CHAPTER I
INTRODUCTION

In polymer processing (extrusion, injection molding) polymer melt flows smoothly through a capillary, a channel or a die at low shear rates producing smooth extrudate. But when a volume flow rate exceeds a certain critical value the flow becomes increasingly unstable and the extrudate can exhibit a variety of defects. These physical defects increase in severity as the extrudate rate is increased. Extrudate distortion is a variation in shape along the length of the extrudate. This effect can range in intensity from a loss of gloss to a gross distortion. A term sometimes used to describe various extrudate distortion effects is "melt fracture". Extrudate production rate is limited by these extrudate distortions such as sharkskin, rippling, helical defect, spurt or stick-slip which are believed to be related to the slip between the polymer melt and capillary. Skin roughness therefore poses a challenging problem for micronsize manufacturing, especially if the products are of mechanical uses; the manufactued products are moving parts which must contact with other parts of a system.

1.1 Extrudate Distortion

There are many factors that influence the type and degree of extrudate distortion depending on melt temperature, capillary geometry, polymer structure, molecular weight and its distribution.

There are many types of surface distortion depending on the regularity and amplitude of the surface variations.

1.1.1 Sharkskin

Sharkskin is the first form of surface distortion encountered when increasing shear rate. The extrudate shows regular ridged surface distortion, with the ridges perpendicular to the extrusion direction and the amplitude of these variations increase with apparent shear rate in this regime, but rarely exceeds 10% of the extrudate diameter (Kalika and Denn,1987).

The mechanism of sharkskin is postulated to be caused by the rapid acceleration of the surface layers of the extrudate when the polymer leaves the die. If the stretching rate is too high, the surface layers of the polymer can actually fail and form the characteristic ridges of the sharkskin surface. High viscosity polymers with narrow molecular weight distribution (MWD) seem to be most susceptible to sharkskin in stability (Dealy,1990).

1.1.2 Oscillating Flow

In the case of oscillating flow at constant piston speed, the extrudate appearance varies in a cyclical manner in accordance with the periodicity of the reservoir pressure. The extrudate produced during a stick-slip cycle consists of two distinct regions: a rough, sharkskin section (corresponding to "sticking") with increasing pressure, and a smooth, glossy section

(corresponding to "slipping") with decreasing pressure (Kalika and Denn,1987).

1.1.3 Wavy Fracture

Wavy fracture is the most severe form of extrudate distortion, with the distortion depth on the order of the extrudate diameter. The degree of distortion at the onset of the wavy fracture region depends on capillary l_c/d_c. Wavy distortion can be quite severe at this transition in short capillaries, while in longer capillaries there may be a narrow stress range where the extrudate is completely smooth. The severity of wavy fracture increase with increasing shear stress (Kalika and Denn,1987).

1.2   Wall Slip

It has long been suspected that high molecular weight polymers could exhibit a non-zero boundary condition for velocity when flowing along a solid wall. Generally the fluid adheres to any wall withwhich it is in contact and that if this wall moves, the fluid in contact with moves at the same speed. The stick hydrodynamic boundary condition is usually an accurate description of viscous interactions at an interface between a solid surface and a liquid. Highly entangled polymeric melts are a unique class of single-component liquids that provide an example of slip behavior under certain experimental conditions. Such slip may originate from the strong dynamic structural discontinuity introduced by a solid surface. Where polymer-wall interfacial interactions diminish at high stresses. Thus, on the other hand, high molecular weight polymer chains interact strongly through chain entanglements in the bulk as illustrated by Figure 1.1(a). On the other hand, when polymer adsorption is

inhibited or disentanglement between adsorbed and free chains occurs in strong flow, the surface is essentially in contact with a molecular thin layer of monomerlike or unentangled liquid, creating extremely large disparity between the viscous interactions taking place across the interface and those taking place in the bulk as illustrated by Figure 1.1(b) (Wang and Drda,1995).

On a hydrodynamic length scale, this could amount to a finite slip velocity that invalidates the law of the stick hydrodynamic boundary condition. The consequence of vanishing polymer adsorption at a solid surface was first discussed theoretically by de Gennes who rediscovered the concept of extrapolation length (Wang and Drda,1995).
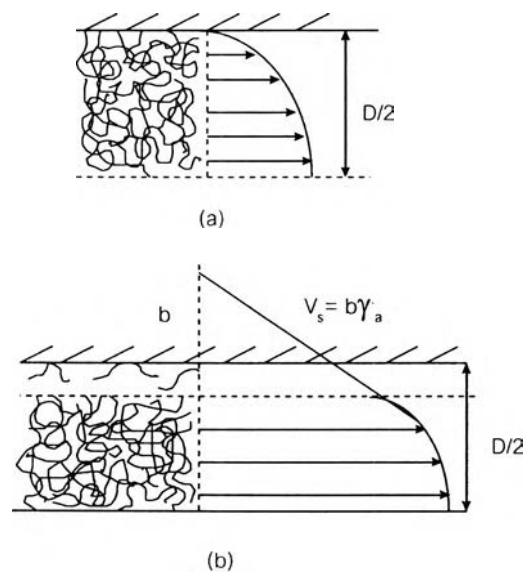

Figure 1.1(a) Velocity field at the stick-slip transition in the capillary corresponding to the "stick" state, with sufficient chain entanglement denoted by the dots and with zero slip velocity.

