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Elongational Rheology of Polyethylene Melts.

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**ELONGATIONAL RHEOLOGY
OF POLYETHYLENE MELTS**

A Dissertation

**Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy**

in

The Department of Chemical Engineering

by

**Bijan Seyfzadeh
B.S., Iowa State University, 1992
M.S., Louisiana State University, 1996
December 1999**

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ABSTRACT

Elongational melt flow behavior is an important and fundamental concept underlying many industrial plastics operations which involve a rapid change of shape as for example fiber spinning and stretching, bottle blow molding, and film blowing and stretching. Under high process loads polymeric materials experience enormous stresses causing the molecular structure to gain considerable orientation. This event has significant effects on the melt flow behavior and can be measured in terms of elongational viscosity and changes in enthalpy and entropy. Different polymeric materials with unique molecular characteristics are expected to respond uniquely to the elongational deformation; hence, molecular parameters such as molecular weight and degree of branching were related to the measurable elongational flow variables.

Elongational viscosities were measured for high and low density polyethylenes using an advanced capillary extrusion rheometer fitted with semi-hyperbolic dies. Said dies establish a purely elongational flow field at constant elongational strain rate. The elongational viscosities were evaluated under influence of process strain rate, Hencky strain (natural logarithm of area reduction of the extrusion die), and temperature. Enthalpy and entropy changes associated with the orientation development of semi-hyperbolic processed melts were also determined.

Results showed that elongational viscosities were primarily affected by differences in weight average molecular weight rather than degree of branching. This effect was process strain rate as well as temperature dependent. An investigation of melt relaxation and the associated first decay time constants revealed that with increasing strain rate the molecular

field of the melt asymptotically gained orientation in approaching a limit. As a result of this behavior molecular uniqueness vanished at high process strain rates, yielding to orientation development and the associated restructuring of the melt's molecular morphology.

Flow induced orientation was measured in form of enthalpy changes that were largest for the highest elongational strain rates and larger Hencky strain. The enthalpy changes were in magnitude one order lower than the polymer's heat of fusion. This explained why peak melt temperatures, evaluated by differential scanning calorimetry, remained unchanged in magnitude with a rise in process strain rate and Hencky strain.

CHAPTER 1: JUSTIFICATION FOR RESEARCH

Whereas the field of shear rheology has been well established and countless publications are communicated through respected journals the related and equally important branch of elongational rheology is still at an early developing stage. Elongational melt flow behavior is an important and fundamental concept underlying many industrial plastics operations which involve a rapid change of shape (Collier et al., 1998). Examples include fiber spinning, extrusion through converging nozzles, film stretching and blowing, bottle blowing, and injection molding. Although in many of these processes the elongational flow dominates, it almost always is accompanied by shearing effects. This implies that it is inherently difficult to establish, control and measure a purely elongational flow field. This statement may also be reworded by saying that it is difficult to prevent, compensate or measure shearing effects that occur along with elongational flow. Moreover, most elongational rheometers operate at elongational rates at least an order of magnitude below those of industrial processes.

When polymer melts are subjected to processing operations such as those mentioned in the previous paragraph, the material experiences enormous stresses which force the macromolecular matrix to gain considerable orientation; i.e., the molecular chains align in a more orderly close-packed fashion. This event has significant effects on the melt flow behavior and can be measured in terms of elongational viscosity and changes in entropy and enthalpy. The orientation development also determines the final product's mechanical and bulk properties such as resistance to stresses, toughness and degree of crystallinity. Knowledge of a polymeric material's elongational melt flow behavior in form of said

measurable parameters is useful information in terms of selecting an adequate polymer grade for a particular application when expecting desired product properties. Moreover, the ability to quantitatively assess the forces that result in an orientation developing flow profile opens the possibility for on-line process control with fast process parameter adjustments and material property selection. Since there is a large number of polymer classes and grades commercially available to plastics processing clients, there are also many material properties to choose from. The uniqueness of a polymer is most frequently measured and expressed in terms of molecular weight, molecular weight distribution, degree of side chain branching, and degree of crystallinity. How these characteristics are brought about depends a lot on operating parameters and conditions during the polymerization and subsequent processes. It is expected that material properties will affect the elongational melt flow behavior. Hence, such molecular characteristics should be related to the previously mentioned measurable elongational flow variables.

Previous research in this group (Pendse, 1995; Kim, 1994) brought forth that polymer melts can be elongationally characterized at processing strain rates. The method used by Pendse involved coextrusion of a polypropylene core with a polyethylene skin, where the skin with its much lower viscosity functioned as a lubricating layer to dissipate shearing effects at the wall. Using a hyperbolic slit and a semi-hyperbolic conical die, measurements showed that the core was essentially in purely elongational flow at constant strain rate. Further attempts to find a correction factor for skinless extrusion lead to the conclusion that the orientation developing effects of the melt are so substantial that shearing gradients near the wall become comparatively insignificant (Romanoschi, 1998; Collier et

al., 1998). This discovery was theoretically justified by developing stream functions expressing the hyperbolic flow convergence and potential functions describing the pressure profiles as the driving force.

As a continuation of these previously established results the concept of purely elongational flow imposed by the unique semi-hyperbolic contour profile is now applied to a broader class of materials. Polyethylenes are at the center of interest for which elongational flow characteristics and molecular orientation development are investigated in view of macromolecular characteristics.

CHAPTER 2: RELEVANT BACKGROUND

2.1 Elongational Rheometry

Rheometry, synonymous with rheology, is the science of deformation of materials, either solids, liquids, or gases, under the influence of stresses (Schramm, 1994). An ideal solid in a rheological sense is one that deforms elastically; i.e., the energy necessary to accomplish the deformation is fully recovered after the stresses have ceased to act. Ideal fluids (liquids and gases) deform irreversibly; i.e., the fluid material cannot sustain a shear stress in the absence of motion (Denn, 1980). The energy necessary to accomplish the deformation is dissipated through the fluid bulk. In reality very few materials behave nearly ideally as just described. Most liquids that are of interest to the rheologist exhibit a behavior somewhat both viscous and elastic, hence the term “viscoelastic” (Schramm, 1994).

In pure extensional flow the deformation of a material occurs along streamlines; i.e., two fluid particles located on the same axis are forced to move further apart. This requires the acting force to be parallel to the normal of the plane on which the force acts. On the other hand in simple shear flow two fluid particles located on the same streamline do not move further apart. Instead, material particles on different streamlines are dislocated relative to each other. This implies that the acting force is perpendicular to the normal of the plane on which the force acts (Dealy et al., 1990). The sketches in Figure 2.1 visually illustrate the difference between elongational (upper illustration) and shear deformation (lower illustration). In purely elongational flow (shear free) the strain rate is the same for all material particles and the strain tensor has only diagonal components. If a non-simple fluid material, previously unoriented, is subjected to simple (uniaxial) extension the molecular

conformation will adjust itself and respond to the extensional stress by alignment of molecular strands along the axis of symmetry. Since most melt processing operations have at least a component of extensional flow, these processes are always accompanied by stretching along stream lines (Dealy et al., 1990).

Figure 2.1: Elongational and Shear Deformation Compared

In converging flow, such as dies and nozzles, the melt experiences an acceleration due to the reduction in cross sectional area. Depending on the geometry of the flow constriction (slit or cone) the fluid will be subjected to planar or uniaxial flow extension. Near the wall where the material adheres to the flow surface shearing effects become more important. However, in operations that involve rapid changes of shape elongational flow is the dominant mode of flow (Collier et al., 1990). A few examples for such processes are fiber spinning and stretching, film blowing, film stretching, injection molding, and extrusion through converging channels. Measuring purely elongational properties and controlling a mixed flow mode is inherently difficult since said shearing effects cannot be easily isolated or diminished. Moreover, commercially available elongational rheometers are typically

operating at strain rates of at least one order lower than those measured in industrial processes (Collier et al., 1990).

In this context it seems appropriate to review the concept of shear viscosity versus elongational viscosity. Newton defined shear viscosity as the ratio of shear stress to shear rate (Agassant et al., 1991) or stated in a different way, an applied shear stress is proportional to shear rate by a proportionality constant, namely viscosity. Analogously, Trouton defined in 1906 the elongational viscosity to be the ratio of normal stress to strain rate. He also showed that for the case of a Newtonian fluid the elongational viscosity equals three times the shear viscosity (Agassant et al., 1991).

2.2 Capillary Rheometers

Rheometers that are capable of measuring flow through a small diameter die are referred to as capillary rheometers. In flow through a capillary the fluid is driven by a pressure difference between the inlet and outlet of the capillary. In a well designed typical capillary rheometer the fluid flows through the straight capillary attaining a parabolic velocity distribution across the radial dimension. This can be compared to visualizing a telescopic-like displacement of tube-like liquid layers sliding over each other (Schramm, 1994). If the flow channel is a slit, the channel width should be much larger than the depth to minimize wall effects. Capillary rheometers differ in their design. Some utilize a variable pressure force to drive the fluid, while in others the fluid is gravity driven. Also, the capillary design itself can vary greatly using conventional straight channels with low or high aspect ratios (length to diameter) or unconventional shapes such as linear or (semi-) hyperbolic cones.

A variable pressure capillary rheometer utilizes a plunger, ram or similar device to force the liquid at programmable speeds through the die contraction. There is at least one pressure sensor located above the capillary entrance far enough from the capillary edge to minimize entrance and exit errors. The pressure transducer's sensitive part is a thin metal membrane that bends in response to the melt pressure. The mechanical deflection is translated into an electronic signal. The melt viscosity depends on the pressure drop measured in the capillary and the melt flow rate. Melt viscosities can be obtained for temperatures well above the melt point of common polymers and for strain rates approaching those in industrial polymer processing. Very high strain rates require the use of so called rod capillaries with diameters ranging from 1 to 3 mm (Schramm, 1994). To minimize entrance effects these capillaries are designed with aspect ratios typically of 20 or higher.

In a gravity force capillary viscometer the liquid sample flows through the capillary by its own weight. The sample runs from a reservoir into the entrance of the capillary orifice. The weight of the liquid column above the exit of the capillary channel is the potential energy of the sample which drives the liquid. A viscosity related time period is measured for a fixed volume of test liquid to flow between two marks. The kinematic viscosity is a function of this time period and a constant related to the dimensions of the capillary orifice.

2.3 Approaches to Measuring Elongational Melt Flow

Significant progress in the study of elongational rheology has only been accomplished in recent years. As mentioned earlier, the presence of shear effects near or at

surfaces of flow channels inhibit the investigation of elongational flow behavior. Also, a steady and controlled elongational flow field is difficult to generate (Collier et al., 1998). Nevertheless, valuable results have been reported from various groups, especially for extensional flow of polyolefins.

