{10} \text{ Dynes/Cm}^2 = 1.1 \times 10^4 \text{ Kg/Cm}^2 = 1.45 \times 10^5 \text{ lb./in}^2 = 0.99 \times 10^4 \text{ Atm.} \]
the residence time of conditioned melt can be increased, by which a
continuous process of highly oriented extrudates can be achieved.
Teflon solution is coated on the wall of the die in this study as in a
previous study (40) in order to reduce the frictional force exerted by
polymer melt.
CHAPTER II
LITERATURE REVIEW

The phenomenon of orientation in polymers is of great importance and can be developed in both glassy, non-crystalline polymers such as atactic polystyrene and semi-crystalline polymers such as Polypropylene and Polyethylene. However, some amorphous polymers do not gain appreciable strength by orientation, because they fail by chain separation rather than by chain scission. In these amorphous polymers, orientation does not increase the chain-to-chain bonds except for a slight increase in strength by van der walls forces due to the closer packing of the chain segments (43). On the other hand, most of the semi-crystalline polymers obtain their strength from tie molecules which connect adjacent spherulites. These tie molecules are the principal sources of the polymer's strength (44).

A spherulite may be envisaged as an isolated morphological super-structure consisting of folded chain lamella arranged radially about its center. The spherulites change from a spherical to an ellipsoidal shape (45). At higher overall deformation, however, the resultant lamellar deformation will be dependent upon the lamellar orientation with respect to the stretch direction. As the spherulites deform further, lamellae reorient themselves along the stress direction and at the yield stress, if necking occurs, the spherulitic structure is replaced by a fibril structure (fig. 1). For a stack of parallel lamellae Peterlin (46) proposed a detailed deformation mechanism (fig. 2). The rate of structural changes and the resulting mechanical properties depend upon size, perfection and organization of the crystalline and amorphous regions (47). The mechanical properties are enhanced, no matter how the
Fig. 1 Samuel's mechanism for lamellar orientation within Spherulites
a) undeformed Spherulite; (b-e) Spherulites deformation and lamellar orientation; (f) fibril formation.

Fig. 2 Formation of "skewed" microfibrils by shearing of a stack of parallel lamellae: (a) stack before shearing; (b) after shearing by one lamella thickness per block width; (c) after shearing by two lamellae thickness per block width.
extended chains are formed (25-36).

**Flow Induced Crystallization**

Flow in a macromolecular system results in orientation and deformation which, in turn, increases the crystallization rate and alters the structure from spherulite to fibrillar structure.

Pennings and Meihuizen (21) obtained a "shish-kebab" structure by allowing fibrillar polyethylene seed crystals to grow longitudinally from supercooled solutions subjected to Poiseuille flow (pipe-pressure flow) and couette flow (coaxial drag flow). They sheared a five percent polyethylene in p-xylene solution by stirring with a teflon rotor. They reported that the fiber with ultra-high modulus and strength has a "shish" which is highly c-axis oriented and parallel to the shear directions while the "kebabs" are lamellae that grow perpendicular to the fiber axis.

Keller and Machin (49) introduced a row structure model to describe the morphology of bulk polymers under stress. According to this model, fibrillar nuclei with extended chains parallel to the flow direction are formed and lamellae with folded chains are overgrown epitaxially on the fibrillar nuclei as shown in fig. 3. This so called row structure is very easily obtained even under very low deformation ratios (50).

**Pressure Bomb Crystallization**

Wunderlich and coworkers (5-8) reported that pressure will affect crystallization. They studied the pressure effect on crystallization of polyethylene up to 7000 atmospheres (0.7 G Pa). They described crystallization as a two-step process: nucleation of each crystallizing molecule to a folded chain conformation, followed by an increase in fold
Fig. 3 Row Structure Model Proposed by Keller (49)

Fig. 4 Continuous Crystal Model Proposed by Clark and Scott (9)
length in a solid-state reorganization step. The reorganization step is enhanced at higher temperature under elevated pressure (5). They observed a small increase in density and melting point for samples crystallized under 2000 atmospheres (0.2 G Pa). Electron microscope observations (6) revealed the presence of extended chain lamellae. In the pressure range of 2000-3500 atmospheres (0.2-0.35 G Pa) they observed a small increase in density and no increase in melting point. It was interpreted that the folded chain lamellae became thinner above 2000 atmospheres (0.2 G Pa) when grown from melt.

The equilibrium melting point increases almost linearly with pressure based on Parks and Richard's equation (51) and for polyethylene as shown by the following equation (8):

\[ \Delta T = T_m - T_c + 0.02 \left( ^\circ C/\text{atms.} \right) P_c \]

where \( \Delta T \) is the subcooling, \( T_m \) is the equilibrium melting point for a perfect polyethylene crystal, \( T_c \) is the crystallization temperature, and \( P_c \) is the crystallization pressure in atmospheres.

**Solid-State Extrusion**

By using an Instron Capillary Rheometer, Southern and Porter (25-28) crystallized polyethylene under combined orientation and pressure effect. Their process involves loading the reservoir of the Rheometer with a crystalline polymer, bringing the temperature of the entire chamber and die to near the melting point of polymer and exerting a pressure around 2000 atmospheres (0.2 G Pa), thereby causing extrusion through a conical die (25). They observed three distinct regions in the sample. The first region, near the capillary entrance was transparent to visible light. The second region was a combination of transparent and opaque material. The third region, which was initially nearer to the
exit of the capillary was opaque. It was reported that the differential scanning calorimeter results gave different melting peaks suggesting that the strand consisted of different crystal formations (26). Scanning Electron Micrographs of region one indicated that it consists of fibrillar structures with probable orientation of the fibers parallel to the axis of the flow (25). The melting peak for region one was 140.1°C (26). The melting point of the third region was low (133.5°C) and was considered to have been crystallized under orientation pressure effects, but remelted as a result of a low pressure, high temperature combination and then recrystallized during the cooling cycle. The strand in region one had a high modulus due to both high crystalline content and the orientation of the crystals (26).

Kolbeck and Uhlmann (52) described the properties of solid-state extruded polyethylene in terms of two primary processing variables, extrusion temperature, and area reduction. It was reported that many properties of the extrudates showed a small dependence on extrusion temperature. But, the area reduction had a major effect on nearly all properties of solid state extruded polyethylene.

Aharone and Sibilia (53) did experiments on thirteen polymers (Table 1) which revealed that solid-state extrusion and malleability occur in semi-crystalline polymers that have a crystalline relaxation (αc) at the temperature $T_{αc}$, and do not occur in semi-crystalline polymers devoid of $αc$. They reported that the solid-state extrusion takes place in the temperature range $T_{αc} \leq T < Tm$ with $Tm$ being melting point.

