CHAPTER I
INTRODUCTION

Surface texture and skin smoothness are one of the critical requirements in fiber spinning process or in plastic processing (extrusion, injection molding) of minute-sized products which require precise manufacturing and/or assembling at later stages. Skin roughness therefore poses a challenging problem for micron-size manufacturing, especially if the products are of mechanical uses; the manufactured products are moving parts of a system.

Fast processing speed reduces cost at expense of the surface waviness or the ***melt fracture***. The cause of extrudate irregularities or ***melt fracture*** has been a topic of discussion in literature since the 1960s (Hoynihan et al.,1990). A comprehensive review by Petrie and Denn in 1976 helped to clarify different types of instabilities previously lumped together under term ***melt fracture*** which refers to the surface distortion of an extrudate of a capillary or a slit extruder. In processing, the surface distortions occur when the volume flow rate exceeds certain critical values. Therefore extrudate production rate is limited by these extrudate distortions: wavy surface, sharkskin, rippling, helical defect, spurt or stick-slip which are believed to be related to the slip between the polymer melt and capillary. Other causes that have been considered to be related with the melt fracture are adhesion and cohesion between melt and extruder, melt compressibility, and possibly some flow instabilities near the capillary contraction.

The central themes in our research efforts are to improve product quality and production rate, and to ensure that precision in manufacturing can be maintained as parts of the assembled products continue to get smaller and smaller whereas tolerances become critically small in proportion. The scientific question is whether there are any universal laws or criteria for the onset of the extrudate distortion. High density polyethylene (HDPE)/ polypropylene (PP) blends are selected to study because HDPE and PP are commodity plastics which have been used widely in Thai plastic industry. One of many reasons for adding HDPE to PP is to improve its low temperature impact and environmental stress cracking properties.

1.1 Background

1.1.1 Extrudate Distortions

At low strain rates, a polymer melt flows through a capillary or die producing smooth extrudates. At high strain rates, several kinds of flow instabilities can develop in which the surface of the extrudate becomes rough or nonuniform in cross section, and the flow rate is no longer steady but oscillates. This extrudate distortion can range in intensity from a loss of gloss to a gross distortion. It is the factor that limits the production rate in certain processes. A term sometimes used to describe the various extrudate distortions is ***melt fracture***.

There are many factors that influence the type and degree of extrudate distortion: chemical nature of polymer, molecular weight and its distribution, branching, entrance geometry, length to diameter ratio and material of construction of the capillary, temperature and flow rate. Several extrudate distortions can be distinguished by their appearances.

1.1.1.1 Sharkskin

Sharkskin is the skin defect that usually has the lowest onset (critical flow rate). The surface texture is orderly, consisting of nearly periodic roughness of about a few percent of the diameter. The semiregular cracks or grooves of the sharkskin surface exhibit itself as a regular ridged surface distortion, with the ridges running perpendicular to the extrusion direction. It is considered to be a short wavelength instability because the disturbance is of small amplitude but of high frequency. Sharkskin does not occur for all polymeric materials (Denn. 1990). The onset of sharkskin depends on the die exit region, the length of the die (Hoynihan et al., 1990) and in some cases the die material and the die coating (Piau et al., 1986). The mechanism of sharkskin is postulated to be caused by the rapid acceleration of the surface layer of the extrudate when the polymer leaves the die. This abrupt change causes a high degree of stretching in the surface layer. If the stretching rate is too high, the surface layer fails and forms the ridge of sharkskin in surface. High viscosity polymers with narrow molecular weight distribution seem to be most susceptible to sharkskin instability (Ramamurthy, 1986). However, later studies of extrudates of linear polyethylenes (Kalika and Denn, 1987), suggest that the onset of this surface fracture is accompanied by the occurrence of wall slip in capillary. Thus, while this type of distortion is clearly an exit effect, it may be associated with slip flow in the capillary.

1.1.1.2 Peeled Orange

This extrudate distortion is a long wavelength instability prior to the occurrence of surface roughness at high strain rate; magnitudes of surface roughness are comparable to the extrudate diameter. It is called ***peeled orange***. This skin defect is different from the sharkskin because the wavelength is longer than the extrudate diameter. It occurs at an onset which is beyond that of the sharkskin. The origin of peeled orange is not well documented as it occurs only for certain materials.