Low-density and linear low-density polyethylene (LDPE and LLDPE) were characterized by the degree of strain hardening during elongation (Bailey et al., 1994). A molten monofilament was drawn and stretched non-isothermally with the aid of a small single screw extruder. The method would allow comparison to typical processing applications such as tubular film blowing by measuring the resistance to elongational flow as a function of apparent elongational strain rates. Said resistance presented as line tension was found to decrease with increasing melt temperature regardless of polymer type. LDPE resins exhibited line tensions much higher than LLDPE resins which was found to be due to the branching distribution and slower rate of crystallization of LDPE. Another group (Müller et al., 1994) investigated the shear and elongational behavior of LLDPE and LDPE blends by capillary rheometry. The blend formulation was chosen with the intention to combine the ease of processing LDPE with the desirable mechanical properties of LLDPE. Results showed that the blends' rheological behavior was dependent upon changes in the molecular weight of LDPE. High molecular weight LDPE blends produced shear viscosities about equal to the LDPE homopolymer for concentrations of LLDPE up to 25%. Low molecular weight LDPE blends exhibited the same shear behavior, but the apparent extensional viscosity of the blend was found to be somewhat higher than that of the LDPE homopolymer.

Martyn and Coates (Martyn et al.) in the UK performed an image analysis of polypropylene (PP) melt fiber stretching. The fibers were extruded by a capillary rheometer and drawn at constant speeds from a computer controlled take up device. The total strain rate and tensile stress were calculated based on the imaged diameter profile of the drawn fiber and load measurements. The draw down characteristics of the melt were found to depend upon the weight average molecular weight. The melt's extensional viscosity decreased with increasing strain rate. Shear and elongational flow properties of PP melts were also investigated by Hingmann and Marczinke of BASF in Germany (Hingmann et al., 1994). Polypropylene melts were subjected to oscillatory shear, capillary rheometry, and uniaxial elongation at constant tensile stress and strain rate. At low stresses linear PP melts produced a threefold elongational viscosity to shear viscosity. With increasing stress both shear and elongational viscosity decreased. Polypropylene melts, intentionally modified to have long chain branches, exhibited a peak in the steady state elongational viscosity.

An isothermal melt spinning experiment of LDPE was performed by Wagner (Wagner, 1998). The investigator concluded that the analysis of extensional flow in polymer processing is complicated by the complex rheological prehistory of the melt in the extrusion die, the length of the spin line, and the fact that extension is performed under controlled force/pressure rather than controlled kinematics.

The response of flexible polymers to a sudden elongational flow was investigated by Smith and Chu (Smith et al., 1998). The authors subjected individual polymers at thermal equilibrium to a sudden elongational flow at a high strain rate and recorded the dynamics with video fluorescence microscopy. The rate of stretching of individual molecules was

found to be highly variable and depended on the molecular conformation that developed during stretching. The variability was thought of being caused by the dynamics on the initial, random equilibrium conformation of the polymer coil.

Findings on elongational flow-induced crystallization under the super cooled state were reported in a series of papers by Okamoto, Kubo, and Kotaka. Polyethylene terephthalate (PET) was investigated with the aid of elongational flow opto-rheometry and temperature-modulated differential scanning calorimetry in the temperature range from 100 to 130°C (Okamoto et al., 1998). Below 110°C spherulite growth was negligible and the effect of crystallization on the up-rising in elongational viscosity as a function of time determined at different strain rates was found to be small for a constant characteristic Hencky strain of 1. Between 120 and 130°C spherulites were formed during the early stages of elongational deformation and contributed significantly to the elongational viscosity as the strain rate increased. Eventually, the spherulites would be deformed or broken down to form oriented crystallites. In a similar effort, polyethylene naphthalate (PEN) was also investigated (Okamoto et al., 1998). It was found that flow induced orientation development was governed by the dimensionless strain rate defined as the ratio of strain rate to the spherulite growth rate under the quiescent state. Either oriented crystallite formation or spherulite growth dominated the elongational behavior, depending on the dimensionless strain rate being above or below a critical Hencky strain of 2.65, respectively.

Many other groups reported equally important and relevant findings such as elongational properties of polymer melts by gravity spinning (Patel et al., 1989), flow visualization for extensional viscosity assessment (Nakason et al.), spinline measurements

for elongational material characterization (Ramanan et al., 1996), influence of elastic properties on drop deformation in elongational flow (Mighri et al., 1997), extensional rheometry of polymer multilayers (Levitt et al., 1997), elongational viscosities of random and block copolymer melts (Takahashi et al., 1998), uniaxial elongational flow of particle-filled polymer melts (Greener et al., 1998), polymer stretching in an elongational flow (Neumann, 1999), uniaxial extensional characterization of a shear thinning fluid using axisymmetric flow birefringence (Burghardt et al., 1999), and necking phenomenon in high-speed fiber spinning based on flow induced crystallization (Kulkarni et al., 1998) to mention the most recent publications.

The above summarized results indicate that the assessment of elongational melt flow is strongly influenced by molecular parameters such as molecular weight and branching, and that extensional measurements are prone to depend on experimental conditions due to the non-uniform extensional history of the polymer and the non existence of an equilibrium strain. Such inherent aspects of extensional melt flow have previously lead this group (Collier et al., 1998) to derive a unique model in combination with appropriate experimental conditions to address and overcome said difficulties in characterizing an elongational melt profile. The relevant details will be presented in a later chapter.

2.4 Polyolefins: Classification and Characteristics

A large variety of polyolefins are commercially available on the market. In this study only polyethylenes were investigated which are the most widely produced polyolefins. In the future polypropylene will be included in the investigation of elongational melt flow as

well, because it is an equally important member of the polyolefin family. For this reason, polypropylene will also be introduced and classified in this chapter.

2.4.1 Polyethylene (PE)

Polyethylenes are synthesized in greater amounts than any other thermoplastic on the market. Manufactured by addition polymerization, their basic structure is the n -repeated ethylene monomer $-(CH_2-CH_2)_n-$. Commonly available PEs are classified according to density ranges, molecular weight, or structure, and are therefore unique with respect to processing and melt behavior and applications: low density polyethylene (LDPE) 0.915-0.935 g/cm³, high density polyethylene (HDPE) 0.941-0.967 g/cm³, linear low density polyethylene (LLDPE) 0.910-0.925 g/cm³, very low density polyethylene (VLDPE) 0.880-0.912 g/cm³, high molecular weight polyethylene (HMWPE) 200,000-500,000, ultrahigh molecular weight polyethylene (UHMWPE) 3,000,000, crosslinked PE, chlorosulfonated PE, copolymer PE (Feldman et al., 1996).

The ethylene monomer along with other olefins is derived from petroleum and natural gas. Petroleum is first separated into broad fractions by distillation, and the fractions are then thermally cracked (pyrolysis). By subsequent fractional distillation individual products are separated. In the case of natural gas, the methane and C₂-C₅ hydrocarbons are converted by thermal cracking to olefins which are subsequently cleansed of impurities. Commercial production of PE dates back to 1939 at Imperial Chemical Industries Ltd., UK. Other manufacturers followed soon with the Ziegler catalyst polymerized process of Hoechst AG in Germany; Phillips Petroleum Co. in 1957 and Standard Oil Co. in 1961 in the U.S., and the low pressure polymerization process of Union Carbide in 1968 to produce

HDPE in the gas phase without solvents (Feldman et al., 1996). In recent years research has been especially devoted to improve existing or derive new catalysts (super high activity Ziegler catalysts, metallocene catalysts) allowing for superior control over the product's molecular weight, polydispersity (MWD), and branching characteristics, as well as copolymer production.

Typical product applications for PEs are electrical insulation, package film, domestic goods (bottles, containers, etc.) and toys, just to mention a few. Applications depend on the polymer's characteristics which in turn depend on properties such as melt index (MI), molecular weight (MW), polydispersity (MWD) and degree of branching (Feldman et al., 1996).

2.4.1.1 Synthesis of Polyethylenes

Low density polyethylenes are commonly synthesized by free radical addition polymerization at high temperatures and very high pressures. The free radical initiator is typically benzoyl peroxide or oxygen. Since the growing polymer radical chains have only a limited life span to interact and react with a new monomer, the latter's concentration needs to be sufficiently high to prevent premature chain termination and allow for high MW polymer yields. This requires process pressures in the range of 150-350 MPa and temperatures of 80-300°C (Feldman et al., 1996). Given these conditions and the highly exothermic nature of the reaction, adequate temperature control is required. At temperatures that are too high ethylene may decompose into methane, hydrogen and carbon, raising the gas phase pressure to an explosive level. Moreover, efficient temperature control must prevent a runaway reaction. These safety considerations are accomplished by carrying out

the polymerization in reactors with high cooling surface to volume ratios, inert diluents (benzene or water) to remove excess heat, and by injecting the initiator at different locations into the reactor to prevent local concentration build-up. The reaction is carried out in long tubular reactors or stirred autoclave reactors.

High density polyethylenes are produced in catalytic processes at fairly low pressures. The choice and nature of catalyst is important with regard to achieving the desired product properties. In the Ziegler process the catalyst forms a coordination complex with the monomer, which controls the approach of the monomer to the growing chain. The catalyst complex consists of a group IV-VIII transition metal (catalyst) and a group I-III organometallic compound (cocatalyst). The choice of the catalyst complex constituents will determine the efficiency of the polymerization and the properties of the product. During the reaction each catalyst site initiates one growing polymer particle. The catalyst particle eventually disintegrates and disperses throughout the polymer particle.

In the Phillips process the catalyst consists of a transition metal compound (chromium oxides) on silica or silica-aluminum support. The reaction is carried out in solution or slurry where the temperature controls the MW of the product. The solution process is carried out at 130-160°C in a liquid hydrocarbon such as cyclohexane. Since the solution temperature is above the melting point of the polymer, the product dissolves and the solution acts as a heat transfer agent. In the slurry process the temperatures are 90-100°C, hence solubility of the PE is very low. The pressures in these processes range from 1.4-3.5 MPa (Feldman et al., 1996).

2.4.1.2 Properties of Polyethylenes

Macromolecular uniqueness of polyethylenes is mostly due to degree and type of branching, MW, and polydispersity as mentioned previously. Branching is affected by processing parameters such as temperature, pressure, selection of catalyst, and transfer agent. A polymer's density is an indirect measure of its degree of branching, since branching prevents the molecular strands from an orderly and close-packed arrangement. Therefore, branching diminishes the polymer's ability to crystallize. The lower the density the higher the degree of branching. Densities of PEs can be as high as 0.98 g/cm^3 for rigorously linear chains. LDPE has a degree of crystallinity of 55-70% as opposed to HDPE with 75-90% (Feldman et al., 1996). PEs have crystalline melt temperatures between 108-132°C varying with degree of crystallinity. With increasing degree of crystallinity also stiffness, hardness, tear strength, yield point, and Young's tensile modulus increase. PEs do not dissolve readily in solvents due to their crystalline, non-polar nature. Dissolution takes place upon heating in solvents with similar solubility parameters. Type of branching influences different polymer characteristics. Short branches affect predominantly crystallinity and density, long branches affect polydispersity. Side chains can be as long as the main chain. The higher the MW, generally the wider the distribution (weight- to number-average MW). Distributions vary from 1.9 to 100. HDPEs have distributions from 4-15 (Feldman et al., 1996). Narrow molecular weight distributions increase impact strength, tensile strength, toughness and softening point of the polymer.