Griswold et al. (29) extruded ultraoriented films of high density polyethylene continuously by a new method called solid-state coextrusion. In this method the polymer billet was split longitudinally and a wafer
TABLE 1
Solid State Extrusion Results

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Solid State Extrudability</th>
<th>Oven Temperature Range, °C</th>
<th>Crystalline Relaxation Temp, °C</th>
<th>Melting Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE</td>
<td>Yes</td>
<td>138 - 145</td>
<td>88</td>
<td>148</td>
</tr>
<tr>
<td>PEO</td>
<td>Yes</td>
<td>34 - 60 60 - 65</td>
<td>24</td>
<td>67</td>
</tr>
<tr>
<td>POM</td>
<td>Yes</td>
<td>174 - 182</td>
<td>102</td>
<td>182</td>
</tr>
<tr>
<td>P4MPI</td>
<td>Yes</td>
<td>170 - 225</td>
<td>160</td>
<td>231</td>
</tr>
<tr>
<td>PVF</td>
<td>Yes</td>
<td>165 - 196</td>
<td>110</td>
<td>196</td>
</tr>
<tr>
<td>PVDF</td>
<td>Yes</td>
<td>162 - 175</td>
<td>90</td>
<td>175</td>
</tr>
<tr>
<td>HALAR</td>
<td>Yes</td>
<td>170 - 228</td>
<td>130</td>
<td>236</td>
</tr>
<tr>
<td>PET</td>
<td>No</td>
<td>-</td>
<td>None</td>
<td>258</td>
</tr>
<tr>
<td>CM-1</td>
<td>No</td>
<td>-</td>
<td>None</td>
<td>326</td>
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<tr>
<td>PBT</td>
<td>No</td>
<td>-</td>
<td>None</td>
<td>223</td>
</tr>
<tr>
<td>TEF ZEL</td>
<td>No</td>
<td>-</td>
<td>None</td>
<td>&lt; 280</td>
</tr>
<tr>
<td>POLY (1-BUTENE)</td>
<td>No</td>
<td>-</td>
<td>None</td>
<td>116</td>
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</tbody>
</table>
(or wafers) of the same polymer was inserted between the two halves of the billet. The whole assembly was then extruded through a conical die. They observed high tensile modulus and transparency which confirmed the continuous attainability of ultradrawn films.

Griswold et al. (30) indicated that high mechanical properties can be obtained using a radial-compression method which involved the gradual buildup of highly-stretched elastomeric filaments around the circumference of a solid high density polyethylene cylinder. The stresses involved in this method are radial and hoop stresses which caused the cylinder to neck down, uniaxially extend, and ultradraw. They observed an increase in degree of crystallinity by six percent, and a raise in melting point by 5°C.

Superdrawn Filament Process

Clark et al. (9, 10) prepared filaments of the polypropylene having high strength and modulus by a two-stage drawing process. The first stage involves free boundary drawing of an unoriented cylindrical billet in a "natural draw" process to a draw ratio of 7 at a rapid rate. In the second stage (superdraw) the sample is drawn slowly at 50 percent per minute to a draw ratio of 20. The data was interpreted in terms of two competing processes in superdrawing which are dependent on both the draw temperature and draw rate. They are a) unfolding of chains to form additional tie molecules and b) shearing displacement of microfibrils. The first process increases the degree of continuity of the covalent bonds along the filament axis and increases the values of the modulus and strength. The second is responsible for the fluid flow behavior which increases the length (draw ratio) without substantial change in structure of the microfibrils or in the mechanical properties.
Figure (4) shows a schematic of continuous crystal model proposed by Clark and Scott (9).

Jarecki and Meier (54) reported that the maximum degree of molecular orientation and deformation obtained by ultradrawing of high density polyethylene in air is limited by formation of internal voids (both longitudinal separation of fibrils and perpendicular cracking), and thus values of Young's modulus which are achievable by ultradrawing techniques are also limited to values much below the theoretical limit for fully extended chains. The temperature has significant effect on critical draw ratio at which internal void formation begins, and also on the draw ratio at which failure occurs during the ultradrawing.

**Fixed Boundary Extrusion**

Collier and coworkers (37-42) demonstrated that controlled levels of orientation could be imparted to polyethylene and polypropylene fibers and films using a single screw extruder and specially designed dies. Biaxial orientation was induced by using a die in which the flow channel widened as the cross-sectional area was reduced by narrowing the thickness (fig. 5). Molecular orientation was retained in the extrudate by crystallizing at least the outer sheath of the oriented melt inside the constant cross-sectional area land of the die. By varying the die geometry and operating conditions, the level of orientation imparted could be controlled with the upper limit being nearly complete chain alignment (55). The operation was continuous until the volume of highly oriented extrudate, which was equal to the volume of the reservoir section of the die, was exhausted. Then plugging occurred, followed by a pressure increase (42). The polymer melt had to be conditioned for a minimum of fifteen minutes at a temperature near its melting
Fig. 5 Schematic Diagram of the 12/1 Die
point prior to extrusion of highly oriented material. Times shorter than fifteen minutes were apparently not sufficient. It was considered that during melt conditioning and subsequent flow, the melt was possibly transformed to a nematic liquid crystalline form which may require conditioning the melt. After conditioning the polymer melt for the limited time, the temperature of the die was raised in increments of $5^\circ C$ until flow commenced and the pressure decreased. It was reported that the extrudate came out after flow was restabilized. The extrudates exhibited high orientation and high mechanical properties (42).

Collier et al. (42) produced uniaxial and biaxial oriented transparent ribbons of polyethylene and polypropylene. It was reported that for polyethylene the highest modulus obtained was $1.9 \times 10^6$ Psi ($13.1 \text{ G Pa}$) ($5.5\%$ of the theoretical value) in the machine direction and $3.63 \times 10^5$ Psi ($2.5 \text{ G Pa}$) in transverse direction (4). For polypropylene the highest initial modulus was $9.421 \times 10^5$ Psi ($5.8 \text{ G Pa}$) ($13.3\%$ of the theoretical value). The highest tensile strength obtained for polyethylene was $43,520$ Psi ($0.296 \text{ G Pa}$) in the machine direction, and for polypropylene the tensile strength obtained was $15,510$ Psi ($0.1069 \text{ G Pa}$) in the machine direction. It had been reported that scanning electron micrographs indicated unbalanced biaxial orientation with the machine direction favored over the transverse direction, which may be due to an effect of layered shearing flow in the reservoir section. The scanning electron micrographs of cut and fractured extrudates exhibited layered structure which was characteristic of the highly oriented samples (42,55). The elevation in melting point was $8.1^\circ C$ for polyethylene from $132^\circ C$ to $140.1^\circ C$ and $10.8^\circ C$ for polypropylene from $164^\circ C$ to $174.8^\circ C$.

It was reported that the initial modulus of the fixed boundary
extrusion samples were higher than those produced by solid state extrusion process at the deformation ratio of 6, 100% higher for polyethylene and 70% higher for polypropylene (55).