(b) Velocity field at the transition corresponding to the "slip" state, with the exaggerated depiction of zero chain entanglements in the interfacial layer and a much larger apparent flow throughput due to a finite slip velocity.

1.3 Extrapolation Length

The slippage of polymer is characterized by the extrapolation length b, defined by the distance to the wall at which the velocity extrapolates to zero (Brochard and de Genn,1992). The extrapolation length is an important quantity in characterizing wall slip if it becomes a macroscopic quantity, much larger than the size of the molecules (Leger,1997). de Gennes suggested that high molecular weight polymers on a smooth non-adsorbing wall should slip, whatever the applied shear rate, with a large extrapolation length b, (a few mm), with a magnitude depending only on the molecular weight of polymer.

The stress at the wall is related to the friction between the monomers in contact with the wall and the wall itself. Brochard and de Gennes suggested the different possible regimes as illustrated by Figure 1.2. Three observable regimes are possible: entanglement, marginal and rouse.

In the entanglement regime: few polymer chains attached to the surface have a drastic effect on the boundary condition for the flow velocity. They strongly reduce the slip velocity at low shear rates, due to a huge friction in the low velocity regime and give b values which are extremely small.

In the marginal regime: above the critical slip velocity, a nonlinear friction regime appears, the polymer chains have been fully extended along the flow and disentanglement from the melt at high-enough shear rates and the extrapolation length is a linear function of the slip velocity.

In rouse regime: at high shear rates, a tendency to attain a linear friction regime, with strong slip appears and the extrapolation length is independent of the slip velocity.
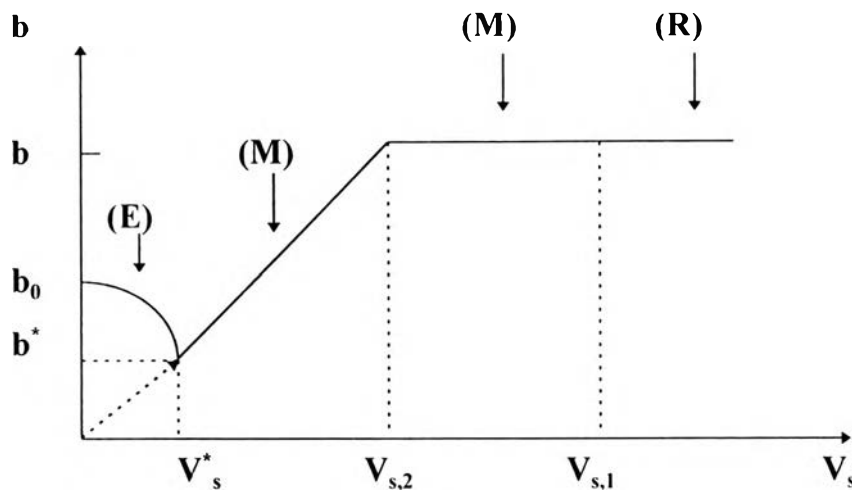
Figure 1.2 The three regimes of slip velocity in the plot between the extrapolation length, b versus the slip velocity, V_S.

1.4   Previous Studies

Ramamurthy (1986) carried out experiments in a capillary rheometer for a variety of HDPE and LLDPE resins. Using the Mooney analysis, he calculated the slip velocity as a function of wall shear stress. He suggestes that the onset of slip occurs at a critical shear stress of approximately 0.1-0.14MPa. When either surface or gross irregularities are present in the extrudate. The critical stress is relatively insensitive to molecular characteristic (molecular weight, MWD, and chain branching), melt temperature and the detailed design of the capilary.

Kalika and Denn (1987) assumed a power-law model and calculated slip velocities of LLDPE from the change of slope. They reported the onset of sharkskin is shown to coincide with the failure of adhesion at the polymer/metal interface. The transition to stick-slip melt fracture is characterized by a catastrophic failure of adhesion, with periodic nearly completed slip over a

capillary residence time adhesion and the onset of sharkskin is in agreement with calculation based on a stability theory of Pearson and Petrie (1976)

Atwood and Schowalter (1989) measured the slip velocity of a high density polyethylene using a hot-film heat flux probe in a slit rheometer. They found that appreciable extrudate roughness was initiated at the same flow rate for heat transfer from the probe departed from the behavior expected for a no-slip condition at the conduit wall. They reported values of slip velocity and a critical shear stress for the onset of slip that were very high compared to those reported by Ramamurthy (1986).