Long chain branches also affect melt flow characteristics. Long branched molecules entangle less than unbranched molecules with other molecules causing lower melt and

solution viscosities. Figure 2.2 illustrates branching characteristics of polyethylenes. Melt properties are also influenced by the weight average MW. With increasing MW tensile strength, tear resistance, low temperature toughness, impact strength and softening point increase. For processing reasons the MW is related to the melt flow index (MI) defined as the mass of polymer in grams extruded under a standard load of 2.16 kg at 190°C in a period of 10 minutes through a 2.095 mm diameter, 8 mm long capillary according to ASTM D1238 (Progelhof et al., 1993). Generally, the higher the MI the lower the MW.

Figure 2.2: Branching Characteristics of Polyethylenes

2.4.1.3 Applications

Due to their unique properties, easy processability and low cost, PEs span a wide range of application possibilities. They are suitable for electrical insulation purposes such as wire coating for undersea cables, and are widely used in the manufacturing of film for packaging (bags, food wrapping, etc.). HDPE is used for toys, electrical fittings, seals, containers, cases, housewares and especially for blow molding applications of milk and water containers. Squeeze bottles are made of LDPE. PEs have also been used for water, gas, and agricultural piping.

2.4.2 Polypropylene (PP)

Polypropylene is one of the fastest growing commodity polymers in the plastics industry. It ranks third in production volume after PE and polyvinyl chloride (PVC) (Feldman et al., 1996). PP is manufactured by stereospecific addition polymerization of the propylene monomer. The monomer is derived from cracking and subsequent fractional distillation of petroleum or natural gas. Commercial production of the polymer was possible due to the discovery of a heterogeneous stereospecific Ziegler catalyst and began in 1957 at Montecatini, Italy, Hercules, U.S.A., and Hoechst AG, Germany. The three stereospecific forms of PP are isotactic with methyl groups located at the same side of the chain, syndiotactic with methyl groups located on alternating sides, and atactic (also called heterotactic) with methyl groups located randomly along the carbon backbone (Figure 2.3). Isotactic and syndiotactic PP are crystalline, atactic PP is amorphous. PP is produced in various grades as homopolymer, copolymer, and blends.

2.4.2.1 Synthesis of Polypropylene

The synthesis of PP depends mostly on the employed Ziegler catalyst in that composition, shape and size of the catalyst determine the polymer's properties. A well chosen and manufactured catalyst will provide high product yields and adequate control over MW. There are three Ziegler based processes, namely the slurry process, the solution process, and the gas phase process.

The slurry process is carried out in a stirred batch or continuous loop reactor. The catalyst, monomer and slurry base (C_4 - C_6 paraffin) are fed separately into the reactor. The

**Isotactic
PP**

**Syndiotactic
PP**

**Atactic
PP**

Figure 2.3: Stereoisomeric Structures of Polypropylene

reactor operates at 50-80°C and 0.5-3.0 MPa (Feldman et al., 1996). Isotactic polymer grows around the catalyst sites and is insoluble in the diluent forming a slurry. Some atactic amorphous polymer develops along and dissolves in the diluent. When the slurry is 30-60% rich in solids the reaction mixture is pumped into a flash unit to separate out and recycle any unreacted monomer. The catalyst is solvated and deactivated by the addition of acidified alcohol. The slurry is centrifuged to claim the crystalline isotactic polymer. The diluent portion contains the atactic polymer. Subsequent purification yields isotactic and atactic PP. Modern improved catalyst performance yields at least 40 kg polymer per gram catalyst.

The solution process is more expensive and used only for special-property PP grades having higher impact strength and lower brittleness temperatures. Reaction temperatures range from 160-250°C at pressures from 2.7-8.0 MPa allowing the polymer to dissolve in the liquid monomer.

In the gas phase process high rates of recycled monomer stabilize fluidization. The reactor consists of two parts, the polymerization zone at the bottom where the engagement and reaction with the catalyst occur and the disengagement zone where the unreacted monomer separates from the solid particles. The product particles collect at the bottom of the reactor and are continuously withdrawn, the unreacted monomer is recycled. Metallocene catalysts are capable of controlling stereoregularity in the propylene chain due to the steric design of the π -ligands which are associated to the metal atom by π -bonds. Four types can be synthesized: isotactic, syndiotactic, atactic, and hemiisotactic. In hemiisotactic PP every other methyl group is on the same side of the chain, the remaining methyl positions are at random.

2.4.2.2 Properties of Polypropylene

The crystallinity of PP depends on its stereoregularity. The microstructure of isotactic PP consists of right- and left-hand helices where the methyl groups are located at the outside of the helix. This allows for a close-packed arrangements of molecular strands and therefore regions of crystallinity. PP grades which are predominantly isotactic may also contain atactic and syndiotactic blocks. The degree of crystallinity depends on the relative amount of the isotactic conformer. In order to obtain high crystallinity PP nucleation agents (organic acids or metal salts) are added to the polymerization process in small amounts to stimulate the growth of smaller and more numerous polymer crystals. The resulting product exhibits tougher bulk properties with regard to stiffness, softening point, tensile strength and hardness.

The melt temperature of isotactic PP is 176°C, its glass transition temperature, T_g , is 0°C, the density is 0.903 g/cm³ (Feldman et al., 1996). Below T_g the polymer becomes brittle. Because of the non-polar nature of PP it has an insulating character similar to PE. PP is insoluble at room temperature and dissolves in hydrocarbons and chlorinated hydrocarbons at 80°C. It is very resistant towards most chemicals and solvents.

The MI of PP can vary from 0.3 to well over 1000 g/10min. The weight-average MW of PP ranges from 220,000-700,000 and the polydispersity can be between 5.6 and 11.9 (Feldman et al., 1996). MW and MWD depend on process factors such as temperature, pressure, concentration of monomer, presence of transfer agents, and of course the composition of the catalyst.

Speciality PP grades have been manufactured by incorporating other materials into the polymer's structural matrix to achieve certain desired properties. Tensile strength and rigidity can be considerably improved by adding glass fiber. Rubbers are employed as fillers to improve impact strength. Foaming agents improve the ratio of stiffness to weight.

2.4.2.3 Applications

PP and its copolymer derivatives are especially used in the production of fibers by extrusion. Resistance towards wear and low cost production provide a multitude of applications in woven and non-woven carpeting, clothing, drapes, tea bags, wall coverings, furniture and automotive upholstery, ropes and netting. Other applications include wire coating, piping, sheet and film for packaging. Injection molded products include toys, laboratory and medical supplies, housewares, appliances, luggage, automotive battery housing, pump housing, dishwasher parts, refrigerator and freezer parts. Atactic PP which has a consistency between that of wax and rubber has been found to be compatible with mineral fillers and bitumens. It is therefore used for roofing materials, as asphalt additive, for sealing and adhesive compounds, and for paper lamination.

2.4.3 Metallocene Catalysis

Metallocene based processes have gained much attention in recent years for that metallocene catalyst systems are extremely efficient and allow for superior control of product quality. Degree of branching, stereoregularity and uniform chain length are well predictable and the catalyst renders precise control over comonomer incorporation. One gram of catalyst can produce product yields in excess of one ton per hour (Feldman et al., 1996). Many comprehensive reviews and publications on metallocene catalyst systems have

been made available to the scientific community (Benedikt et al., 1998; Benedikt et al., 1999).

The metallocene complex has the basic structure L_2MX_2 , where M is a group IV transition metal (titanium, chromium, zirconium, hafnium), X is a halogen, an alkyl, phenyl, or benzyl group, and L is a ligand to the transition metal through its π -bonds such as cyclopentadienyl, indenyl, or fluorenyl (Figure 2.4). The ligands can be unsubstituted or include substituents attached to their ring structure. In some cases the ligands may be linked

Figure 2.4: Structures of Typical Metallocene Ligands

by an ethylene or isopropylene bridge. There are two types of metallocene complexes in use, bicomponent systems and single component systems. The bicomponent system contains an alumoxane compound as the cocatalyst. The function of the alumoxane is to produce and stabilize active metallocene cations. During the polymerization process, the monomer approaches the highly electrophilic cationic complex such that the unsaturated π -electrons coordinate with the positively charged metal complex. A four-center transition state follows in which the monomer is incorporated through a metal-carbon bond. Through the migration of the polymer chain a vacant catalyst site is regenerated at the location originally occupied by the polymer chain (Feldman et al., 1996):

where P = polymer, x = vacant site, and M = group IV transition metal. The termination of the polymer chain occurs through chain transfer to aluminum, to monomer, or to hydrogen eliminations.

Proper design of the catalyst complex is necessary to assure metallocenes of desired productivity rate and ability to control MW and MWD. Factors such as the composition of the cocatalyst, the ratio of catalyst to cocatalyst, and unique operating temperature for each metallocene system influence the productivity, MW and the kinetic profile of the polymerization process.

Single-component metallocene systems are ionic complexes of form $[\text{Cp}_2\text{MR}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. Polymerization of olefins occurs without the aid of alumoxane cocatalyst. The active part is the cationic constituent which is stabilized by the anionic counterpart. For the synthesis of PE the MW, MWD and yield depend on the nature of the ligands, metal and counterion in the ionic complex and on the polarity and temperature of the solvent.

CHAPTER 3: EQUIPMENT AND MATERIAL SPECIFICATIONS

Melt flow behavior of selected polyethylenes having unique molecular characteristics was investigated by the aid of a capillary rheometer. The instrument provides data for shear viscosities at varying strain rates when using straight capillary dies and when properly altered enables determination of elongational viscosities based on recorded equilibrium melt pressures. A separate conventional shear rheometer with rotational and oscillatory shearing functions was used to broaden the rheological investigation and to fully characterize the melt behavior of said polymer samples at processing temperatures.

The acquisition of the polymeric materials required a careful selection of class representative, uniquely defined polymer grades to meet the research objectives. All samples are commercially manufactured. All results presented in this work relate to LDPE and HDPE grades.