Collier (55) reported that the characteristics of the extrudates by fixed boundary extrusion are quite similar to those resulting from solid state extrusion; i.e. a high degree of transparency was induced, a fibrous structure was revealed by scanning electron microscope, elevation in melting point, and higher degree of crystallinity.
CHAPTER III
THEORY

In an extrusion process oriented chain molecules are formed by the extensional flow through the entrance region. Main stream lines of flow are indicated by numbers 1, 2 and 3 in figure 6. The velocity at the centerline of flow should be higher than that on out-board stream lines in the region upstream of and very close to the die entrance region. Upon approaching the entrance region the velocity distribution changes and the flow pattern changes to a "wineglass stem" shape (55) as a result of normal forces that develop as a result of chain alignment during extensional flow.

The stream lines converge very rapidly in this region producing an extensional effect on the randomly coiled polymer chains. The chains tend to uncoil and align with respect to each other. In a biaxial die, the fluid near the entrance region is accelerated in the flow direction due to the reduction in cross section and in the transverse direction due to the expansion in width.

The change in Gibbs free energy in a system undergoing change in state under isothermal condition can be defined by equation (56)

\[ \Delta G = G_{\text{out}} - G_{\text{in}} = \Delta H - T \Delta S \]  

(1)

where \( \Delta G \) is the change in Gibbs free energy, \( \Delta H \) is the change in enthalpy, and \( T \) is the absolute temperature. If the isothermal condition occurs at a first order thermodynamic transition such as melting, boiling, crystallization, etc., the change in free energy will be zero. For fusion, the equation (1) can be written as:
Fig. 6 Schematic Representation of Non-Newtonian Flow Process
\[ \Delta G = 0 = \Delta H_f - T_M \Delta S_f \]

OR

\[ T_M = \frac{\Delta H_f}{\Delta S_f} \quad (2) \]

For a steady state flow (kinetic and potential energy are negligible) \( \Delta H \) can be written as:

\[ \Delta H = Q - W \quad (3) \]

For an isothermal process, the portion of the enthalpy change due to orientation is small, where there is no shaft work and the amount of heat required during the process is very small as indicated by the stability of the temperature controller.

For polymer melts the entropy change will be significantly larger for high elongational flow (i.e. \( \frac{\partial \gamma}{\partial z} \) is high) than it is in the quiescent melts at atmospheric pressure. Hence the change of entropy from disordered polymer melt to disordered crystalline state would be much higher than that of change of entropy from oriented polymer melt to oriented crystalline state. This is shown in figure 7.

If we define \( \Delta T_{ME} = T_{ME} - T_M \), where \( \Delta T_{ME} \) is the difference between melting point of the oriented polymer \( (T_{ME}) \), and melting point of the quiescent polymer \( (T_M) \), then:

\[ \Delta T_{ME} = T_{ME} - T_M \]

\[ = \frac{\Delta H_{ext}}{\Delta S_{ext}} - \frac{\Delta H_{Quiescent}}{\Delta S_{Quiescent}} \]
Static crystallization

Disordered melt \rightarrow \text{Disordered crystalline}

\[ S_1 \rightarrow S_2 \]

Flow crystallization

Disordered melt \rightarrow Oriented melt \rightarrow Oriented crystalline

\[ S_1 \rightarrow S_3 \rightarrow S_4 \]

Since \[ S_1 \gg S_3 > S_2 > S_4 \]

\[ \Delta_{\text{quies}} = S_1 - S_2 \quad \Delta_{\text{ext}} = S_3 - S_4 \]

\[ T_M = \frac{\Delta_{\text{quies}}}{\Delta_{\text{quies}}} \quad T_{ME} = \frac{\Delta_{\text{ext}}}{\Delta_{\text{ext}}} \]

and

\[ \Delta_{\text{quies}} \propto \Delta_{\text{ext}} \]

so

\[ T_{ME} > T_M \]

Fig. 7 Schematic Representation of the Effect of Flow Upon the Melting Point
If the alignment and orientation are a function of $\frac{\partial v_z}{\partial z}$ in the flow direction near the entry, then alignment would be increased as the velocity gradient $\frac{\partial v_z}{\partial z}$ increases. Since the entropy is a measure of disorder, the entropy change during orientation should be proportional to the velocity gradient $\frac{\partial v_z}{\partial z}$. Thus, the entropy change during transition ($\Delta S_{ext}$) is inversely proportional to the elongational velocity gradient $\frac{\partial v_z}{\partial z}$. i.e.,

$$\alpha \frac{1}{\Delta S_{ext}} \frac{\partial v_z}{\partial z}$$

$\Delta S_{Quiescent}$ is a constant for static crystallization. Therefore from equation 4

$$\Delta T_{ME} \propto \frac{1}{\Delta S_{ext}} \frac{\partial v_z}{\partial z}$$

Equation 5 suggests that the greater the velocity gradient, the lower the entropy change upon crystallization and the greater the change in melting point. However, $\Delta T_{ME}$ would approach a limit where velocity gradient is at critical point beyond which no change in alignment would occur (i.e. for a fully aligned crystalline structure). The development of extended chain crystals may be related to the development of the nematic liquid crystal or mesomorphic state. This state would correspond to axially aligned polymer chains but not necessarily matched end to end as shown in figure (8).

The quiscent melt below a critical pressure should tend upon cooling
Fig. 8  Nematic Liquid Crystalline Form
to go directly from the disordered liquid melt state to the solid crystalline state, as shown by the free energy versus temperature relationships in figure 9; whereas, above a critical pressure, as shown in figure 10, the liquid melt upon cooling could go first to the nematic state and then to the solid crystalline state. This would result in extended chain domains. However, in this study, the pressure could be below a critical pressure, therefore not favoring a nematic state as shown in figure 9. This difficulty could be circumvented by flow induced crystallization, where the extended chain form could be produced at the entrance region of the die and crystallized in the land of the die expressing indirectly that the nematic form is metastable under certain flow conditions.
Fig. 9 and 10 Free energy as a function of temperature for a liquid crystal.
Let \((V_1, V_2, V_3)\) be velocity components in the rectangular coordinate directions \((X, Y, Z)\). Where \(Z\) is the direction of the flow, \(Y\) is the transverse direction, and \(X\) is the normal (thickness) to the polymer ribbon.

Biaxial orientation in ribbons was induced by using an extensional flow which can be represented by a deformation tensor:

\[
d = \begin{bmatrix}
  d_{11} & 0 & 0 \\
  0 & d_{22} & 0 \\
  0 & 0 & d_{33}
\end{bmatrix}
\]  

(6)

Where \(d_{11}\), \(d_{22}\) and \(d_{33}\) are strain rates defined as:

\[
d_{11} = \frac{\partial V_1}{\partial x}, \quad d_{22} = \frac{\partial V_2}{\partial y}, \quad d_{33} = \frac{\partial V_3}{\partial z}
\]

(7)

In the case of incompressible fluids (constant density), the continuity equation becomes (57):

\[
d_{11} + d_{22} + d_{33} = 0
\]

so,

\[
d_{11} = -(d_{22} + d_{33})
\]

(8)

Substituting equation 8 in equation 6, we obtain:

\[
d = \begin{bmatrix}
  -(d_{22} + d_{33}) & 0 & 0 \\
  0 & d_{22} & 0 \\
  0 & 0 & d_{33}
\end{bmatrix}
\]

For equal biaxial orientation

\[
d_{22} = d_{33}
\]

and \(d_{11} = -2d_{22} = -2d_{33}\). 

