CHAPTER I
INTRODUCTION

Surface texture and skin smoothness are one of the critical requirements in plastic processing (extrusion, injection molding) of minute-sized products which require precision in manufacturing. Extrusion processes are often limited at high processing speed by the appearance of different types of surface defect: wavy surface, sharkskin, melt fracture, helical defect, spurt or slip-stick. These defects depend on the nature of the polymer, flow instability, polymer-metal interaction and others.

The plastic production rates are limited by the appearance of surface irregularities. In a capillary extruder, different types of defect may be encountered. A low shear rate, the extrudate is smooth. Increasing the shear rate, a small defect occurs which is often called sharkskin defect. Then, at high shear rate, large distortion occurs: the well-know *melt fracture defect*. Increasing processing speed saves cost at the expense of skin defects.

For technical significances: a) Processing speed is limited by these skin defects. To save energy and labor cost, the issue of the large variation in the critical onset conditions must be resolved. b) Minute-sized manufacturing, if the products are of mechanical uses on the manufactured products are moving parts thus require contact with other parts of a system. c) surface gloss and surface smoothness quality are ones of many requirements for consumer appeal. In industry time is money we must take the least time to process and to obtain quality products. When we increase processing rate, melt fracture will occur. We want the highest processing speed possible with suitable operating conditions for a smooth surface.

1.1 Extrudate Distortion and Sharkskin Texture

It is generally believed that extrudate distortions are intimately related with and possibly are the results of the melt flow instability of some kinds that can be distinguished by their appearances. The factors that influence the type and degree of extrudate distortion include; chemical nature of polymer, molecular weight and its distribution, branching, entrance geometry, length to diameter ratio of the capillary, material of construction of the capillary, temperature, and strain rate.

Sharkskin is the first form of surface distortion at low shear rate. The sharkskin texture is orderly, consisting of nearly periodic roughness less than one percent of extrudate diameter. The semiregular cracks or grooves of the sharkskin surface are always perpendicular to the flow direction (*Larson, 1992*). It is considered a short wavelength instability because the disturbance is one of small amplitude but of high frequency. The mechanism of sharkskin is postulated to be caused by the rapid acceleration of the surface layer of the polymer leaves the die. This abrupt change cause a high degree of stretching in the surface layer. If the stretching rate is too high, the surface layer fails and form the ridges of sharkskin surface. This type of instability has some ordering and can be differentiated from another type of instability.

Peeled -orange is a skin defect which is similar to the sharkskin except that the wavelength is longer than the extrudate diameter and skin roughness or amplitude is comparable to the diameter. It occurs at an onset which beyond that of the sharkskin.

Melt fracture is easily distinguished from others by random surface appearances in which the magnitude of surface roughness is comparable to the diameter. It is the most severe form of the extrudate distortions and its onset is the largest. At the onset of the melt fracture, there is a jump in the flow rate at a given stress.

This study investigated the sharkskin defect and flow instability of HDPE, LLDPE and MDPE polymer melts from the capillary extrusion. Skin defects are a result of a flow instability of some kind; it may originate from a failure at the interface, and adhesion failure. Sharkskin defects occur at τ_W = 3.3×10^5 N/m^2 where τ_W is the wall shear stress at the capillary die. The recoverable shear (local value) is 1.5. Stability diagram of sharkskin defects can be constructed by the normalized scale of wavelength and amplitude of sharkskin surface and recoverable shear (S_R).

Previous normalizations of the wall shear stress was by the recoverable shear factor, S_R, defined as

$$S_R = \frac{\tau_{w,c}}{G'}, \qquad (1)$$

where $\tau_{W,c}$ is the critical wall shear stress and G′ is the plateau value of the storage modulus in the limit of large frequency. In this normalization, the conjecture was that it should be unique as it represents the ratio of two dominant forces: viscous and elastic forces.

S_R for each skin defect has been found to be nonunique; in the case of the sharkskin defect S_R varies between 1-10 (*Larson, 1992*). The variation is too large to attach any physical meaning or theory to it. The failure to observe consistent S_R might be due to the following reasons: a) there are more than two types of forces that are relevant; b) normalizations were not properly done, as rheological properties were not throughly measured; c) instabilities might be of the subcritical type where the lowest nonlinear term destabilizes the flow system a hysteresis occur.