3.1 The Advanced Capillary Extrusion Rheometer (ACER)

The ACER is a state-of-the-art pilot scale capillary rheometer made by Rheometric Scientific® Inc. The existing instrument has been software-upgraded for advanced fully automatic control at precise strain rate operation. The ACER deforms a sample by forcing it through a capillary channel and calculates an apparent viscosity. The flow of the melt is accomplished by a ram which moves at constant velocity through a precisely-bored cylindrical barrel of known diameter as illustrated in Figure 3.1. From the barrel the melt enters the die with known length and diameter. A pressure transducer located just above the entrance of the die measures the melt pressure and translates the analog deflection of the

Figure 3.1: The Advanced Capillary Extrusion Rheometer (ACER) Fitted with a Hencky 6 Semi-Hyperbolic Die

transducer's membrane into an electronic signal. The transducer communicates the measured signals to the computer. A measurement at a set strain rate comes to completion when the pressure has reached an equilibrium plateau. The pressure values are continuously plotted against time and are updated and displayed every 10 seconds on the terminal screen.

The barrel can be heated by three independent electrical band heaters located around the outside of the cylindrical barrel. Each heater is fitted with a thermocouple to measure and report temperature. The instrument is capable of performing Bagley and Cogswell entrance corrections.

3.2 The Rotational Shear Rheometer

Rotational and oscillatory shear measurements were obtained using a Bohlin VOR Rheometer made by Bohlin Instruments, Inc.. The apparatus is capable of performing said rheological measurements at controlled temperature via an attached heating unit. In the viscometry mode a steady rotational speed is applied. The rotational motion is obtained by a DC motor drive with the clutch disengaged (Figure 3.2). Shearing rates are software controlled. The DC drive's electronics are equipped with a brake function enabling rapid velocity decrease or stop. During shearing the sample's response to deformation is transmitted through the plate's shaft to a torsion bar suspended in an air bearing. The torsion of the bar causes a lever arm to deflect. The deflection of the torsion arm is translated into an electronic signal and fed to the computer for calculations. In the oscillation mode the angular deflection of the stage holding the plate assembly is brought about by a position servo actuator with the clutch engaged. Shear viscosities are measured and displayed on the screen as a function of set frequencies. Storage and loss modulus are also displayed.

Figure 3.2: The Bohlin Shear Rheometer and its Basic Functions

3.3 Selected Polymer Grades

Five commercial LDPE pelletized grades have been acquired, three of which are copolymers and two of which are homopolymers. There are also five commercial, pelletized HDPEs that were used, three of which are blow molding grade copolymers and two of which are high molecular weight extrusion/blow molding copolymers. Table 3.1 below summarizes the known specifications. The measured elongational viscosities were related to the branching and molecular weight characteristics.

Table 3.1: Polymer Grades and their Molecular Characteristics

Material	MI (g/10 min)	Density (g/cm ³)	MW GPC analyzed	MWD GPC analyzed
LDPE-A	1.2	0.9	97,550	2.22
LDPE-B	7.5	0.9	56,950	1.99
LDPE-C	2.2	0.895	83,350	2.24
LDPE-D	2.3	0.919	86,650	6.85
LDPE-E	2.0	0.923	80,350	5.15
HDPE-A	0.3	0.943	105,200	9.74
HDPE-B	0.3	0.95	125,400	8.09
HDPE-C	0.3	0.954	125,700	13.0
HDPE-D	0.1	0.949	183,200	14.77
HDPE-E	0.1	0.949	154,100	12.63

CHAPTER 4: METHODOLOGY

4.1 Theoretical Basis to Data Acquisition

As mentioned earlier, the theoretical foundation for the analysis of elongational melt flow data was established previously in this group for the semi-hyperbolic converging die geometry (Collier et al., 1998). In order to facilitate the reader with a better understanding of those concepts underlying the data processing and the results to be discussed, the theoretical development is sketched out here. A complete and detailed analysis has been reported elsewhere (Collier et al., 1998).

The semi-hyperbolic die was designed for the melt or solution to maintain a constant elongational strain rate throughout the core. This is accomplished by describing the channel surface with the equation $R^2z = C$, where z is the axial flow direction, R is the radius of the flow channel, and C is a constant. Two of the semi-hyperbolic dies used in this research were ones having a Hencky strain, ϵ_h , equal to 6 and 7. The Hencky strain is defined as the natural logarithm of the ratio of die entrance area to exit area; therefore, $\epsilon_h=6$ corresponds to an area ratio of approximately 400, and $\epsilon_h=7$ to 1100. A sketch of the $\epsilon_h=6$ die appears in Figure 3.1.

When the melt flows through the semi-hyperbolic channel it assumes the shape of the die surface; i.e., layers of the melt may be viewed as stream lines experiencing the same conditions. These stream lines can be described by the stream function, Ψ , forming a two dimensional surface. The stream function is defined to satisfy the continuity equation, and in shear free flows the potential function, Φ , can also be defined. Hence, ψ and Φ are mutually orthogonal and for shear free flows Φ satisfies the irrotationality equation and for

pressure driven flows describes a constant pressure surface. For the axisymmetric die geometry a cylindrical coordinate system seems most appropriate, for which the stream function is defined as:

$$\Psi = -\frac{\dot{\epsilon}}{2} r^2 z \quad (4.1)$$

and the potential function is given as:

$$\Phi = \dot{\epsilon} \left(\frac{r^2}{4} - \frac{z^2}{2} \right) \quad (4.2)$$

The pressure, P , is directly proportional to $\rho \dot{\epsilon} \Phi$, where $\dot{\epsilon}$ is the elongational strain rate, and ρ is density. The velocity components in cylindrical coordinates are (Bird et al., 1960; Collier et al., 1998):

$$v_z = -\frac{1}{r} \frac{\partial \Psi}{\partial r} = -\frac{\partial \Phi}{\partial z} = \dot{\epsilon} z \quad (4.3)$$

$$v_r = \frac{1}{r} \frac{\partial \Psi}{\partial z} = -\frac{\partial \Phi}{\partial r} = -\frac{\dot{\epsilon}}{2} r \quad (4.4)$$

The non-zero velocity gradients are:

$$\frac{\partial v_z}{\partial z} = \dot{\epsilon}, \quad \frac{1}{r} \frac{\partial (rv_r)}{\partial r} = -\dot{\epsilon}, \quad \frac{\partial v_r}{\partial r} = -\frac{\dot{\epsilon}}{2} \quad (4.5)$$

The fundamental equations describing the flow are the equation of continuity (conservation of mass), conservation of energy expressed in terms of enthalpy per mass unit, $\dot{H}$, conservation of momentum, and the irrotationality equation for potential flow. Mass, momentum and energy balances are conserved separately. An internal body force term must be taken into account. It represents the force per unit volume required for orientation development and can be viewed as the force necessary to overcome the resistance towards developing the orientation imposed onto the melt by the converging shape of the die. As mentioned earlier, the semi-hyperbolic shape is one that provides a constant strain rate and constant resulting stress. The flow is therefore at constant acceleration as shown by the velocity gradient equations. This is not the case in shearing flow where a stress gradient acts in normal direction to the sheared surface and the stress tensor includes a shearing component gradient. Because of the constant elongational strain rate and strong dominance of the orientation development, the flow through the semi-hyperbolically converging die is expected to be essentially purely elongational. The only significant non-zero velocity gradients are in flow and transverse direction; hence, the only significant non-zero components of the deformation rate tensor, Δ , are the normal components.

Apart from what has been mentioned up to this point, the theoretical development is founded on the following considerations: 1. The strain rate state determines the stress state; i.e., the fluid can be described by a generalized Newtonian constitutive equation (not necessarily a Newtonian fluid, but a general viscous or viscoelastic model). Moreover, the die geometry, assuming negligible shearing gradients, dictates that the only significant non-zero deformation rate components are the normal components and these components are not

a function of position; therefore, the only significant non-zero stress components are the normal components, and the stress components are not a function of position. 2. The melt is incompressible. 3. The system is in an isothermal state. 4. The flow is steady state. 5. The inertial terms are negligible.

The constant elongational strain rate of the flow channel forces the axial and transverse normal components of the stress tensor, τ_{zz} and τ_{rr} , to be constant. Their values depend on the strain rate. Experimental data for these semi-hyperbolically convergent dies has proven that the body force term strongly dominates shearing effects and thus causes the shear stress gradient to be negligible. This dominance along with the constant strain rate implies that the stress gradients in the momentum balance are negligible. Furthermore, this coupled with the low Reynolds number implies that the inertial terms are also negligible. With the previous statement of pressure P being proportional to $\rho \dot{\epsilon} \Phi$ the momentum balance reduces to the statement that the pressure gradient, ∇P , is equal to the body force term. Furthermore, since:

$$v_z = \dot{\epsilon} Z \text{ and } \epsilon_h = \ln\left(\frac{r_o^2}{r_e^2}\right) \quad (4.6)$$

the energy balance can be integrated from entrance to exit, and the stress component gives:

$$\tau_{zz} = \frac{2 \Delta P}{3 \epsilon_h} + \frac{2 \rho \Delta \hat{H}}{3 \epsilon_h} = \frac{2 \Delta P}{3 \epsilon_h} + \frac{2 \Delta H}{3 \epsilon_h} \quad (4.7) \text{ in cylindrical coordinates.}$$

The pressure drop, ΔP , is defined as entrance minus exit pressure, and ΔH is defined as exit minus entrance enthalpy change per unit volume. In Cartesian coordinates the analysis leads to the normal stress component given by:

$$\tau_{zz} = \frac{1}{2} \frac{\Delta P}{\dot{\epsilon}_h} + \frac{1}{2} \frac{\rho \Delta \hat{H}}{\dot{\epsilon}_h} = \frac{1}{2} \frac{\Delta P}{\dot{\epsilon}_h} + \frac{1}{2} \frac{\Delta H}{\dot{\epsilon}_h} \quad (4.8)$$

The elongational viscosity, η_e , is defined as:

$$\eta_e = \frac{\tau_{zz} - \tau_{rr}}{\dot{\epsilon}} = \frac{3}{2} \frac{\tau_{zz}}{\dot{\epsilon}} \quad (4.9) \text{ in cylindrical coordinates and}$$

$$\eta_e = \frac{\tau_{zz} - \tau_{xx}}{\dot{\epsilon}} = 2 \frac{\tau_{zz}}{\dot{\epsilon}} \quad (4.10) \text{ in Cartesian coordinates.}$$

Therefore, in both cylindrical and Cartesian coordinates the elongational viscosity is:

$$\eta_e = \frac{\Delta P}{\dot{\epsilon} \dot{\epsilon}_h} + \frac{\rho \Delta \hat{H}}{\dot{\epsilon} \dot{\epsilon}_h} = \frac{\Delta P}{\dot{\epsilon} \dot{\epsilon}_h} + \frac{\Delta H}{\dot{\epsilon} \dot{\epsilon}_h} \quad (4.11)$$

The enthalpy term represents either a real phase change or an apparent one that may be induced by the orientation developing process in the melt. The effective elongational viscosity, η_{ef} , is related to η_e in both coordinate systems by:

$$\eta_{ef} = \frac{\Delta P}{\dot{\epsilon} \dot{\epsilon}_h} \quad (4.12)$$

$$\eta_e = \eta_{ef} + \frac{\Delta H}{\dot{\epsilon} \epsilon_h} \quad (4.13)$$

Therefore, the definition for the effective elongational viscosity includes any potential enthalpy change. The elongational strain rate is defined as:

$$\dot{\epsilon} = (v_o / L)(\exp \epsilon_h - 1) \quad (4.14)$$

where ϵ_h is the Hencky strain as previously defined, L is the centerline length of the die, and v_o is the initial velocity.