Therefore, the deformation rate for equal biaxial orientation may be represented as:

\[
d = \mathbf{\dot{Y}} = \begin{bmatrix}
-2 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{bmatrix}
\]  

(9)

Where \( \mathbf{\dot{Y}} \) is the strain rate defined as:

\[
\mathbf{\dot{Y}} = \frac{dv_3}{dz}
\]

Equation (9) corresponds (in a constant volume process) to an acceleration in the machine direction, an equivalent expansion in width (2 and 3 directions), and a decrease in thickness (1 direction). Therefore, for a constant volume process and the deformation rate given in equation (9), a balanced biaxial orientation should result when the thickness decreases twice as fast as the width increases.

The above mathematical development assumed negligible effect from shearing flow. In the dies used in previous studies (39-41) the shaping section elongational strain rate was significantly lower than the shear rate at the wall in the land and of similar to lower magnitudes to the shear rate at the wall in the reservoir. Therefore, the shear rate should not be neglected. A layered flow is possibly produced by the shear component in the conditioned melt. The differential motion between layers would tend to orient the molecules at the boundary of each of the layers in the flow direction (55) since the cross-sectional area in the land is small, the shear rate at the wall is higher than in the reservoir. The shearing flow contribution can be reduced by having a large cross-sectional area reservoir section, and short machine direction length in both the reservoir and land section. To compensate
for a shearing flow contribution, the transverse elongation would need to be increased relative to the machine direction.
CHAPTER IV
EQUIPMENT

Extruder:

The equipment used for extruding the polymer was a Model 200 Brabender Single Screw Extruder with a barrel diameter of 0.75 inch and L/D (length to diameter) ratio of 20. There were two 800 watt heaters on the extruder barrel, controlled by two West Model JPC On-Off Proportional Controllers. There were two thermocouple wells for the above two heaters at 8 inches (Zone 1) and 15 inches (Zone 2) from the feed end along the barrel and both were 1/8 inch away from the inside wall of the barrel. The pressure was monitored by a Dynisco Strain Guaze Transducer Model TPT 432A-10M-6/18 and indicated by a West instrument Model IS 86 with a range of 0-10,000 Psig. The transducer was located at the discharge end of the barrel. The screw torque was indicated by a counter balance swing arm on the Brabender Plasticorder. The screw speed was indicated by a tachometer with 2 rpm graduations and was also monitored by a stop watch.

Die and Adaptor:

The reservoir, land, shaping section and cooling section of the die were built as a split die from 416 stainless steel. The interior or flow portions, reservoir, shaping and land sections were designed to be identical to an immersion die used in a previous study (41). The die in the study reported herein was internally cooled and allowed horizontal extrusion. Both dies had a cross-sectional area reduction ratio of 12 to 1 which produced ribbons with a width of 1.5 inches and thickness of 1/32 inch (fig. 11). The volume of the reservoir of the die was 1.125 cubic inches. This die had been designed with an internal circulation of coolant.
in the die wall of the land section. The rest of the die can be independently temperature controlled. As shown in figure (11) the thermal separation of the land region from the remainder of the die was enhanced further by recessing the external portion of the die. The shaping section was overlapped into the land of the die (cooling section).

The cooling section of the die had a total of 42 holes (21 in each half of the die) of 1/4 inch diameter for inlet of coolant and 6 holes (1/4 inch each, 3 in each half of the die) for outlet of coolant as shown schematically in figure (12). Two adaptors (one for each half of the die) were designed to distribute inlet coolant equally to all the holes in the die. The adaptors were attached to the die by twelve screws (six for each). Two small adaptors (one for each half of the die) were attached on the side of the die to collect outcoming coolant and were attached by four screws (two for each). The above adaptors were detachable from the die. As heat source for the reservoir of the die, a 500 watt heater (Zone 4) was used and was controlled by a West Model JPC On-Off Proportional Controller. A thermocouple in the reservoir section was used to monitor the temperature of the molten polymer. The connections on the die were designed to use with or without the melt conditioner. The two halves of the die were fastened together with 6 bolts (0.5 inch diameter, 3.5 inches length).

The die was fastened to the end of the extruder by a specially designed adaptor (fig. 13). The die was attached to the adaptor with six screws. A 200 watt band heater (Zone 3) was used as a heat source to the adaptor and was controlled by a Weathermeasure Model TPC-PID On-Off Temperature Controller. Schematic diagram of process equipment is shown in figure (14).
Fig. 12 Schematic Diagram of The Internal Cooling Die (With Cooling Section)
Fig. 14 Schematic Diagram of the Process
Differential Scanning Calorimeter:

For melting point and degree of crystallinity observations of the polymer, a Perkin-Elmer Differential Scanning Calorimeter Model DSC 1B with 8 scan speeds of 0.625 to 80°C per minute and a range of 1 to 32 (millicalories/second) for full scale deflection was used. The endotherms were recorded on a Perkin-Elmer Recorder Model 56 with event marker.

Tensile Testing Machine:

For tensile tests an Instron Universal Testing Instrument Model TT-D with 20,000 pound capacity and testing speed range of 0.002 to 20 inch/minute was used. A GR load cell used in the high sensitivity range (0-4000 pound). Model G61 - 10FA grips were used to hold the sample. Load versus elongation was recorded on a variable speed recorder.
CHAPTER V

EXPERIMENTAL PROCEDURE

Two polymers were used in this study. They were Marlex® (registered trademark of Phillips Petroleum Corporation) HGZ-050-02 polypropylene with melt index of 5 and Fortiflex® (registered trademark of Soltex Polymer Corporation) A60-70R high density polyethylene with melt index of 0.7. These two were chosen because of their moderate value of melt index, which would give optimum operating conditions (36). Since more stable conditions were reported by Collier and coworkers (42) using polypropylene in the biaxial die, most of the experiments in this study were done on polypropylene.

The variables in this study were screw speed, pressure and the temperatures of the four zones. In the beginning of this study, the experiments were planned to do in conjunction with the melt conditioner. Because of the delay in obtaining melt conditioner components, the work was done without the melt conditioner. Most of the experiments were done using water as coolant. Prestone Ethylene Glycol® (registered trademark of Union Carbide Corporation) was also used as coolant in some of the experiments.

Without Teflon® Coating:

In the beginning of experiments, the die was used without Teflon® coating. In these experiments only polyethylene was used. At start up, the temperature profile in the extruder, adaptor and die was set at 175 - 175 - 165 - 155°C in Zone 1, Zone 2, Zone 3 and Zone 4 respectively. About 45 minutes from the start up were allowed to insure complete melting of the polymer in the barrel and die from the previous runs. When the equilibrium conditions were attained, which were indicated by the steadiness of on-off controllers, the molten polymer from the previous run was
purged out with fresh resin to eliminate any degraded material.

