CHAPTER I

INTRODUCTION

In the extrusion process of polymers through a capillary die, different skin defects and flow instability occurs. These defects are of commercial importance because both of large and small products, surface gloss and surface smoothness quality are ones of many requirements for customer appeal. Skin defects occur when the flow rate exceeds critical values. Therefore extrudate production rate is limited by the skin defects. To save energy and labor cost, the issue of the large variation in the critical data must be resolved. Further step may be a control of the skin defects. The other application in this area of polymer processing is minute-sized of manufacturing. For the small scale of plastic products require assembling before use. 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 and require contract with other parts of a system.

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.

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. It is considered a short wavelength instability because the disturbance is one of small amplitude but of high frequency.

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 is beyond that of the sharkskin.

Melt fracture is easily distinguished from others by the 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.

For the sharkskin extrudate; it does not occur for all polymeric materials (Denn, 1990). The mechanisms of sharkskin has been proposed by Kurtz (1984). The occurrence of the sharkskin depends to the same extent on the state of stress of the material transported to the exit region. At the exit, there is a stress singularity or the stress discontinuity (Larson, 1992). It is possible that the sharkskin defect derives from an instability at the die exit of a material which has been pre-stressd by its flow through the capillary. Another hypothesis has been given on the origin of the sharkskin. It was proposed that cavitation or bubble formation takes place, 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 instabilities.

1. 2 Flow Instability and Mechanisms

Flow instability is a change in flow behavior from being a steady state to another steady state or oscillating state. For example, a smooth extrudate of a steady flow can change to a sharkskin extrudate of a steady state flow or a sharkskin extrudate of a steady flow can change to an alternating sharkskin/smooth extrudate of an oscillating flow. The precise instability mechanism has not been yet completely elucidated, and seems to be influenced by various properties, such as fluid rheology, capillary die exit geometry, molecular structure and thermal effects. One explanation given by Tordella (1957) and Bagley (1961) is that the liquid polymer is fractured by elongational stresses. Bagley gave a critical capillary wall recoverable shear strain criterion for melt fracture. White (1964) gave a different explanation based on experimental observations of the flow of viscoelastic fluid through a contraction. He argued that a hydrodynamic instability is initiated in the form of a spiral flow when a critical Weissenberg number is reached. In his opinion, this instability is the initial mechanism of polymer melt extrudate distortion.

There are two mechanisms that cause the failure of the surface distortion, the first one is adhesive force which is the interaction at the interface of polymer melt and metal of the die, it depends on the material of construction or lubricating layer of the die. The other is cohesive force which is the interaction between covalent bonding of the polymer melt itself. These explanations are referred to as wall slip, and constitutive instability, respectively (Denn, 1990). Wall slip is often modeled by replacing the conventional no-slip boundary at the wall condition (Pearson and Petrie, 1968; Renardy, 1990; Hill et al., 1966). A constitutive instability, on the other hand, will occur if the constitutive relationship between shear stress and strain rate is non-monotonic (Huseby, 1966). Although these two mechanisms of extrudate distortion are different in principle, they are in practice difficult to distinguish, because both predict the same macroscopically observable phenomenon.

Bifurcation diagram implies a non-monotonic stress-strain rate relation, or the constitutive instability. We constructed bifurcation diagrams using the stress as the system property and the apparent strain rate as the system parameter. A point in parameter space where the flow changes qualitatively is called the critical value or bifurcation point. From a bifurcation point emerges several solution branches, either stable or unstable. The representation of any characteristic properties of the flow is a function of the bifurcation parameter. There are several types of bifurcation: saddld-node, transcritical, pitchfolk and Hopf (Berge, 1984). The first three types refer to bifurcation from a steady state to another steady state. 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 easier to identify unambiguously Hopf bifurcations or the change in melt flow behavior from steady state to a limit cycle.