The enthalpy change associated with the orientation development in the melt can be calculated as follows. Making the assumption that the non-Newtonian character of the melt in excess of that caused by the shear viscosity, η_s , at equal value shear rate is due to the resistance towards orientation, the actual Trouton ratio would be $\eta_e/\eta_s=3$. Hence, the elongational viscosity can be expressed in terms of a measured shear viscosity and combined with the above given expression for η_e to give:

$$\Delta H = -\epsilon_h \dot{\epsilon} (\eta_{ef} - 3\eta_s) \quad (4.15)$$

The entropy change, ΔS , is an indicator as to what extent orientation develops. It can be determined using $\Delta G = \Delta H - T\Delta S$, where ΔG is the Gibbs free energy and T is the absolute temperature. Assuming that due to the orientation development the flow reaches a quasi or transient steady state equilibrium, then $\Delta G=0$ and $\Delta S=\Delta H/T$.

4.2 Data Acquisition and Analysis

The ACER records equilibrium pressures at set strain rates via a pressure transducer. Due to their narrow channels, capillary dies don't allow the transducer to come into contact with the die surface itself which it ideally should. Instead, the transducer is located right above the entrance of the die which can cause the transducer to sense entrance effects and may require appropriate corrections. The ACER uses the equilibrium pressures and their respective strain rates to calculate and plot apparent viscosities as a function of strain rates based on user defined die specifications. Since commercial capillary rheometers' software like that for the ACER do not take into account the unconventional semi-hyperbolic shape (Rheometric Scientific® is considering providing the user with an upgraded software based on this group's experimental work) the recorded equilibrium pressures must be processed separately to obtain elongational viscosities at elongational strain rates. To accomplish this task, the ram velocity, v_o , needs to be back calculated based on the computer controlled strain rates and the barrel and die dimensions. Using

$$\dot{\epsilon} = \left(\frac{v_o}{L}\right)(\exp \epsilon_h - 1) \text{ and } \eta_{ef} = \frac{\Delta P}{\dot{\epsilon} \epsilon_h}$$

from the previous section, the elongational viscosity and its true elongational strain rate can be calculated.

Elongational viscosities were measured for high and low density polyethylenes at typical processing temperatures ranging from 175 to 250°C. The polymers were characterized regarding their molecular parameters with $\epsilon_h=6$ and 7 semi-hyperbolic dies.

In order to determine enthalpy and entropy changes associated with the orientation developing flow through the semi-hyperbolic dies, shear viscosities had to be measured using constant diameter dies in the capillary rheometer and for a parallel plate rheometer in the continuous rotational mode for lower rates and in the oscillatory mode for higher rates. Enthalpy and entropy changes were calculated for all polyethylenes at 200°C for $\epsilon_h=6$ and 7 die geometries. Moreover, melt relaxation experiments were conducted to evaluate the effects of relaxation versus orientation development. Pressure relaxation curves were recorded with the ACER and fitted as second- and third-order exponential decay functions using Origin® software. Also, differential scanning calorimetry (DSC) measurements were obtained to measure peak melt temperatures and enthalpy changes required to accomplish the first- order thermodynamic transition of crystalline melting. This DSC information indicates what degree flow-induced orientation (higher T_m) occurred when the polymer melts were extruded through the capillary dies.

CHAPTER 5: DISCUSSION OF RESULTS

The following sections discuss the results and conclusions that were derived from the analysis of the experimental data with the intent to establish a relation between molecular characteristics of low and high density polyethylenes and their elongational melt flow behavior. Preceding the presentation of results is a section on differential scanning calorimetry (DSC) to discuss structural differences among the selected polyethylenes. Although the molecular weights are known, any information on the branching characteristics was not made available by the manufacturer. To establish meaningful comparisons between the effects of molecular weight versus branching on elongational melt flow behavior at least a relative order of the extent of branching needed to be determined. This was accomplished by comparing crystalline peak melt temperatures and relating these to the known polymer densities.

Following the discussion on DSC results are four sections covering the influence of molecular parameters, i.e. MW and degree of branching (density), on elongational viscosities, an assessment of melt pressure relaxation and its relation to orientation relaxation, the effects of Hencky strain and temperature on elongational viscosity, and enthalpy and entropy changes of the orientation gain by the melt when extruded through the semi-hyperbolic flow profile.

5.1 Differential Scanning Calorimetry (DSC)

Knowledge of the molecular differences among the chosen high and low density polyethylenes was essential to characterize polyolefin class representative melt flow behavior and to interpret the results in a manner relevant to the research objective. Since

MW specifications of the commercial polymers were available, but branching characteristics were not, DSC crystalline peak melt temperatures were recorded using a Seiko Exstar differential scanning calorimeter to establish a comparison on the basis of the relative difference in peak melt temperature in relation to the known densities. It is expected that for a homologous series of polymers with different MW's and degree of branching the DSC curves will be different (Progelhof et al., 1993). Although DSC measurements may not reveal definite information in numerical format on the degree of branching; nevertheless, a relative order of magnitude or extent of branching for a group of samples analyzed under equal conditions can be established.

The Seiko DSC unit was operated to provide measurements for the first heating, followed by cooling, followed by second heating. The first heating was accomplished at a rate of 5°C/min for a temperature range of around 0°C to 200°C. Cooling followed at a rate of 1°C/min from 200°C to 10°C where the temperature was held constant for thirty minutes. Second heating followed with a rate of 5°C/min back to a temperature of 200°C. The first and second heating DSC peak melt temperature curves for the HDPEs are shown in Figure 5.1. The slow cooling rate followed by the temperature-hold affects the crystalline morphology in that spontaneous nucleation and spherulitic growth preferably occur at low cooling rates, whereas fast cooling rates prevent the mobility of the chains traveling to the growth sites, therefore limiting the size of the spherulites. With the crystalline morphology fully developed the polymers are expected to display peak melt temperatures in accordance with their ability to crystallize. This will depend on the degree of branching for that highly branched polymers (low in density) are sterically too hindered and insufficiently able to fold

Figure 5.1: DSC Peak Melt Temperatures for HDPEs

and pack tightly to crystallize to as high a level as low branched (high in density) polymers are. A highly crystallized, well ordered morphology will require a higher melt temperature to become disordered through melting than a morphology of low crystallinity does. Thus, degree of branching is expected to decrease with an increase in peak melt temperature. Whereas, the quality or perfection of crystallinity relates to the crystalline peak melt temperature as just described, the extent or degree of crystallinity will depend on the measured thermal energy requirement, i.e. the enthalpy change, necessary to accomplish melting. This enthalpy change is related to the area under the melt peak.

Bearing these facts in mind DSC peak melt temperatures for the second heating curve of the unprocessed pellets were compared for both low and high density polyethylenes. The comparison is shown in the form of bar charts in Figure 5.2. The second heating melt temperature was chosen over the first, because after second heating any effects on the melting process related to the manufacturing of the pellet are removed. Clearly, for HDPEs a slight increase and for LDPEs a pronounced increase in crystalline peak melt temperature was observed with increasing density (decrease in degree of branching). This was accompanied by an increase in the enthalpy change for the LDPEs, but a somewhat random order of enthalpy changes for the HDPEs. This observation conforms with the above discussed relation of branching to density and was also recorded by Brandrup (Brandrup et al., 1989) as a decrease in number of methyl groups per 1000 C-atoms at increasing melt temperature for polyethylene. It is also noticeable that the two HDPE grades D and E of equal density but different MW's have nearly the same melt temperatures. The same is true for LDPE grades A and B. This suggests that MW does not affect the peak melt

Figure 5.2: Peak Melt Temperatures for HDPEs and LDPEs in Relation to Density

temperatures in as much as branching (density) does. The order in melt temperature therefore allows to establish a branching order which for HDPEs is $A > D > E > B > C$ and for LDPEs is $C > A > B > D > E$. As already mentioned above the rise in peak melt temperatures along with the rise in enthalpy change among LDPEs is more pronounced than the only slight rise of melt temperatures among HDPEs. This makes sense knowing that LDPEs are generally more branched than the linear HDPEs whose molecular uniqueness is dependent mostly on their MW's. As expected the range of peak melt temperatures is much broader for the LDPEs than it is for the HDPEs.

Furthermore, process effects on melt temperature were evaluated by comparing first heating peak melt temperatures of samples extruded through Hencky 6 and 7 semi-hyperbolic and $L/D=20$ linear dies. Obviously, bearing in mind the objective to analyze capillary extrusion process effects, the first heating was of primary interest, since with subsequent cooling and second heating the thermodynamic and process history of the sample is erased. For example for HDPE-A first heating peak melt temperatures were compared for elongational process strain rates of 2.52s^{-1} , 5.03s^{-1} , and 25.2s^{-1} , all Hencky 6 extruded. The peak melt temperatures were 129.7°C , 129.6°C , and 129.6°C ; and the enthalpy changes were 132.7 mJ/mg , 139.4 mJ/mg , and 139.7 mJ/mg , respectively. The $L/D=20$ straight conventional die produced a first heating melt temperature of 127.7°C and an enthalpy change of 140.1 mJ/mg at a process rate equivalent in ram velocity to the 2.52s^{-1} extruded Hencky 6 melt. The Hencky 7 extruded melt yielded a first heating peak melt temperature of 127.4°C with an enthalpy change of 138.5 mJ/mg at process strain rate of 5.03s^{-1} . Hence, an increase in Hencky 6 process strain rate did not noticeably elevate or

decrease the crystalline melt temperature and caused only a slight increase in enthalpy change between process strain rates of 2.52s^{-1} and 5.03s^{-1} . Indeed, extrusion through any of the capillary die channels, semi-hyperbolic or straight, did not seem to have enhanced solid crystallinity that may have resulted due to the melt attaining a prearranged, oriented morphology prior to sudden cooling and the onset of crystallization. A possible explanation for this behavior is that for crystallization to happen to the highest perfection and degree, the conditions influencing the crystallization kinetics would have to be appropriate. This would include a slow, controlled cooling rate as previously mentioned. Moreover, pressure will influence the dynamics of the crystallization process as well. Generally, an elevated pressure will allow the molecular chains to prearrange and sterically become oriented in a way suitable for crystallization to occur in an ideal manner. However, as much as a fast cooling rate suppresses the crystallization kinetics by limiting mobility, backbone rotation and folding of the chains, so can excessive pressures prevent a sterically ideal approach of the chains to the growth site and an ideal folding for a tightly packed crystallite. This may explain the lower melt temperatures and enthalpy changes resulting from the higher Hencky strain processed extrudates.