After purging the polymer the screw speed was set at 10 rpm. The pressure was 100 Psi ($6.89 \times 10^{-4}$ G Pa) before any coolant was used. Then water was introduced as coolant to the die. The pressure increased to about 5000 Psi ($3.44 \times 10^{-2}$ G Pa), and a non-uniform cross-section extrudate was produced. Eleven experiments were carried out under different conditions of temperature and pressure, however extrudates with uniform cross-section could not be produced as discussed in the results and discussion section.

With Teflon® Dispersion Coating:

In another series of experiments, Teflon® dispersion was used for coating. Before any coating the Teflon® was thoroughly cleaned with fresh water. The cleaned Teflon® was then dried in an oven at 100°C for 8 hours. The reservoir, shaping section and land of the die were thoroughly cleaned and polished with a fine grade emery paper. The dried Teflon® was cooled to room temperature and applied to the die. A thin layer of Teflon® was applied by rubbing with a fine smooth cloth on the surface of the reservoir and shaping sections and the land of the die. Then a second layer of Teflon® was applied using the same application technique on the surfaces of reservoir and shaping section and the land of the die. The experimental procedure was similar to that used without Teflon® coating. In these experiments Marlex® polyethylene was used. A similar temperature setting for this was 175 - 175 - 165 - 155°C in Zone 1, Zone 2, Zone 3 and Zone 4 respectively. After the equilibrium conditions were insured, the molten polymer from the previous run was purged out with fresh resin. After purging the previous resin, the screw speed was set at 10 rpm. The pressure was around 100 Psi
(6.89 x 10^{-4} \text{ G Pa}) before coolant was introduced. After the coolant introduction the pressure increased to nearly 5000 Psi (3.44 x 10^{-2} \text{ G Pa}). Again similar to the experiments done without Teflon® coating, the non-uniform extrudates were produced. Nine experiments were done with different combinations of temperature and pressure, but extrudates with uniform cross-section could not be produced.

With Teflon® Coating:

After the above two procedures failed to obtain extrudates with uniform cross-section, a series of experiments were done similar to the previous studies (40, 41) with different type of Teflon® coating. The reservoir, shaping section and the land of the die were cleaned and polished with a fine grade emery paper. Teflon® dispersion and the etching solution (mixture of 16.33% of concentrated sulfuric acid, 16.33% of concentrated phosphoric acid, 16.33% of concentrated chromic acid and 50% of water) were diluted to 50% in water. The etching solution was used to achieve a coating which has a reasonable porosity and adhesion.

The diluted solution was mixed in a ratio of 2 to 1, two parts being Teflon® solution and one being the etching solution. The Teflon® solution was deposited with a dropper on reservoir and shaping sections and the land of the die. A thin layer of Teflon® solution was formed by blowing air across the faces of the die. The die was heated in a preheated furnace at 700°F for 20 minutes. A second coating was applied similar to the first except that the etching solution was not used to cover the cracks produced by the first heating. After the second coating the die was again heated in the furnace at 700°F for 10 minutes. After the die was coated with Teflon® the die was tightened together using a torque of 55 - 60 lbs. to withstand high pressures. In the series of
experiments Marlex® polypropylene was used. The temperatures in the four zones, two in the barrel, one on the adaptor and the last on the die were preset to 175 - 175 - 160 - 155°C for polyethylene and 225 - 225 - 215 - 190°C for polypropylene. Forty-five minutes were allowed to insure complete melting. To prevent plugging initially, some molten polymer was extruded. Then the coolant (water) was introduced to the die. The polymer in the extruder was purged out with fresh resin to insure that the samples do not contain any degraded material. After purging the polymer, the screw speed was set at 10 rpm. At this temperature setting, which was higher than the atmospheric pressure melting point of the polymer (polyethylene or polypropylene), the extrudate came out with uniform cross-section. The pressure at this stage was about 500 Psi (3.44 x 10⁻³ G Pa).

The temperature of the die (Zone 4) was lowered by 5°C decrements until the die plugged. The pressure was rising throughout the time of lowering the temperature. Pressure did not increase or decrease after plugging. The screw speed was decreased to almost one (1) rpm. Then the polymer was held plugged at the same temperature and pressure for a minimum of 15 minutes. Then the temperature of the die (Zone 4) was raised at 2 - 5°C increments approaching equilibrium at every step. The ribbon exited out of the die at 210°C for polypropylene and 185°C for polyethylene. When the pressure was dropped to 450 Psi an opaque ribbon with poor mechanical and thermal properties was extruded. Then the operation was stopped and the above procedure was repeated again (starting with Teflon® coating) using different combinations of pressures and temperatures.
Sample Preparation:

The oriented samples were examined and tested by a Differential Scanning Calorimeter (DSC) for melting behavior and by an Instron Universal Testing Unit for tensile testing.

For DSC analysis approximately 3 - 9 milligrams samples were taken. The samples were cut from the ribbon and weighed on a balance in a sample pan supplied with the DSC unit and crimped in a crimper along with the supplied lid. The DSC unit was calibrated using an heavy Indium sample with melting point of 156°C. The peak of the curve was taken as the melting point and the area under the curve was taken to calculate heats of fusion.

For tensile testing, the samples were cut into pieces of two and a half inches long and trimmed on both sides by using templates and the Tensilekit Model 10 - 68 machine into a dog-bone shape as recommended by ASTM Test No. D638 as discussed in the results section. The tensile tests were performed on an Instron Universal Testing Model TT-D with gage length of one(1) inch long, cross-head speed of 0.5 inches per minute and chart speed of 2 inches per minute. The Instron machine was calibrated with a 50 lbs. dead weight. The calculations of yield stress and secant modulus are shown in figure (15).
Secant modulus = \( \frac{\text{slope of secant line} \times \text{gage length}}{\text{sample cross-sectional area}} \)

Yield Stress = \( \frac{\text{yield load}}{\text{sample cross-sectional area}} \)

Fig. 15 Determination of Secant Modulus and Yield Stress from A Typical Load versus Elongation Recording.
CHAPTER VI
RESULTS AND DISCUSSION

The samples of Polyethylene and polypropylene were analyzed for melting behavior and degree of crystallinity. A Perkin-Elmer Differential Scanning Calorimeter Model DSC 1B was used in this study. The unit was calibrated using heavy Indium sample with a melting point of 156°C (figure 16) and heat of fusion of 6.75 calories per gram (58). A heating rate of 10°C and full scale range of 8 millicalories was used throughout this study. The mechanical testing of the samples was carried out using an Instron Testing Machine. The samples were machined (figure 17) as required by ASTM Standards (59).

Polyethylene:

The endotherm in figure (18) is of Sample I, extruded at a pressure of 100 Psi (6.9 x 10^{-4} G Pa) with a temperature profile of 175°C - 175°C - 175°C - 165°C and a screw speed of 8 rpm. This sample demonstrated no elevation in melting point.

The endotherm in figure (19) is of Sample II, extruded at a pressure of 2500 Psi (1.72 x 10^{-2} G Pa) with a temperature profile of 175°C - 175°C - 175°C - 150°C and a screw speed of 2 rpm. This sample had 3°C elevation in melting point and the extrudate was translucent. This sample could be a mixture of oriented and unoriented material but dominated by unoriented material.