Our experimental objective in this thesis are two folds. We wish to obtain unique condition with a consistent physical picture for the onset of sharkskin, in terms of molecular weight, die geometry and melt temperature. Secondly, we wish to examine the dependences of the sharkskin wavelength and amplitude on molecular weight, die geometry and melt temperature.

We divided our experiment into three parts. The first part summarizes the flow regimes or skin characteristics ($\tau_{w,c}$ and $\gamma_{a,c}$) of the two LLDPE (L2009F, L2020F), one MDPE (M3204RU) and three HDPE (N3260, H5690S, R1760) investigated. The second part presents the results of rheological properties (G' vs. ω, G'' vs. ω, b_TG' and b_TG'' vs. $a_T\omega$, and master curves), the determination of the onset conditions and the sharkskin parameters (λ_s/ε_s), and finally the third part is the unique LLDPE, MDPE and HDPE sharkskin stability diagram (S_R vs. λ_s/ε_s).

1.2 Previous Studies

The small amplitude periodic distortion distortions appearing on the surface of extrudates in several polymer processes (sharkskin melt fracture) have been the subject of investigation of several research groups over the part 50 years.

A sharkskin defect is generally believed to occur when a certain stress level has been reached for linear low density polyethylenes of a certain molecular weight range. *Vinogradov et al. (1972)* reported that a polybutadienes sharkskin defect occured when the critical wall shear reached a value of 2.75×10^6 dyne/cm^2, the corresponding recoverable shear S_R was found to be 0.43.

On the other hand, *Vlachopoulos and Alam (1972)* reported that the product of the critical wall shear stress and a group of molecular weights, $\tau_{w,c}M_zM_{z-1}/M^2_w$ remains constant and equal to 2.65, independent of molecular weight or it distribution. As the weight average molecular weight increases the shear stress $\tau_{w,c}$ decreases.

Bergem (1976) performed capillary experiments for a variety of polymers. Using a tracer technique, he concluded that sharkskin arises from a tearing of the melt at the exit of the capillary.

Cogswell (1977) proposed that sharkskin results from rupture of polymer under tensile stress which develops around the die exit singularity.

Welli (1980) proposed that his relaxation oscillation theory explains the origin of sharkskin: the high frequency oscillatory flow is created at the entry, propagates through the tube and finally imposes its frequency to the stretching flow which creates the rupture on the skin of the melt.

Sornberger et al. (1987) studied the sharkskin defect in linear low density polyethylene using bifringence and roughness measurements, suggesting the defect is associated with high values of local stress at the die exit.

A more recent study by *Kalika and Denn (1987)* reported that the recoverable shear stress measured was approximately 1.5. There are many other investigators who pointed out some consistencies with regard to the onset conditions for the sharkskin extrudate. They suggested that the onset of sharkskin coincides with the failure of adhesive at the polymer/metal interface. The onset of sharkskin is in agreement with a calculation based on a stability theory of *Pearson and Petrie (1965)*. The memory slip boundary condition has been proposed to lead to short-wave instability or Hadamard instability and consequently sharkskin. It is generally agreed that sharkskin is initiated at or near the die exit and that the onset depends on the die materials as well as the lubricants used. Only for a short l_C/d_C die could 'pre-stressing' in the entry region initiated sharkskin is an exit phenomenon related to relaxation of stretch chains at the orifice outlets, whereas instabilities are generated in the upstream region for which melt fracture appears downstream. *Moynihan (1990)* agreed with the point of view, with the addition that the melt should be first "pre-stressed" critically at the entry region of the die.

The mechanisms of sharkskin has been proposed by *Kurtz (1984)*. He proposed that we have two types of slip i.e., continuous and discontinuous. Discontinuous slip is analogous to that of elastomers over metal interfaces. Sharkskin melt fracture due to discontinuous slip and both adhesion and slip promoters may eliminate surface defects, if they provide the conditions for continuous slip. This scenario was also discussed by *Hatzikiriakos and Dealy (1991)*.