However, enthalpy and entropy measurements indicate that at least flow induced orientation occurs through semi-hyperbolic flow channels. This issue will be discussed in a later section. The LDPEs very much behaved in the same way as did the HDPEs regarding the insensitivity of peak melt temperature towards capillary die processing.

It shall be noted here that the first heating DSC curves of all LDPEs exhibited a second order transition usually appearing near 50°C for the pellet as well as the capillary die

processed extrudate. After cooling and second heating this transition disappeared in all cases, but instead a shoulder type secondary peak would appear earlier than and near the main peak melt temperature for the copolymers A, B, and C. No such shoulder would appear for the homopolymer grades D and E. The appearance of the second order transition seems to be related to the manufacturing of the pellet (possibly due to stereospecific metallocene catalysis) or the inherent structure of the polymer, but not to capillary die processing, since it was present in all cases. The disappearance of this transition after cooling and second heating is most likely due to the controlled, slow cooling rate which provides a maximum crystallization rate and therefore a reorganization of the molecular morphology according to the polymer's ability to crystallize. The appearance of the secondary minor peak for the copolymers as opposed to non-appearance of this peak for the homopolymers seems to be related to the structural differences of both types. The cause of secondary peaks may be due to a variation in the type of crystallization. Due to manufacturing related structural and/or molecular uniqueness a material may pass through a series of crystalline growth transitions such as orthorhombic, monoclinic, hexagonal, etc.. As the material solidifies the crystalline morphology is fixed thereby possibly causing different morphological structures to be established within the bulk. When the material is subjected to melting once again the crystallization history is revealed in form of subordinate secondary, tertiary, etc. peaks. Apart from being beyond the scope of this project, a sound interpretation for the above mentioned observations is difficult, because details about the manufacturing process of these polyethylenes, especially the composition of the catalyst

complex and its interaction with the monomer as well as control on stereoregularity, are not known.

5.2 Influence of Molecular Characteristics on Elongational Viscosities

High and low density polyethylenes were elongationally characterized using the Hencky 6 semi-hyperbolic die geometry at temperatures of 175, 200, 225, and 250°C. These temperatures were chosen because they cover a typical polyethylene processing temperature range, and the range is limited by other considerations. Above 250°C polymer degradation, as evident by melt discoloration started to become apparent, whereas below 175°C the melts became exceedingly viscous limiting the ACER to low process rates due to pressure overloads. Elongational strain rates were chosen as to cover as wide of a strain sweep as possible. For each polymer grade the same 10 rates were applied. If a particular grade could not be extruded at high strain rates, the upper limit on strain rate was dictated by the transducer upper safety threshold pressure limitation of 35 MPa. The equilibrium pressures were recorded and the elongational viscosities were determined as described in the previous chapter.

Graphs of effective elongational viscosity dependence on elongational strain rate were prepared and are shown in Figures 5.3 and 5.4 for HDPEs and Figures 5.5 and 5.6 for LDPEs. In all cases viscosities decreased in a non-Newtonian power law fashion with increasing strain rate as expected. Among HDPEs noticeable differences in elongational viscosities were observed between the groups comprised of grades A, B, C with lower MW's and D, E with higher MW's. At lowest elongational strain rate of 2.52s^{-1} the relative difference between these two groups was approximately four tenth of a decade; i.e., 400,000

Figure 5.3: Elongational Viscosity as a Function of Elongational Strain Rate for HDPEs at 175°C and 200°C

Figure 5.4: Elongational Viscosity as a Function of Elongational Strain Rate for HDPEs at 225°C and 250°C

Pas, and this difference stayed relatively constant with temperature. However, with increasing strain rate the viscosity differences appeared to diminish and the lines converged at higher strain rates. The point of convergence was dependent upon temperature in that a low temperature caused an earlier convergence than a high temperature did. For example, at 175°C (Figure 5.3 upper graph) lines converged at about 10s^{-1} , at 200°C (Figure 5.3 lower graph) at about 20s^{-1} , at 225°C and 250°C (Figure 5.4) the point of convergence was outside the measured range. For the five HDPEs the order of magnitude of viscosity at equal strain rate followed the order of magnitude of MW; i.e., grade A with the lowest MW=105,000 exhibited the lowest viscosity values at rates prior to convergence of the lines. Grades B and C have essentially equal MW's with 125,400 and 125,700, respectively, although their densities differ. Indeed, their lines are essentially superimposed. Grades E and D follow in order with MW's of 154,100 and 183,200, respectively, having also the highest viscosities. The basically equal MW grades A, B, and C having different densities did not exhibit significant viscosity differences. These observations suggest that viscosity differences are predominantly controlled by MW rather than degree of branching (density). In fact, HDPEs are linear polyolefins with minor branching characteristics. The long, linear, high MW chains are prone to entangle and hence are expected to cause high melt viscosities. The diminishing effect of molecular influence on elongational viscosity with rising strain rate is thought to be the result of asymptotic approach to a limiting orientation in which the polymer chains are increasingly oriented with respect to each other and are not as influenced by entanglement and sliding effects related to molecular structure as they are at lower strain rates. This issue will be discussed in more detail in the following section.

LDPE elongational melt viscosities were evaluated under the same aspects (Figures 5.5 and 5.6). As for HDPEs the melt viscosities were decreasing power law functions of strain rate. The previously mentioned converging effect of the viscosity lines can also be seen here, in particular for the copolymer grades A, B, and C. Again, MW controlled the spread along the viscosity axis when comparing grade B with MW=56,950 versus grades A and C with MW's= 97,550 and 83,350, respectively. The homopolymer grades D and E at about equal MW of 86,650 and 80,350, respectively, but different densities of 0.919 and 0.923, respectively, were insensitive to strain rate or temperature variations. This behavior of MW control as opposed to the insignificant branching effect on elongational viscosities as seen for HDPEs is again reflected in the comparison of LDPEs.

It shall be mentioned at this point that the observed differences between elongational viscosities of different grades do not fall within the margins of experimental error. Tests have shown that the ACER is an extremely precise instrument that allows for repeated measurements at equal conditions with marginal deviations of usually no more than 1.5%. Therefore, viscosity differences displayed on the logarithmic scaled figures are the result of variations in molecular uniqueness rather than seemingly due to potential experimental inconsistencies or errors.

5.3 Pressure Relaxation

As mentioned in the previous section asymptotic approach to a limiting orientation in which the polymer chains are increasingly oriented with respect to each other; thereby diminishing the influence of entanglement and sliding related to molecular structure has a

Figure 5.5: Elongational Viscosity as a Function of Elongational Strain Rate for LDPEs at 175°C and 200°C

Figure 5.6: Elongational Viscosity as a Function of Elongational Strain Rate for LDPEs at 225°C and 250°C

significant effect on the elongational rheology. This is believed to be responsible for the apparent effects of molecular parameters at low process strain rates, whereas increasingly high process rates along with the diminishing influence of simultaneous melt relaxation as orientation increases caused molecular uniqueness to vanish. In order to substantiate this observation melt pressure relaxation was measured at varying elongational strain rates using the ACER. The curves were obtained for the melts extruded through the Hencky 6 semi-hyperbolic die at 200°C. Graphs were prepared as time dependent, exponentially decaying pressure functions and were parameter fitted using Origin® software. Graphs are shown for the HDPEs at process strain rates of 2.96s^{-1} , 20.12s^{-1} , and 35.21s^{-1} in Figures 5.7, 5.8 and 5.9, respectively. A logarithmic scale was chosen for the time dimension for display purposes allowing for more spread between the curves and ease of comparison. Figure 5.7 shows the relaxation spectrum at a low 2.96s^{-1} process rate. The curves are second order decay of form: $P=P_o+A_1\exp(-t/\lambda_1)+A_2\exp(-t/\lambda_2)$, where A_1 and A_2 are the first and second pre-exponential factors and λ_1 and λ_2 are the first and second time constants. The first time constant is the location at which the tangent to the onset of relaxation intercepts with the time axis. Estimates show that at this time the pressure has decayed to about 63% of its original value which is equivalent to $1-(1/e)$. By nature of the exponential decay function the rate of decrease is most rapid during the initial short time period. Hence, the first decay constant is an important measure for the extent and rate of relaxation and a useful tool to differentiate between melts of unique molecular characteristics. Table 5.1 summarizes the dependance of the first decay constant on elongational strain rate for pressure relaxation at

Figure 5.7: Pressure Relaxation for HDPEs at 200°C, Hencky Strain=6, and Elongational Strain Rate=2.96s⁻¹

Table 5.1: First Decay Constant for HDPEs at 200°C and Hencky 6 Die Geometry

Polymer	Strain Rate = 1.04s ⁻¹	Strain Rate = 2.07s ⁻¹	Strain Rate = 2.96s ⁻¹	Strain Rate = 20.12s ⁻¹	Strain Rate = 35.21s ⁻¹
HDPE-A	26.68	19.09	14.89	4.03	6.01
HDPE-B	32.58	25.42	17.47	5.92	4.06
HDPE-C	28.92	20.89	16.96	7.16	5.73
HDPE-D	37.98	25.46	19.80	7.15	6.16
HDPE-E	43.25	39.72	23.91	8.92	8.44

200°C and Hencky 6 die geometry. The time constants decrease with increasing strain rate as well as their relative differences decrease. The rate of relaxation is related to the degree

of orientation that has developed prior to relaxation. A large thermodynamic driving force for relaxation will cause the time constants to be smaller for more highly oriented melts as reflected by higher strain rates. Moreover, the difference of time constants between strain rates decreases as the orientation level increases indicating an asymptotic approach to a limiting value. Evidently, as will be discussed in a later section, the calculated entropy changes for Hencky 6 and 7 extruded samples increased in magnitude with increasing elongational strain rate which is indicative of the just mentioned increase in orientation at asymptotically decreasing relaxation time constants.