Sample III, which has demonstrated the highest melting point at 136.5°C and a shoulder at 133°C is shown in figure (20) with 3.5°C elevation in melting point. For this sample, the pressure was 2750 Psi (1.9 x 10^{-2} G Pa) and temperature profile was 175°C - 175°C -
Fig. 16 DSC Endotherm for Heavy Indium

Fig. 17 Schematic Diagram of Tensile Testing Sample
Fig. 18 DSC Endotherm for Sample No. I of Polyethylene

Fig. 19 DSC Endotherm for Sample No. II of Polyethylene
Fig. 20 DSC Endotherm for Sample No. III of Polyethylene
165° C - 150° C and the screw speed was 2 rpm. This sample also has the highest heat of fusion and percent crystallinity recorded in this study (Table 2).

Sample I was extruded without coolant and the extrudate did not have a uniform cross-section. Sample II was extruded with water as coolant. The extrudate came out as a ribbon but plugging occurred 3 minutes after coolant was introduced. Then the melt started leaking through the sides of the die and the pressure increased to 7200 Psi (4.96 x 10^-2 G Pa). Then the temperature profile was changed to 190° C - 190° C - 190° C - 185° C. After 20 minutes, the pressure decreased slowly, but no further extrudate could be produced. Sample III was also extruded with water as a coolant. Plugging occurred just as in the case of Sample II.

The relaxation time of a polymer melt is inversely proportional to the absolute temperature (57). During extrusion, at high temperatures, the relaxation time is sufficient for the polymer chains to relax back to disoriented state. Therefore, Sample I could not be obtained as highly oriented ribbon. But when using a coolant, a sharp temperature gradient developed and the polymer chains may not have sufficient time to relax back. Therefore, the orientation was locked in the land of the die as in the case of Sample II and Sample III.

Peterlin (60) proposed that when entangled macromolecules flow past a cold wall of the die, some of the molecules will solidify at the surface while the remainder of the polymer is still in a molten state. When the coolant is introduced, crystallization is induced in the land of the die. If the temperature gradient causes the crystallization front and the front moves up to the entrance region (between shaping section
# TABLE 2

DSC Data for Polyethylene With A Heating Rate of 10°C Per Minute

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Melting Peaks (°C)</th>
<th>Melting Peaks After Recrystallization (°C)</th>
<th>Heat of Fusion (Cals/Gm)</th>
<th>Crystallinity (Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>133</td>
<td>133</td>
<td>16.6</td>
<td>26.68</td>
</tr>
<tr>
<td>19</td>
<td>133</td>
<td>130</td>
<td>18.377</td>
<td>29.5</td>
</tr>
<tr>
<td>20</td>
<td>136 133</td>
<td>132.5</td>
<td>20.0</td>
<td>32.17</td>
</tr>
</tbody>
</table>
and land of the die), plugging will result. Just before plugging occurs, nuclei are probably induced by molecular flow and pressure. As the die temperature is lowered, massive crystallization takes place in the shaping section and land of the die as a result the exit of the die is plugged. Due to the plugging the back pressure will increase causing leakage.

In the beginning of this study, the bolt size of 0.085 inches was used to fasten the two halves of the die. When the leakage was observed, the bolt size was increased to 0.5 inches. Double layers of aluminum foil were used between the two halves of the die to prevent the leakage between the faces of the die. Two 4 inch clamps were used to tighten the cooling section of the die. For Sample III the above modified set-up was tried, but leakage occurred on the sides of the die at the recessed section between cooling section and shaping section (figure 12).

As the die temperature was lowered and coolant was introduced, a large temperature gradient was imposed on the land section and, the melt apparently crystallized in the land. Because the cooling section is near to the shaping section (figure 12), the crystallization front in the land of the die could move up into the entrance region which could cause plugging. By opening the die and extracting the solidified polymer, it was observed that the crystallization front indeed moved up into the shaping section. Because of the area reduction in the shaping section and the crystallization front near the entrance of land section, the polymer could not move into the land section even after the temperature of the die increased. As the temperature is subsequently increased the polymer near the walls of the die melts, and the pressure reinstates
the flow.

For Sample II and Sample III, after the plugging occurred, the coolant was removed and the temperature of the die was increased to reinstate the flow. But oriented ribbon could not be extruded successfully. For Sample II and Sample III only a length of less than 1.5 inches of oriented ribbon was obtained. Because of its length no tensile tests could be done.

Polypropylene:

Highly oriented and transparent Polypropylene ribbons were extruded using a 12/1 biaxial die (figures 21 to 23) designed by the author for this study. The endotherms in figures (24) to (27) show the melting peaks of samples removed (at different die temperatures) from a highly oriented and transparent ribbon extruded with Prestone® as coolant.

The samples are of the oriented ribbon extruded with 150 milliliters per minute (in each cooling section) of Prestone® as coolant. The extrusion was started with a temperature profile of 225° C - 225° C - 210° C - 190° C in Zone 1, Zone 2, Zone 3 and Zone 4 respectively. The die temperature, i.e. Zone 4, is reduced at a decrement of 5° C. The samples shown in figures (24 to 27) were taken from a ribbon at die temperature of 165° C, 155° C, 150° C and 145° C and pressure of 2000 Psi (1.38 x 10^-2 G Pa), 2000 Psi (1.38 x 10^-2 G Pa), 2200 Psi (1.52 x 10^-2 G Pa) and 2300 Psi (1.59 x 10^-2 G Pa) respectively.

The endotherm shown in figure (28) exhibited the highest melting point and highest heat of fusion. This sample had the highest elevation in melting point of about 7.5° C with melting peaks at 171.5° C, 169° C and 168° C (the highest value used for evaluation of elevation in
Fig. 21 Polypropylene Ribbon (plugged) (Prestone® as coolant)

Fig. 22 Polypropylene Ribbon (unplugged) (Prestone® as coolant)
Fig. 23 Polypropylene Ribbon (plugged) (water as coolant)
Fig. 24 DSC Endotherm of Polypropylene (Die Temperature - 165° C)

Fig. 25 DSC Endotherm of Polypropylene (Die Temperature - 155° C)
Fig. 26  DSC Endotherm of Polypropylene (Die Temperature - 150°C)

Fig. 27  DSC Endotherm of Polypropylene (Die Temperature - 145°C)
Fig. 28  DSC Endotherm of Polypropylene (Die Temperature - 140° C)
The melting point was 171.5° C. The melting peak after recrystallization was at 164° C. This sample was from the same ribbon of above samples and extruded at the same conditions, except the die temperature which was 140° C. The extrusion rate was 9.8 inches per minute. This sample plugged after about 3 minutes of operation at a die temperature of 140° C and at a pressure of 6100 Psi (4.2 x 10^{-2} G Pa). The temperature of the coolant (Prestone®) was 35.2° C.