1.1.1.3 Oscillatory Flow

For several linear polymers, at higher flow rates where a sharkskin occurs, a regime is reached in which the flow rate and pressure oscillate between upper and lower bounds. In this regime, the extrudate usually consists of regularly alternating zones of relatively rough and relatively smooth surface textures. This behavior corresponds to periods during which the melt alternatively sticks and slips at the wall capillary. Benbow et al. (1961) have postulated that the polymer melt losed adhesion at the metallic wall and slipped when the shear stress exceeded the critical value. The wall shear stress then decreased to a value lower than the critical one and adhesion was promoted. The shear stress increased again as observed by the cyclic flow. Kalika and Denn (1987) noted that in the oscillating flow regime flow, the extrudate exhibited alternatively a gloss section and a severe sharkskin section. They reported that the glossy segment corresponded to the slip at the wall or as the pressure was falling.

1.1.1.4 Gross Fracture

Further increases in the flow rate above the range over which oscillating pressure is observed lead to an intense random distortion of extrudate. For these skin defect appearances, 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. The degree of distortion at the onset of the gross fracture region depend on capillary l_c/d_c. It can be quite severity at transition in short capillaries, while in longer capillaries there might be a narrow stress range where the extrudate is completely smooth. The severity of fracture increases with increasing shear stress. Nearly complete slip follows the onset of the gross fracture.

1.1.2 Concept of Bifurcation

Slip velocity is used as the property of the system and the apparent strain rate is the system parameter in constructing a bifurcation diagram (Berg et al., 1984). A point in parameter space where the flow changes qualitatively is called a critical value or a bifurcation point. From the bifurcation point emerges several (two or more) solution branches, either stable or unstable. The representation of any characteristic properties of the flow as a function of the bifurcation parameter constitutes ***a bifurcation diagram***. There are several types of bifurcation: saddle-node, transcritical, pithflok and Hopf (Berg et al., 1984). The first three types refer to bifurcations from a steady state to another steady state, whereas the last refers to a bifurcation form a steady state to a limit cycle (time-dependent). Although the first three types of bifurcation may exist following a change from a skin texture to another, it is very difficult to detect and identify with existing apparatus. It is much simpler to identify unambiguously Hopf bifurcations or the change in the melt flow behavior from a steady state to a limit cycle. Hopf bifurcations will be determined whether they are of supercritical or subcritical type, depending on the continuity of the flow curve at the bifurcation point or whether hysteresis occurs. Supercritical type occurs when the lowest nonlinear term of the melt flow equation stabilizes the system and the bifurcations is often unique. Subcritical type implies the lowest order nonlinear term in the melt flow equation destabilizes the system. It is sensitive to noise and therefore the critical parameters or bifurcation are not expected to be unique. We propose to identify the type of the Hopf bifurcation because it is closely related to and will help explaining the outcome and the result of the critical parameters.

1.1.3 Stick - Slip Transition at Polymer Melt/Solid Interfaces

Stick hydrodynamic condition is usually an accurate description of viscous interactions at an interface between a solid surface and a liquid (Drda and Wang, 1995). For Newtonian fluids the assumption of no-slip at a fluid/wall interface leads to a good agreement with experiment observations. For non-Newtonian fluids the assumption of no-slip at wall sometimes leads to inaccurate predictions. Highly entangled polymeric melts are a unique class of single component liquids that may provide an exceptional example of slip behavior under certain experiment conditions. Such slip may originate from the strong dynamic structural discontinuity introduced by solid surface where polymer/wall interfacial interactions can diminish at high stresses. Whereas, high molecular weight chains interact strongly through chain entanglements in the bulk. A sufficient entanglement or ***stick*** condition is present between the adsorbed and free chains at the polymer/wall interface as illustrated by Figure 1.1(a). When polymer adsorption is inhibited or disentanglement between adsorbed and free chains occurs in the strong flow, the surface is essentially in contact with a molecularly thin layer of monolike or unentangled liquid, creating an extremely large disparity between the viscous interactions taking place across the interface and those taking place in the bulk (Drda and Wang, 1995) The interfacial layer experiences a structural transition that may be thought of as a flow induced disentanglement between adsorbed and free chains at the polymer/wall interface and it is referred to as the ***slip state*** as illustrated in Figure1.1(b). 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 (1992) who rediscovered the concept of extrapolation length.