Turning to the relaxation curves, for the low strain rate of 2.96s^{-1} (Figure 5.7) the staggered order of curves follows the order of MW in the same way as it did for the elongational viscosities in Figure 5.5. The two MW groups of HDPEs A, B, C and D, E are also clearly distinguishable here. As the process rate increases to 20.12s^{-1} (Figure 5.8) which is the point of convergence of elongational viscosities at 200°C as shown in Figure 5.5, the decay curves become third order. The order of MW is now more or less random and the two MW groups are not distinguishable anymore, probably due to the effect of orientation approaching an asymptotic limit causing the relaxation to be less sensitive to MW effects. At even higher process rate of 35.21s^{-1} (Figure 5.9) the relaxation curves remain third order and appear yet more crowded. The decrease of MW order with increasing strain rate reflected in the relaxation spectrum thus conforms with the convergence of the strain rate dependent elongational viscosity lines at higher process strain rates. Hence, at high loads

Figure 5.8: Pressure Relaxation for HDPEs at 200°C, Hencky Strain=6, and Elongational Strain Rate= 20.12s^{-1}

Figure 5.9: Pressure Relaxation for HDPEs at 200°C, Hencky Strain=6, and Elongational Strain Rate= 35.21s^{-1}

molecular uniqueness vanishes, yielding to orientation development and the associated restructuring of the melt's molecular morphology. Molecular chains start to disentangle and align in a more organized, layered fashion, thereby lowering the melt viscosity.

When comparing the relaxation time constants of Hencky 6 to Hencky 7 extruded melts no differences were observed other than that the latter were larger in magnitude than the former, which agrees with the generally higher melt viscosities produced by the Hencky 7 over the Hencky 6 semi-hyperbolic die.

5.4 Influence of Hencky Strain and Temperature on Elongational Viscosities

In order to investigate the influence of the semi-hyperbolic die geometry of particular Hencky strain as well as process temperature on the melt viscosities, experiments were conducted at temperatures of 175°C, 200°C, 225°C, 250°C and Hencky strains of 6 and 7. While all HDPEs and LDPEs exhibited the same general trends, only one polymer grade of each class, HDPE-C (Figure 5.10) and LDPE-E (Figure 5.11), shall be presented here for discussion.

In Figure 5.10 (upper plot) lines of strain rate dependent elongational viscosities for the eight possible combinations of temperature and Hencky strain ran parallel for most of the process strain rate range, especially throughout the first decade. Hencky 7 extruded samples yielded higher melt viscosities than their Hencky 6 extruded counterparts at equal temperature. Also, with increasing temperature the viscosities decreased at equal Hencky strain as expected. The well ordered, parallel staggered lines allow for shifting along the strain rate axis to collapse all data points onto one reference line, thereby creating a master line (lower plot, Figure 5.10) The same was done for LDPE-C in Figure 5.11 where the data

Figure 5.10: Elongational Viscosities for HDPE-C as a Function of Temperature and Hencky Strain

Figure 5.11: Elongational Viscosities for LDPE-E as a Function of Temperature and Hencky Strain

correlated even better with lines running parallel over the entire process strain rate range (upper plot, Figure 5.11). In both cases, the data for $T=200^{\circ}\text{C}$ and $\epsilon_h=6$ was chosen as the reference line for it is more or less centered within the stack of lines. The shifting factors, summarized in Table 5.2, were determined as to provide the best possible regression correlation for the superimposed data points. When comparing the factors, there does not seem to be a definite correlation between shift factors and Hencky strain/temperature process conditions. For the Hencky 6 processed melts the step size of the shift factors seems

Table 5.2: Shifting Factors for Master Lines of HDPE-C and LDPE-E

Process Condition	HDPE-C	LDPE-E
$T=175^{\circ}\text{C}, \epsilon_h=6$	0.95	0.74
$T=200^{\circ}\text{C}, \epsilon_h=6$	1.00	1.00
$T=225^{\circ}\text{C}, \epsilon_h=6$	1.17	1.41
$T=250^{\circ}\text{C}, \epsilon_h=6$	1.36	2.10
$T=175^{\circ}\text{C}, \epsilon_h=7$	0.49	0.39
$T=200^{\circ}\text{C}, \epsilon_h=7$	0.58	0.53
$T=225^{\circ}\text{C}, \epsilon_h=7$	0.68	0.79
$T=250^{\circ}\text{C}, \epsilon_h=7$	0.82	1.15

to increase more rapidly with increasing temperature than for the Hencky 7 processed melts.

Both master lines can be expressed in form of a regressed equation which turned out to be for HDPE-C:

$$\eta_c = 10^{6.23144} \cdot m(T, \epsilon_h) \dot{\epsilon}^{-0.68247} \quad (5.1)$$

and for LDPE-E:

$$\eta_e = 10^{5.87373} \cdot m(T, \epsilon_h) \dot{\epsilon}^{-0.59045} \quad (5.2)$$

where m is the shift factor depending on temperature and Hencky strain. Used in this manner the correlation can predict elongational viscosities for particular combinations of Hencky strain and process temperature and represents the dependence of elongational viscosity on process conditions.

5.5 Enthalpy and Entropy Changes

Enthalpy and entropy changes were calculated based on the relevant equations presented in chapter 4. To accomplish this task shear rheological data had to be obtained using the Bohlin rheometer in the continuous rotational and oscillatory mode. The shearing range covered shear rates in order of magnitude equivalent to the elongational strain rates used to obtain data from the ACER. In case of the HDPEs the ACER also had to be used with a linear, $L/D=20$, die to measure shear viscosities at shear rates that were too high to be obtained from the Bohlin rheometer. When using the straight $L/D=20$ die a Bagley entrance correction was performed to correct for the equilibrium pressure offset caused by die entrance effects. The details for the Bagley procedure are provided in Appendix A.

In Figures 5.12 and 5.13 are shown the enthalpy and entropy changes for HDPEs and LDPEs, respectively. For the HDPEs at 200°C, the measured enthalpy and entropy changes increased in magnitude (became more negative) as the process strain rate increased for both die geometries. This may be restated by saying that the melt dissipated more thermal energy at decreasing molecular randomness while the process strain rate was increasing, i.e. the melt was increasingly more transformed to a more ordered state corresponding to a lower

Figure 5.12: Enthalpy and Entropy Changes for HDPEs at 200°C

Figure 5.13: Enthalpy and Entropy Changes for LDPEs at 200°C

entropy and greater magnitude latent heat of transformation with increasing strain rate. Moreover, at comparable strain rate, the Hencky 7 extruded melts produced larger enthalpy and entropy changes than their Hencky 6 counterparts. The same was observed for the LDPEs at 200°C. The enthalpy and entropy changes in HDPEs indicated a greater magnitude change being required for higher molecular weight samples. The discrimination by molecular weight was more distinct for the Hencky 6 die than it was for the Hencky 7, probably because the increased orientation forced by the more restrictive die dominated the less influential molecular weight contribution. The LDPE samples having nearly the same relatively high branching content (i.e. density) and polydispersity, samples A, B, and C, indicated the same dependence as the HDPE samples on molecular weight and Hencky strain. However, the less branched and higher polydispersity samples, D and E, indicated significantly smaller magnitude enthalpy and entropy changes than did the other LDPE samples. The HDPE samples in general exhibited larger magnitude enthalpy and entropy changes at equivalent lower strain rates than did the LDPE, but all samples seemed to be asymptotically approaching a common limit at higher elongational strain rates. This common limit probably is indicative of a limiting orientation and the rate at which it is approached is dependent upon molecular characteristics.

These general observations suggest that at least flow induced orientation occurs in semi-hyperbolic flow with the extent being dependent upon the elongational strain rate. For Hencky 6 extruded HDPE-A the enthalpy change ranged from -1.2×10^7 to -3.2×10^7 J/m³ for a strain rate range from 2.52 to 50.3 s⁻¹. The literature reports for the heat of fusion for polyethylene an experimental value of 8.22 KJ/mol/monomer unit (Van Krevelen, 1990).

For HDPE-A this would be equivalent to $-2.77 \times 10^8 \text{ J/m}^3$. This last value is one order of magnitude higher as expected for the solid crystalline state having a significantly higher degree of orientation than the meta stable liquid form. Values very much comparable in magnitude with those presented here were reported by Collier (Collier et al., 1998) when investigating flow induced orientation in polypropylene melts. The lower ordered flow induced orientation did not cause a significant shift in peak melt temperature as noted earlier when discussing DSC results. This would explain the insensitivity of melt temperature and melt enthalpy change to capillary die processing.

CHAPTER 6: CONCLUSIONS AND FUTURE WORK

The discussion of results as presented in the previous chapter revealed and explained some of the effects of molecular characteristics on the elongational melt flow behavior of high and low density polyethylenes. Whereas there is likely to be a wealth of information still to be uncovered regarding the research objective and its related issues, this work focused on particular aspects establishing several fundamental conclusions. These conclusions may be summarized as follows:

With the aid of DSC measurements a branching order for HDPEs and LDPEs was determined on the basis of comparing crystalline peak melt temperatures and the enthalpy changes required to accomplish the first order thermodynamic transition of melting. DSC curves also revealed that processing through capillary profiles, semi-hyperbolic or straight, did not have any significant effect on the extent or perfection of solid crystallinity. This was apparent when noticing the insensitivity of peak melt temperature and melt enthalpy towards capillary die processing of any shape and process strain rate tested. Furthermore, when comparing strain rate dependent elongational viscosities of the molecularly uniquely characterized HDPEs and LDPEs it was observed that viscosity differences were primarily controlled by MW rather than degree of branching, and that this effect was process strain rate as well as temperature dependent. At low elongational strain rates viscosity differences among HDPEs and LDPEs were visibly dependent upon molecular weights, whereas at higher and highest strain rates viscosity differences diminished. To further investigate the causes of said observations, pressure melt relaxation curves were recorded, regressed and parameter fitted to determine the pressure relaxation time constants. Time constants were

observed to decrease with increasing elongational strain rate as well as their relative difference decreased indicating that with increasing strain rate the molecular field of the melt asymptotically gained orientation in approaching a limit. As a result of this behavior molecular uniqueness vanished at high process strain rates, yielding to orientation development and the associated restructuring of the melt's molecular morphology.

When testing each polymer grade for the response of elongational viscosity to Hencky strain and temperature, the strain rate dependent viscosity lines appeared stacked in parallel. Shifting of the data points along the strain rate axis would allow the lines to superimpose and constitute one single line. A regression of such master line produced a power law correlation including a temperature and Hencky strain dependent shift factor that expressed the dependence of elongational viscosity on process conditions.

In an effort to investigate flow induced orientation of the polyethylenes in semi-hyperbolic dies, enthalpy and entropy changes were calculated from ACER and continuous rotational as well as oscillatory shear data. With increasing strain rate the melts released more energy and the molecular structure became more ordered as the enthalpy and entropy changes increased in magnitude. With the Hencky 7 die larger enthalpy and entropy changes were achieved at equal strain rate than with the Hencky 6 die. Therefore, flow induced orientation was achieved to an extent dependent upon the Hencky strain and elongational strain rate. Said flow induced orientation was found to be one order of magnitude lower than the heat of fusion which explained the previously mentioned insensitivity of solid crystalline melt temperature to the effect of capillary die processing.