The endotherms in figures (24 to 28) has one or more shoulders which may be due to the presence of different morphologies or different levels of orientation in machine and transverse directions, which melt at different temperatures. Table 3 summarizes the thermal analysis done on these samples of plugged Polypropylene ribbon. To test the reproducibility, similar extrusion conditions were maintained and cooling was with Prestone® at a flow rate of 150 milliliters per minute (in each cooling section). The temperature of the coolant was 38° C, about 3° C higher than the previous run. The ribbon did not plug at 140° C and was extruded until the die temperature was reduced to 125° C. The extrusion rate was 10.1 inches per minute. The thermal analysis done on this ribbon has been summarized in Appendix I.

In figure (29) the percent of crystallinity of plugged and unplugged samples were plotted against die temperature. For plugged samples, the percent of crystallinity is increasing from 43.67% to 77.33% between the die temperature of 165° C - 140° C. But for unplugged samples, the percent of crystallinity is approximately constant (ranging from 63.93% at 165° C to 60.87% at 145° C) and increased to 75.44% at the die temperature of 125° C. At die temperatures of 145° C and 150° C, both plugged and unplugged samples have the almost same percent
TABLE 3

DSC Data for Polypropylene (plugged) With A Heating Rate of 10°C Per Minute

<table>
<thead>
<tr>
<th>Figure Number</th>
<th>Melting Peaks (°C)</th>
<th>Melting Peaks After Recrystallization (°C)</th>
<th>Heat of Fusion (Cals/Gm)</th>
<th>Crystallinity (Percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>24</td>
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<td>27.17</td>
<td>43.67</td>
</tr>
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<td>25</td>
<td>166</td>
<td>162</td>
<td>32.6</td>
<td>52.4</td>
</tr>
<tr>
<td>26</td>
<td>166</td>
<td>160</td>
<td>37.38</td>
<td>60.1</td>
</tr>
<tr>
<td>27</td>
<td>165.5</td>
<td>161</td>
<td>38.22</td>
<td>61.46</td>
</tr>
<tr>
<td>28</td>
<td>171.5 169 168</td>
<td>164</td>
<td>48.1</td>
<td>77.335</td>
</tr>
</tbody>
</table>
(o) unplugged samples (Prestone as coolant)

(o) plugged samples (Prestone as coolant)

Fig. 29 Crystallinity versus Die Temperature for Polypropylene
of crystallinity.

Instron fractured sample of Polypropylene are shown in figure (30). The samples delaminated while testing in the machine direction. All the tensile tests were conducted at room temperature. The results are shown in figures (31) to (33). Figures (31) to (33) were of samples taken from plugged and unplugged ribbons of Polypropylene using Prestone® as coolant and plugged ribbon of Polypropylene using water as coolant. In figure (31), tensile strength was plotted against die temperature and in figure (32), secant modulus (two percent elongational base) was plotted against die temperature. In figure (33), ultimate percent elongation was plotted against die temperature. The tensile test values for figures (31) to (33) were given in Appendix II.

The tensile strength of many samples of Polypropylene was between 5000 - 9000 Psi (3.4 x 10^{-2} - 6.2 x 10^{-2} G Pa). The tensile strength of the sample (Prestone® as coolant) produced just before plugging was 57,600 Psi (0.397 G Pa) and tensile strength of the sample (water as coolant) produced just before plugging was 67,850 Psi (0.468 G Pa). All the Polypropylene samples were extruded at a coolant rate of 150 milliliters per minute (in each cooling section).

The extrusion of transparent and highly oriented Polypropylene ribbons was dependent upon the Teflon® die coating. The best samples reported in this study were obtained immediately after coating the die.

Collier (55) points out that nematic liquid crystals could be forming in the die due to the existing thermal and flow conditions. The melt upon cooling could go first to a nematic state and then to solid crystalline state which would give rise to extended chain alignment. This orientation could be locked in if the ribbon
Fig. 30 Instron Fractured Sample of Polypropylene (delaminated)
(○) plugged samples (Prestone as coolant)

(□) unplugged samples (Prestone as coolant)

(△) plugged samples (water as coolant)

Fig. 31 Tensile Strength versus Die Temperature for Polypropylene
(o) plugged samples (Preston as coolant)

(□) unplugged samples (Prestone as coolant)

(△) plugged samples (water as coolant)

Fig. 32  Secant Modulus versus Die Temperature for Polypropylene
(○) plugged samples (Prestone as coolant)

(□) unplugged samples (Prestone as coolant)

(▼) plugged samples (water as coolant)

Fig. 33 Ultimate Percent Elongation versus Die Temperature for Polypropylene
crystallize before the chains have sufficient time to relax. During plugging, the inner core of the solidified polymer could act as a wall. Again the orientation process occurs due to drag flow which orients the outer sheath. The dual peaks and shoulders of DSC endotherms could be due to different crystallographic or morphological forms present in the machine and transverse direction. By controlling the temperature and flow rate of the coolant, Polypropylene can be extruded with controlled orientation mainly in the die temperature range of 145°C - 160°C.

As shown in figure (31), the tensile strength for all the ribbons lies between 7500 Psi (5.17 x 10^2 G Pa) and 9000 Psi (6.2 x 10^2 G Pa) using die temperatures of 145°C - 160°C. At 140°C both water cooled and Prestone® cooled (plugged) samples have shown very high tensile strength of 67,840 Psi (0.468 G Pa) and 57,600 Psi (0.397 G Pa) respectively.

Figure (32) shows the secant modulus versus die temperature. The secant modulus for unplugged samples (Prestone® as coolant) varied very little (1.176 x 10^5 to 1.336 x 10^5 Psi) (0.81 to 0.92 G Pa) between the die temperatures of 125°C to 165°C. For plugged samples (Prestone® as coolant) the variation in secant modulus was smaller (0.94 x 10^5 to 1.074 x 10^5 Psi) (0.648 to 0.74 G Pa) between the die temperatures of 145°C to 190°C but increased very rapidly at plugging (die temperature is 140°C) to 6.14 x 10^5 Psi (4.23 G Pa). The sample which was cooled with water had a lower secant modulus than those samples cooled with Prestone®. For this sample the secant modulus increased at plugging (die temperature is 140°C).

Figure (33) shows the ultimate per cent elongation versus die
temperature. For unplugged samples (Prestone® as coolant) the ultimate percent elongation varied from 12.5% to 17% between the die temperatures of 125°C to 165°C. For plugged samples (Prestone® as coolant) the ultimate percent elongation varied between 14% to 50% between die temperatures of 145°C to 190°C. At 140°C, where the plugging occurred the value of ultimate percent elongation could not be obtained because the sample slipped out of the Instron grips. For the sample where water was used as coolant, the ultimate percent elongation was dropped from 341.5% to 17.2% between the die temperatures of 160°C to 140°C.