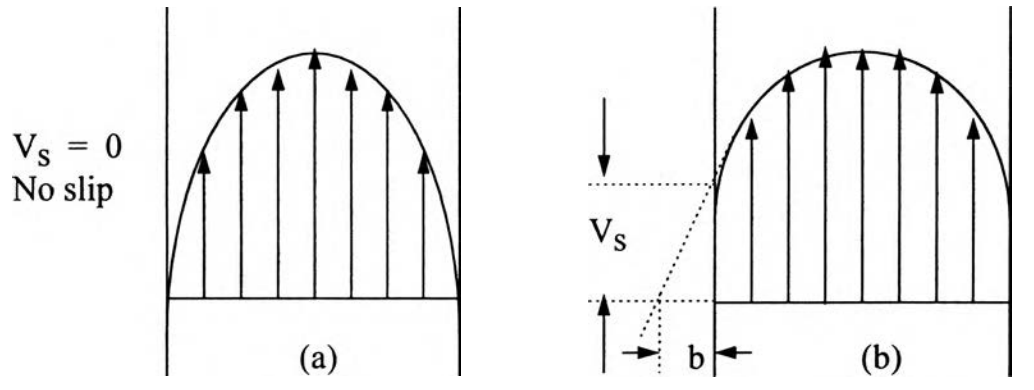

Figure 1.1(a) Velocity field of the stick-slip regime corresponding to the "stick" state.

Figure 1.1(b) Velocity field of the stick-slip regime corresponding to the "slip" state.

1.1.4 Theory of Brochard & de Gennes

The condition where the flowing material at the interface has nonzero velocity is called the ***wall slip***. The slip layer and hypothesis have received considerable attentions lately (Brochard and de Gennes, 1992). The slip velocity, normalized by the average velocity and collapsed well for many diameters, is a strong function of the wall shear stress; the slip velocity and the slippage length have been postulated to be functions of the shear stress imposed (Hill et al., 1990). There is a thin slip layer near a wall in a disentangled state where polymer melt moves at a uniform velocity. Refering to Figure 1.2, three observable regimes are possible: entanglement, marginal and Rouse. In the entanglement regime; slip occurs with melt chains assuming random coil configurations. In the marginal state; melt chains have been fully extended and the slippage length is a linear function of the slip velocity. The Rouse regime corresponds to the situation where the slippage length is independent of the slip velocity.

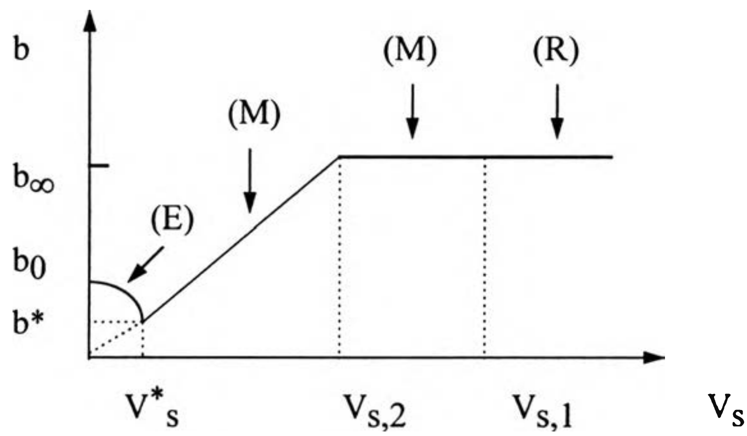

Figure 1.2 The three regimes of slip velocity in the plot between the extrapolation length, b versus the slip velocity, V_S.