In the future the elongational flow analysis will extend to a broader scope of tasks. The strain thinning and orientation gaining behavior should be explored at elongational strain rates considerably higher than the current limit of about 50 s^{-1} . This requires the acquisition of a new pressure transducer for the ACER that is capable of sensing pressures past the current limit of 35 MPa. Furthermore, two additional semi-hyperbolic dies of Hencky strains 4 and 5 should be custom electron discharge manufactured (EDM). This should provide opportunity to broaden the investigation of the effect of Hencky strain and temperature on elongational viscosities. It is expected that the additional data derived from the new dies will also correlate in the form of parallel lines over at least two decades of elongational strain rates. An analysis of the shift factors should follow to explore if there exists a definite dependence of shift factor to a Hencky strain/temperature combination. Moreover, as an alternative, the data could be correlated using an Arrhenius type of equation with an activation energy to be determined. This analysis should lead to two independent shift factors, one depending only on temperature and one only on Hencky strain. Also, stress relaxation measurements should be performed using the rotational shear rheometer. The relaxation spectrum can be measured to yield exponential decay time constants based on a shearing deformation. These time constants can be compared to those derived from the ACER's pressure relaxation experiments using straight capillary dies. The ACER does not provide continuous time dependent stress data. Therefore, the pressure dependent stress profile needs to be determined. Decay time constants derived from the ACER in shear flow should theoretically agree with those derived from the continuous rotational shear

rheometer. If so, time constants can also be found for elongational flow by measuring relaxation with the semi-hyperbolic dies.

The analytical techniques presented and proposed in this work should also be applied to different grades of polypropylene, in particular to the isotactic and syndiotactic forms. The results can be compared to those discovered previously by this group (Collier et al., 1998). Eventually, efforts will focus on designing an on-line process control rheological sensor. Process control data of continuous polymer fabrication processes is currently based only on shearing flow data; however, the elongational contribution is at least equally important in processes in which orientation is intentionally or consequently imposed. Polymer processing can be better controlled and made more cost efficient if elongational responses are measured in real time. The rheological data will allow for quick process parameter adjustments to compensate for changes in molecular characteristics during the fabrication process. This ensures the continuity of uniform product quality with increased product yields and less recycle. With the addition of an elongational on-line sensor, process control can be significantly enhanced, because elongational rheology reflects the orientation development characteristics of polymer melts.

BIBLIOGRAPHY

Agassant, J. F., P. Avenas, J. Ph. Sergent, and P. J. Carreau. Polymer Processing. Hanser Verlag, Munich, Vienna, New York 1991.

Bailey, L. E., D. G. Cook, J. Pronovost, and A. Rudin. "Elongational Flow Properties of Low-Density Polyethylene and Linear Low-Density Polyethylene from Nonisothermal Melt Spinning Experiments." Polymer Engineering and Science 34(19): 1485 (1994).

Benedikt, G. M., and B. L. Goodall. Metallocene-Catalyzed Polymers. Plastics Design Library, 1998.

Benedikt, G. M., and B. L. Goodall. Metallocene Technology and Modern Catalytic Methods in Commercial Applications. Plastics Design Library, 1999.

Bird, R. B., W. E. Stewart, and E. N. Lightfoot. Transport Phenomena. Wiley, New York, 1960.

Brandrup, J., and E. H. Immergut. Polymer Handbook. Wiley, New York, 1989.

Burghardt, W. R., J. Li, B. Khomami, and B. Yang. "Uniaxial Extensional Characterization of a Shear Thinning Fluid Using Axisymmetric Flow Birefringence." Journal of Rheology 43(1): 147, 1999.

Collier, J. R., O. Romanoschi, and S. Petrovan. "Elongational Rheology of Polymer Melts and Solutions." Journal of Applied Polymer Science 69: 2357, 1998.

Dealy, J. M., and K. F. Wissbrun. Melt Rheology And Its Role In Plastics Processing. Van Nostrand Reinhold, New York, 1990.

Denn, M. Process Fluid Mechanics. Prentice Hall, Inc., 1980.

Feldman, D., and A. Barbalata. Synthetic Polymers. Chapman and Hall, London, UK, 1996.

Greener, J., and J. R. G. Evans. "Uniaxial Elongational Flow of Particle-Filled Polymer Melts." Journal of Rheology 42(3): 697, 1998.

Hingmann, R., and B. L. Marczinke. "Shear and Elongational Flow Properties of Polypropylene Melts." Journal of Rheology 38(3): 573, 1994.

Kim, H. C., A. Pendse, and J. R. Collier. "Polymer Melt Lubricated Elongational Flow." Journal of Rheology 38(4): 831, 1994.

Kulkarni J. A., and A. N. Beris. "A Model for the Necking Phenomenon in High-Speed Fiber Spinning Based on Flow-Induced Crystallization." Journal of Rheology 42(4): 971, 1998.

Levitt, L. and C. W. Macosko. "Extensional Rheometry of polymer Multilayers. "A Sensitive Probe of Interfaces." Journal of Rheology 41(3): 671, 1997.

Martyn, M. T., and P. D. Coates. "Image Analysis of Polypropylene Melt Fibre Stretching." Unpublished Paper.

Mighri, F., A. Ajji, and P. J. Carreau. "Influence of Elastic Properties on Drop Deformation in Elongational Flow." Journal of Rheology 41(5): 1183, 1997.

Müller, A. J., V. Balsamo, F. Da Silva, C. M. Rosales, and A. E. Saez. "Shear and Elongational Behavior of Linear Low-Density Polyethylene Blends from Capillary Rheometry." Polymer Engineering and Science 34(19): 1455, 1994.

Nakason, C., M. Kamala, M. Martyn, and P. D. Coates. "Flow Visualization for Extensional Viscosity Assessment." Unpublished Paper.

Neumann, R. M. "Polymer Stretching in an Elongational Flow." Journal of Chemical Physics 110(15): 7513, 1999.

Okamoto, M., H. Kubo, and T. Kotaka. "Elongational Flow-Induced Crystallization of Polyethylene Terephthalate Under the Supercooled State." Polymer 39(14): 3135, 1998.

Okamoto, M., H. Kubo, and T. Kotaka. "Elongational Flow-Induced Crystallization and Structure Development in Supercooled Polyethylene Naphthalate." Macromolecules 31(13): 4223, 1998.

Patel, R. M., and D. C. Bogue. "Measurement of the Elongational Properties of Polymer Melts by Gravity Spinning." Journal of Rheology 33(4): 607, 1989.

Pendse, A. V. Elongational Rheometry of Coextruded Polymer Melts. Unpublished Ph.D. Dissertation, Louisiana State University, 1995.

Progelhof, R. C., and J. L. Throne. Polymer Engineering Principles, Hanser Verlag, Munich, Vienna, New York, 1993.

Ramanan, V. V., S. e. Bechtel, V. Gauri, K. W. Koelling, and M. G. Forest. "Exploiting Accurate Spinline Measurements for Elongational Material Characterization." Journal of Rheology 41(2): 283, 1997.

Romanoschi, O. Processing of Value-Added Textile and Geotextile Products from Sugar Cane and Kenaf. Unpublished Ph.D. Dissertation, Louisiana State University, 1998.

Schramm, G. A Practical Approach to Rheology and Rheometry. Gebrüder Haake GmbH, Federal Republic of Germany, 1994.

Smith, D. E., and S. Chu. "Response of Flexible Polymers to a Sudden Elongational Flow." Science 281(5381): 1335, 1998.

Takahashi, T., J. Takimoto, and K. Koyama. "Elongational Viscosities of Random and Block Copolymer Melts." Journal of Applied Polymer Science 69: 1765, 1998.

Van Krevelen, D. W. Properties of Polymers. Elsevier Science Publishers, 1990.

Wagner, M. H. and A. Bernat. "The Rheology of the Rheotens Test." Journal of Rheology 42(4): 917, 1998.

APPENDIX: THE BAGLEY CORRECTION

In rod capillary dies entrance effects cause false pressure readings which require correction. Because the die cross section is so small, the pressure transducer cannot be positioned inside the die channel where it ideally should be located to guarantee a correct pressure reading that reflects a pressure drop due to the difference between die entrance and exit, only (Schramm, 1994). Instead, the transducer is located near and above the die entrance plane. However, at that location the transducer will sense pressure losses due to flow turbulence in the entrance region caused by the sudden change of the large barrel diameter to the small die diameter. Furthermore, energy losses are also caused by the need to accelerate the melt in passing at low speed from the barrel to a much higher speed in the narrow capillary channel. Thus, measuring a steady state flow would only be possible within the die channel.

Bagley proposed an experimental method to correct for said pressure/energy losses. The procedure requires a series of experiments for a particular polymer using dies of different aspect (length/diameter) ratios, but otherwise equal test conditions. Each die will cause the same type of entrance effects; however, the smaller the L/D ratio of the die, the larger the percent error will be at the entrance. It is possible to extrapolate from dies with high L/D ratios to those with low L/D ratio by decreasing the die length L . This extrapolation leads to a die of zero length; i.e., $L/D=0$. Such die will cause a pressure loss due to the entrance effect only which represents the pressure correction value. Thus, for chosen strain rates a plot of pressure drop versus aspect ratio will give a series of straight lines. These lines are extrapolated to intersect with the ordinate at a value which is the

correction pressure, ΔP_c . Alternatively, one can extrapolate the lines beyond the ordinate to intersect with the negative abscissa. This will provide a negative L/D value from which a ΔL can be found. The extra, imaginary length added to the actual die length, L , will give rise to a pressure drop reading which accounts for the entrance effect. The corrected shear stress is then determined on the basis of subtracting ΔP_c from the measured pressure drop or alternatively adding the imaginary length, ΔL , to the capillary die. Therefore:

$$\tau_c = (\Delta P - \Delta P_c) \cdot \frac{R}{2L}$$

or

$$\tau_c = \Delta P \cdot \frac{R}{2(L + \Delta L)}$$

For the HDPE grades used in this research Bagley entrance corrections were performed by using three capillary rod dies of L/D ratios of 20, 10 and 5. In Figure A.1 is shown an example for HDPE-A. The graph's legend displays the regressed equations for the lines of pressure versus aspect ratio at selected shear rates. The intercept is the correction pressure. For the LDPEs a Bagley correction was not necessary, since all shear viscosity measurements needed to calculate the enthalpy and entropy changes associated with the orientation development in the semi-hyperbolic dies fell within the range of oscillatory shearing rates. Thus, ACER generated shear viscosity measurements were not necessary for the LDPEs.

Figure A1: Bagley Entrance Correction for HDPE-A at 200°C

VITA

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DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Bijan Seyfzadeh
Major Field: Chemical Engineering
Title of Dissertation: Elongational Rheology of Polyethylene Melts

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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