Moynihan, Baird and Ramanathan (1990) investigated the surface melt fracture behavior of linear low-density polyethylene (LLDPE). They examined the effect of l_c/d_c ratios in the capillary experiment and slit-die experiments when surfaces were coated with a fluoro-elastomer. The roles of the entry, land and exit regions in the surface melt fracture behavior were examined and the results seem to suggest that the surface melt fracture arises at the die with the aid of pre-stressing conditions upstream of the exit.

Hatzikiriakos and Dealy (1991a) carried out steady uniform shear experiments at ambient pressure in a sliding plate rheometer for a high density polyethylene, and found that above a critical shear stress the curve of shear stress versus nominal shear rate (plate velocity over plate spacing) depends on the gap between the plates, implying that the melt slip at the wall. They used Mooney technique to calculate the slip velocity as a function of shear stress.

Hatzikiriakos and Dealy (1991b) also carried out experiments in a capillary rheometer with long dies (lc/dc>40) for the same high density polyethylene and found that the apparent flow curve was a function of the diameter of the capillary when the wall shear stress was greater than the critical value. It implies that slip was occuring.

Brochard and de Gennes (1992) studied shear flows of a polymer melt near a solid wall surface onto which a few chains have been grafted. They found that at low shear rates $\tau < \tau^*$ they expected a strong friction. Above a certain critical shear τ^* the grafted chain should undergoes a coil stretch transition. In the stretched state, they are not entangled with the melt, and a significant slippage is expected when $\tau > \tau^*$. They suggested that this transition may be important in the processing of polymers, where a few chains from the melt can be bound on an extruder wall and play the role of the grafted chains.

Hatzikiriakos and Dealy (1992) studied the roles of slip and fracture in the oscillating flow of HDPE in constant piston speed rheometer. They concluded that on the high-flow-rate branch of the flow curve there was slip along a cylindrical fracture surface near the wall. The jump to the high-flow-rate branch occured when this fracture occured, at an upper critical value of the shear stress, while the jump back to the low-flow-rate branch occured when adhesion was established at the fracture surface at a lower critical shear stress.

Hatzikiriakos (1994) studied the capillary die flow of high density and linear low density polyethylene simulated under slip conditions to investigate the origin of sharkskin melt fracture. They found that sharkskin originates at the exit of the die and is due to the acceleration (high stretching rate) of the melt as it exits the die. They also found 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. They also found the sharkskin was more pronounced in short dies, and it was suggested that applied pressure at the capillary exit suppressed surface defects.

Wang and Drda (1995) studied a striking superfluid like stick-slip transition and semiquantitatively analyzed for a series of highly extangled linear polyethylene melts subjected to capillary flow. They found that the

observed violation of the law of the stick hydrodynamic boundary condition was significant and unambiguous, and can be conveniently characterized by the extrapolation length, b. It was shown that b at the transition was independent of temperature and sharply increased with molecular weight in confirmation with a simple scaling relation introduced by de Gennes.

Brochard and de Gennes (1996) studied the slippage of a highly viscous polymer melt on a solid substrate grafted by a few smaller chains in the mushroom regime. The friction was provided by the sliding motion of the highly viscous polymer melt of the "skin" which were entangled with the tethered chains. They found that at low grafting densities, only a fraction of the highly viscous polymer melts were coupled to the smaller chains in the mushroom regime and the friction on the mushrooms was additive. Above a threshold grafting density, all highly viscous polymer melts of the skin were trapped, and the low velocity friction become independent of the grafting density. Above certain threshold slippage velocity the smaller chains in mushroom regime were strongly stretched and reach a "marginal state" , corresponding to a constant shear stress. They predicted a cascade of regimes, where the smaller chains in mushroom regime may be ideal, stretched, or " marginal", while the trapped chains may be ideal or stretched and progressively disentangled from the smaller chains in mushroom regime.

Wang and Drda (1996,a) explored rheological characteristics of molecular mechanism for superfluid like stick-slip transition occuring under controlled pressure in capillary flow of a series of highly entangled linear polyethylene (PE) melts and establishes its connection with the spurt flow phenomenon. The transition was signified by a large discontinuity in the flow rate at a critical stress, resulting in a double value within the flow curve. They found the flow transition depended on the surface condition of the die wall and

occured at a considerably lower critical stress when the wall was treated by depositing a fluorocarbon elastomer to weaken the PE adsorption.

Wang and Drda (1996.b) studied molecular characteristics and temperature dependence of a superfluid like stick-slip transition in a series of highly entangled high density polyethylene (PE) resins and their rheological behavior in a pressure driven capillary flow. They found that at sufficiently high stresses the capillary flow characteristics were largely dictated by the stick-slip transition occured at the PE/die wall interfaces. The transition magnitude was found to have an explicit and strong molecular weight dependence reminiscent of bulk chain entanglement.

1.5   Research Objectives

This work has the following objectives:

- To investigate the extrudate distortion phenomena and the slip phenomena of HDPE and LLDPE by a capillary rheometer.

- To determine slip velocities in a capillary rheometer in terms of molecular weight and temperature.

- To determine the extrapolation length from a capillary rheometer in terms of molecular weight and temperature.