1.1.5 Normalizations

Previous normalizations of the wall shear stress was by the recoverable shear factor (S_R). In this normalization, the conjecture was that S_R should be unique as it represents the ratio two dominant force such as viscous and elastic forces. As stated in the objective section, 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 and for the melt fracture S_R varies between 5-8 (Kalika and Denn, 1987). The variations are 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 force that are relevant

(b) normalizations were not properly done, as rheological properties were not thoroughly measured

(c) instabilities might be of the subcritical type where the lowest nonlinear term destabilizes the flow system, and a hysteresis occurs

S_R can be normalized by two method; the asymptotic and local methods. In the first method, S_R is obtained using the glassy storage modulus which is independent of frequency at a particular temperature or at a reference temperature of a master curve. The second method, S_R is done by the local storage modulus which corresponds to the apparent strain rate at which the skin defect occurs. Our conjecture is that since the glassy storage modulus is not the actual elastic force incurred in the capillary, the local value of the storage modulus might be a more appropriate elastic force. It is expected that S_R obtained this way would be closer to order one with a smaller variation, for skin defects whose origins are of cohesive nature.

1.2 Literature review

Benbow et al. (1961) have studied the slip-stick phenomenon. They have postulated that the polymer melt lost adhesion at metallic wall and slippage occurred when the wall shear stress exceeded a critical value. The wall shear stress then decreased to a value lower than critical one and adhesion was promoted. The shear stress increased again as observed by the cyclic flow of HDPE.

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 the wall shear stress. He suggested that the onset of slip occurred at a critical shear stress and was accompanied by both a matte appearance of the extrudate and a change in the slip of the flow curve.

Kalika and Denn (1987) assumed a power-law model and calculated slip velocities from the change of slope. They reported slip velocities and a critical wall shear stress for the onset of the slip that were significantly higher than those reported by Ramamurthy (1986).

Hatzikiriakos and Dealy (1991) carried out steady uniform shear experiments at ambient pressure in a sliding plate rheometer for HDPE, and found that above a critical shear stress the curve of shear stress versus nominal shear rate depended on the gap between the plates, implying that the melt slips at the wall. They used the Mooney technique to calculate the slip velocity as a function of shear stress. They also carried out experiments in a capillary rheometer with long dies for the same HDPE 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, which implied that slip was occurring.

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

Wang and Drda (1995) have studied a striking superfluidlike transition in which a series of high entangled linear polyethylene melts were subjected to a capillary flow. They observed violation of the law of the stick hydrodynamic boundary condition to be significant and unambiguous, and can be conveniently characterized by an extrapolation length, b. It was shown that b at the transition was independent of temperature and it sharply increased with molecular weight, consistent with a simple scaling relation introduced by de Gennes (1992).

Wang, Drda and Inn (1996) have studied extensively of the capillary flow and extrudate behavior of LLDPE. They found the characteristic curvature (i.e., a slope change) in the flow curve originates from partial slip in dies exit region. Due to the singularly strong stretching a stress field was generated by the boundary discontinuity at die exit. They suggested the slope change arises from a combination of the interfacial slip and cohesive failure because of chain disentanglement. As the disentanglement state is unstable for the adsorbed chains within a certain stress range below the critical stress for the global stick-slip transition, a partial slip flow cannot support itself and occurs only periodically. The discontinuity of the interfacial boundary condition at die exit diminishes whenever significant slip occurs between LLDPE and the die wall. When the die wall is made nonadsorbing and slippery by a fluoroelastomer coating or when LLDPE undergoes an interfacial stick-slip transition, severe sharkskin abruptly diminishes and the extrudate turns completely smooth.

Wang and Drda (1997) indicated that an interfacial stick-slip transition occurred in capillary flow of linear polyethylenes beyond a critical stress because of a reversible coil-stretch transition of the absorbed chains leading to their disentanglement from unbound chain. The interfacial process caused the melt/wall hydrodynamic boundary condition (HBC) to become indeterminate and oscillatory and the extruded melt to undergo flow oscillation under a constant extrusion rate such as fixed piston speed. The slip occurred at the same amplitude because of the stress-induced polymer desorption on a weakly adsorbing die wall. In addition, debonding of adsorbed chains restored a steady slip HBC and eliminated instability of oscillating flow, then offering a satisfactory explanation for how the empirical method of modifying the surface condition can remove the flow oscillatory symptoms.

1.3 Objectives of Research

- To study a variety of the extrudate distortions of HDPE/PP blends by a capillary rheometer.
- To determine the type of the flow bifurcation in the oscillating regime.
- To measure the slip velocity and determine the characteristic extrapolation length in the oscillating regime.
- To investigate the effect HDPE/PP blend composition pertinent to the oscillating and the melt fracture regimes.
- To determine the recoverable shears for the skin defects and to see if they are unique.