Piau (1988) used a photographic technique to show that cracks on the surface of extrudates always originate at the exit of the die. In general, there seems to be agreement in the literature that sharkskin melt fracture is an exit phenomenon.

For the sharkskin extrudate; it does not occur for all polymeric materials *(Denn, 1990)*.

Plau, Kissi and Tremblay (1990) investigated the flows of four different linear or branched silicones through thin-walled orific dies which were visualized. The observation of the extrudate downstream of the orifice allowed a through examination of the appreance and evolution of the various flow regimes. Depending on the rheology of the fluids considered, these defects may evolve into more severe forms commonly designated by "loss of gloss'' or "sharkskin". Moreover, for all the silicones studies, the well-known melt fracture phenomenon was observed. This defect first appears in forms of regular helix, and then evolves into a chaotic regime as flow pressure increases.

It is possible that the sharkskin defect derives from an instability at the die exit of a material which has been pre-stressed by its flow through the capillary. Another hypothesis has been given on the origin of sharkskin. It was proposed that cavitation or bubble formation take places, similar to that is involved during crazing *(Trembley, 1991)*. The bubbles are supposed to coalesce to form the characteristic surface cracks of sharkskin. *Chen and Joseph (1991)* have proposed that high stresses near the capillary wall could cause a segregation of polymer from the solvent or high molecular weight components from those of low molecular weight components. The low molecular weight polymer then become concentrated in a thin wall layer. In effect, there is a stratification of elasticity accompanying polymer segregation leading to short wavelength instability.

Tremblay (1991) has recently simulated the capillary flow of a linear polydimethylsiloxane melt, which exhibited significant sharkskin. His calculation have show that a large negative pressure (hydrostatic tension) exists at the die exit. He suggested that this tension cavitates the polymer melt very close to the die lip, thus leading to surface defects. Finally he pointed out that slip in the die land cannot explain the origin of the sharkskin phenomenon.

Hatzikiriakos and Dealy (1991) carried out experiments in a sliding plates rheometer to diameter the effect of the presence of two fluoropolymers on the slip velocity of a HDPE (Scalair 56B). They found that in one case slip increased while in the second case (a sprayed-on coating) slip decreased.

The occurrence of the sharkskin depends to the same extent on the state of stress of the material transports to the exit region. At the exit, there is a stress singularity or the stress discontinuity *(Larson, 1992)*.

Hatzikiriakos (1993) studied the effect of both these fluoropolymers on the extrudate appearance of a HDPE. Surprisingly, they found that both fluoropolymers eliminated surface defects. These observations show that wall slip is not the only causative factor for the occurance of surface melt fracture.

Hatzikiriakos (1994) proposed that sharkskin originates at the exit of the die and was due to the acceleration (high stretching rate) of the melt as it exits of the die. It was also shown that both adhesion and slip promoters eliminated surface defects by decreasing the stretching rate of the polymer melt at the exit region of the die. It was found that sharkskin was more pronounced in short die.

Recently, *Wang and Drda (1996)* proposed that sharkskin originated from an unsteady hydrodynamic boundary condition at the exit where LLDPE departs from the die in either a stick state or a slip state, causes by a local entanglement-disentanglement transition.

Wang and Drda (1997) studied molecular instabilities in capillary flow of polymer melt. They found that the severe roughness of sharkskin originated from the interfacial process at the melt/wall boundary near the exit. *Wang and Drda* conjectured that sharkskin phenomenon may involve not only some degree of localized wall slip near the die exit but also cohesive failure involving disentanglement among bulk chains situated away from the die wall near the exit. It occurs when stress level near the exit drops less than the critical stress, the adsorbed chains can no longer remain in their disentangled state and may remain entangled with the exit chains.

1.3 Research Objectives

- To determine the dependence of sharkskin onset parameters and the sharkskin characteristics on the molecular weight, die geometry, and melt temperature.

- To construct the stability diagram of sharkskin defect by normalization of recoverable shear (S_R).