Figure (21), shows the plugged Polypropylene ribbon extruded with Prestone® as coolant. Figure (22), shows unplugged Polypropylene ribbon extruded with Prestone® as coolant. Figure (23), shows the plugged Polypropylene ribbon extruded with water as coolant. The ribbon in figure 23 is more clear and transparent and also has the highest tensile strength. The ribbon in figure (22) is more clear and transparent than the ribbon in figure 21. This might be due to the plugging and resultant high pressure extrusion. The polymer at higher pressures showed higher tensile strengths than the polymer at lower pressure regions. The surface defects in figures (21) to (23) might be due to high local heating.

For the flow induced crystallization process, the temperature profile of the polymers in the reservoir may not be identical within the same transversal cross-sectional area. The difference in temperature should be larger when the flow rate is increased, since the polymer in Zone 3 is always higher than that in the die. Furthermore, since the polymers have low thermal conductivities (about 70 to 250 times smaller than that of steel), the temperature in the core of the
reservoir might be higher than that near the wall of the die. Thus as the temperature of the die was dropped to 125°C, Polypropylene could still be extruded out due to the higher temperature in the core of the reservoir (unplugged sample). Because the polymer near the wall is colder than that in the core, the viscosity of the polymer near the wall would be larger than that in the core. During heating, the inner core of the solid polymer acts as a wall, and the orientation process due to drag effect again occurs. The oriented polymer flowing through the entrance region under high shear will be aligned further, particularly where the elongational viscosity gradient is the largest near the wall. This, coupled with high pressure, high induced shear, and a steep temperature gradient along the land of the die, should cause the polymer to crystallize rapidly (plugged sample).

The Polyethylene could not be extruded successfully because the rate of crystallization of Polyethylene is much higher than the rate of crystallization of Polypropylene. The coolant rate, die temperature and the pressure are probably the difficult factors involved. In this study, the coolant rate and temperature of coolant are more critical factors than die temperature and pressure. Due to the leakage that occurred in most of the experiments, the runs were not fully successful and it was not possible to obtain many highly oriented ribbons and bring the process to a steady state operation.
CHAPTER VII

CONCLUSIONS

1. Highly oriented and transparent ribbons of polypropylene can be obtained using a 12/1 internally cooled biaxial die at moderate pressure (4000 - 6100 Psi) (0.028 - 0.042 G Pa).

2. Using the internal cooling die, horizontal extrusion can be done successfully.

3. The surface defects which were observed in the previous studies were removed by extruding horizontally.

4. Different levels of orientation can be achieved by controlling the flow rate and temperature of the coolant.

5. The highest elevation in melting point obtained was 7.5°C for polypropylene from 164°C to 171.5°C and 3.5°C for polyethylene from 132.5°C to 136°C.

6. The highest heat of fusion obtained for polypropylene was 48.1 calories per gram corresponding to 77.33% crystallinity. For polyethylene, highest heat of fusion obtained was 20 calories per gram corresponding to 32.17% crystallinity.

7. The highest tensile strength obtained for polypropylene (water as coolant) in this study was 67,850 Psi (0.468 G Pa). The highest tensile strength obtained for polypropylene (Prestone® as coolant) was 57,600 Psi (0.397 G Pa).

8. The Teflon® coating made extrusion operation smooth by apparently reducing the friction between the die walls and polymer.

9. Highly oriented polyethylene ribbons could not be extruded successfully.
CHAPTER VIII

RECOMMENDATIONS

1. By controlling the coolant rate precisely, the relationship between flow rate and orientation (and tensile strength) of the polymer may be determined.

2. The distance between the cooling section and the shaping section should be long enough to prevent any unnecessary plugging and longer than in the die used in this study.

3. A better cooling section should be designed, such that there will be a uniform temperature gradient at all points in the cooling section.

4. To prevent leakage, the center bolt should be nearer to the center to have more closeness between two halves of the die.

   i.e. instead of

   it should be

5. To prevent eddies in the land section, the walls of land section should be curved (e.g. parabola shape).

6. Polymers which have slow rate of cooling should be tried.
BIBLIOGRAPHY


38) Tam, Y. Y. T. Dissertation, Chemical Engineering, Ohio University.


58) Morton, L. Report submitted to Chemical Engineering Department, Ohio University.

<table>
<thead>
<tr>
<th>Die Temperature (°C)</th>
<th>Melting Peaks (°C)</th>
<th>Melting Peaks After Recrystallization (°C)</th>
<th>Crystallinity (Percent)</th>
<th>Heat of Fusion (Cal/gram)</th>
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APPENDIX II

Tensile Test Data for Polypropylene (unplugged) (Prestone® as coolant)
at Two Percent Elongation

<table>
<thead>
<tr>
<th>Die Temperature (°C)</th>
<th>Tensile Strength at Yield (Psi)</th>
<th>Ultimate Percent Elongation (Percent)</th>
<th>Secant Modulus (Psi x 10^-5)</th>
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Tensile Test Data for Polypropylene (plugged) (water as coolant)
at Two Percent Elongation

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<th>Secant Modulus (Psi x 10^-5)</th>
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APPENDIX III

Calculation of Heat of Fusion and % Crystallinity for Polypropylene (Fig. 28):

Heat of Fusion of standard sample = 6.75 calories/gram
standard (Indium) peak area = 27 units (measured with Planimeter)
weight of standard = 5.34 milligrams
sample (Polypropylene) peak area = 227 units
weight of sample = 6.3 milligrams
at 100% crystallinity (for Polypropylene), the heat of fusion is 62.6 calories/gram

Heal of Fusion of sample = \[
\frac{(6.75 \text{ cals/gm}) \times (5.34 \text{ mgms.}) \times (227)}{(27) \times (6.3 \text{ mgms.})}
\]
= 48.1 calories/gram

% Crystallinity = \[
\frac{(48.1 \text{ cals./gram.}) \times 100}{(62.2 \text{ cals./gram.})}
\]
= 77.335
The objective of this work was to design a biaxial die, with which extrusion could be done horizontally, thereby allowing better control of the temperature in the land and improvements in the operating conditions. The land temperature gradient was impressed previously by immersion of the exit end of the die under water. This improved design should be used with or without a melt conditioner.

Polyethylene and polypropylene were extruded through a 12/1 (deformation ratio of 12 to 1) biaxial die, using a C.W. Brabender Model 200 Single Screw Extruder. The die was cooled with Teflon® to reduce friction between the walls of the die and polymer. The ribbons extruded were highly oriented and had high tensile properties and were 1.5 inches wide and 1/32 inches thick. Prestone® and water were used as coolant. For polypropylene the maximum extrusion rate of oriented ribbon was 9.2 inches per minute. Oriented polyethylene could not be produced successfully using this die.

Thermal analysis of polypropylene samples demonstrated a 7.5°C melting point elevation and polyethylene samples demonstrated a maximum of 3.5°C elevation in melting point. For polypropylene samples the maximum crystallinity obtained was 77.5%, maximum tensile strength was 67,840 Psi (0.468 G Pa). There were no changes in dimensions when kept in an oven at 100°C and at 140°C for a maximum of one hour.

It was demonstrated that the horizontal extrusion can be done without producing surface defects and can enhance the orientation. The work suggests that the samples can be reproducible if the flow
rate and temperature of the coolant are controlled.