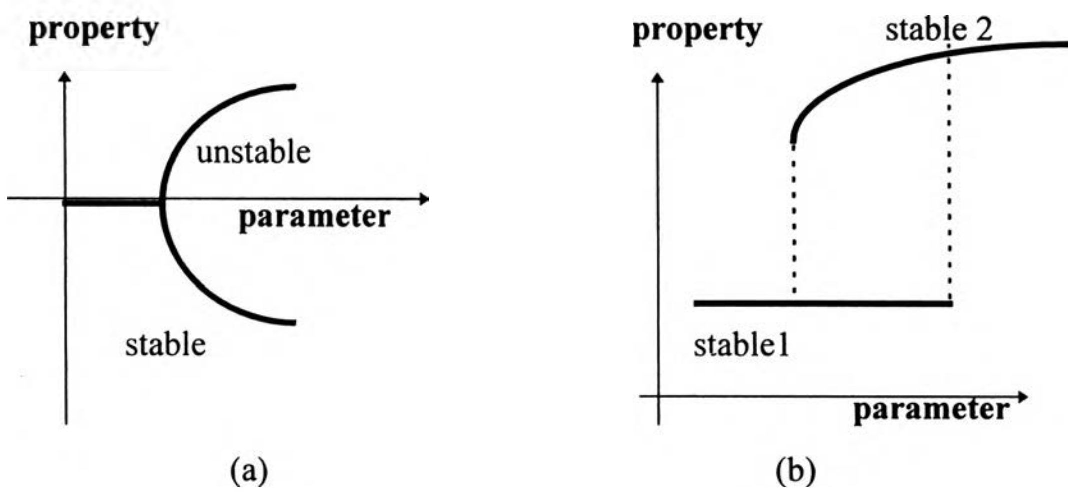

Figure 1.1 Bifurcation diagrams (a) supercritical and (b) supercritical.

We identified Hopf bifurcation from several polymer melts in the oscillating regimes, and we will determine whether they are of *supercritical* or *subcritical* type, depending on the continuity of the flow curve at the bifurcation point or whether hysteresis occurs. Subcritical type implies that the lowest order nonlinear terms in the melt flow equation destabilizes the system. It is sensitive to noise and therefore the critical parameters or bifurcations are not expected to be unique. Supercritical type occurs when the lowest nonlinear term of the melt flow equation stabilizes the system and the bifurcation point is often unique.

1. 3 Previous Studies

Kalika and Denn (1987) studied on wall slip and extrudate distortion in LLDPE and the onset of extrudate distortion (sharkskin) in LLDPE is shown to coincide with the failure of adhesion of the polymer/metal interface. The transition to slip - stick melt fracture is characterized by a catastrophic failure of adhesion, alternating between completely slip and adhesion (stick) over a capillary residence time. The onset of sharkskin is in agreement with a calculation based on a stability theory of Pearson and Petrie (1965). A critical value of the recoverable shear of sharkskin is 1.5.

Sornberger (1987) studied the sharkskin defect in LLDPE. They used roughness measurements to detect accurately the onset of the sharkskin defect and to quantify its amplitude. With increasing flow rate, the sharkskin defect appears at a critical value of flow rate and then grows. This critical value and maximum amplitude of defect increase with temperature. Flow birefringence pattern was used to obtain the information on the stress distribution at the die. At the appearance of the sharkskin defect, all birefringence patterns are identical and independent of the flow rate and temperature.

Weill (1980) studied about the origin of sharkskin that they gave results of LLDPE melt flow instability and sharkskin phenomenon. They are presented in terms of relaxation oscillator theory, and permit us an understanding of the influence of experimental parameters on the period of the oscillatory flow. Sharkskin is interpreted to be the same phenomenon as the other instability, but to occur in the die exit region rather than the whole die itself. Theory on sharkskin mechanisms show that the length of the perturbation of the pressure gradient within the entry of the capillary is two times of diameter of the capillary.

EL Kissi and Piau (1990) studied on the different capillary flow regimes of entangled polydimethylsiloxane (PDMS) polymers. It was shown that the flow is perfectly stable at first. The appearance of the extrudate was smooth and transparent, then the extrudate become scratched when increasing the flow speed. The extrudate presents a sharkskin effect. Above a certain pressure, it triggers a melt fracture. As far as stable flow is concerned, most of results apply to highly entangled PDMSs following through long capillary. These PDMSs to allow large - scale cracks in the fluid, giving the appearance of the sharkskin, by the existence of warp - around corresponding to the edges of each crack.

Moynihan (1990) studied on the additional observations on the surface melt fracture behavior of LLDPE that the onset of sharkskin is observed at an apparent shear rate of 27 s^{-1} and the severity increases with increasing shear rate. The effect of coating is to eliminate the surface by coating the entry region indicating that the entry region plays an important role in the sharkskin behavior. The results of coating the exit region suggests that it is ultimately the exit region which is responsible for initiating fracture in LLDPE and not the entry. The explanation in the coating studies is that the fracture is initiated in the entry region and that coating the exit serves to attenuate the fracture.

Piau (1989) studied the influence of upstream instabilities and wall slip on the melt fracture and sharkskin phenomenon during silicones extrusion through orifice dies. Extrudates found were scratches, loss of gloss and cracks typical of the sharkskin phenomenon. All these defects can appear when the upstream flow is perfectly stable. They are basically exit phenomena, resulting essentially from the detailed structure of emerging zone of free surface, and from the high tensile stresses acting on the fluid at the outlet from the orifice dies. These defects occur only under free jet conditions, and are thereby related to the presence of a free surface in downstream region. Furthermore, whereas scratches appear for relatively low stresses and may therefore be observed for all the fluids studied, it has to be noted that the two other phenomena are typical of thick and fragile products, likely to undergo high tensile stresses responsible for cracks and sharkskin. Thus, these phenomena have been observed with the gums but not with the oils. Note that such a phenomenon has to be studied right at the die exit, where the tensile stresses are maximum and the cracks most severe, and not on rods cut off far downstream of exit region which generally show only the secondary phenomenon of surface roughness following fluid relaxation.

Wang, Drda and Inn (1996) studied the molecular origins of sharkskin, partial slip, and slope change in flow curves of LLDPE. The interfacial condition at the LLDPE wall boundary clearly plays a crucial role in the generation of slope change and sharkskin. When a die wall is sufficiently adsorbing, the boundary condition is that of no slip for a significant fraction of time in the sharkskin regime. This may cause a boundary discontinuity across the die exit and generates an exceedingly large stretching flow field in the exit region that may initiate a cohesive entanglement-disentanglement transition away from the first interfacial layer. The bulk (cohesive) disentanglement does not occur in high molecular weight HDPE because it can resist much higher stresses before a cohesive failure can occur, but lower molecular weight HDPE can display sharkskinlike extrudate distortion. A coating of the die wall enables stress-induced chain debonding and insures a steady boundary condition, which apparently relieves the strong stretch field by diminishing the discontinuity in the boundary condition across the exit. By a coating treatment of the die, they were able to eliminate sharkskin.

Wang and Drda (1997) studied about the molecular instabilities in capillary flow of polymer melts focusing on interfacial stick-slip transition, wall slip and extrudate distortion. They found that the severe roughness of sharkskin originated from interfacial process at the melt/wall boundary near the exit. The self-similarity characteristic of sharkskin and the intensity of the slope change, both supported a proposal that the 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 regain entanglement with the exit chains.

1. 4 Research Objectives

This work has the following objectives:

- To investigate the type of the flow bifurcation diagram in the oscillation regime and its relation to the sharkskin defect.
- To relate the flow bifurcation with the slip velocity.
- To determine the dependence of sharkskin critical parameters and the sharkskin characteristics on the molecular weight and die geometry.
- To construct the stability diagram of sharkskin defect by normalization of Weissenberg number (W_i) and recoverable shear (S_R).