CHAPTER II
LITERATURE SURVEY

The occurrence of the extrudate distortion in the extrusion processing was the preliminary problem for many researches There are several surface skin defects: matte, sharkskin, peeled orange, bamboo-like and gross melt fracture (Leonov and Prokunin, 1994). The cause of these skin defects was attributed to the instabilities of extrusion flow. Petrie and Denn (1976) suggested that low Reynolds number instabilities in shear flow and in extrusion, commonly referred to collectively as melt fracture, are two different phenomena. For linear polymers, the characteristic was probably an instability of the shear flow in the die. For branched polymers, the other characteristic was probably instability on the converging flow at the die entry. Both instabilities occurred at a value of the recoverable shear (shear stress/shear modulus) of order 1 to 10. Previous published results indicated that instability and fracture behavior were in some cases very sensitive detectors of such variations in molecular structure. Here literature on the slip phenomena is reviewed.

Weill (1980) proposed that the oscillatory flow of HDPE in capillary extrusion can be considered as a succession of temporary condition governed by the mass conservation and it may be described in terms of relaxation oscillations: the compressibility of the melts in the melt in the reservoir acting as the capacitor of the oscillator. The whole die was considered as the resistive part of the pressure. But if only the entry region contributes to the resistive part of the oscillator, the die itself acts as a damping element and melts flow at the exit give rise to the sharkskin phenomenon.

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 suggested that the onset of slip occurs at a critical shear stress of approximately 0.1-0.14 MPa. When either surface or gross irregularities were present in the extrudate, the critical stress was relatively insensitive to molecular characteristic (molecular weight, MWD, and chain branching), melt temperature an the detailed design of the capillary.

Moynihan, Baird and Ramanathan (1990) investigated the surface melt fracture behavior of linear low-density polyethylene (LLDPE). They studied the effect of L/D ratios of rounded die and slit die and the coated surfaces with a fluoro-elastomer. The roles of the entry, land and exit regions in the surface melt feature behavior were examined and the results seemed to suggest that the surface melt fracture arose at the die with the aid of pre-stressing conditions upstream of the exit.

Brochard and de Gennes (1992) expressed the disentanglement model for shear flow of a polymer melt near a solid surface onto which a few grafted chains are present (chemically identical to the melt). At low shear rates, $\sigma < \sigma^*$, they expected a strong friction. Above a certain critical shear stress, σ^*, the grafted chains should undergo a coil stretch transition. In the stretched state, the grafted chains are not entangled with the melt, and a significant slippage is expected when $\sigma > \sigma^*$. 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 (1994) investigated the origin of sharkskin melt fracture of HDPE and LLDPE by simulating slip conditions. He found that sharkskin originated at the exit of the die and was due to the acceleration (high stretching rate) of the melt as it exited the die. Both adhesion and slip promoters were able to eliminate surface defects by decreasing the stretching rate of the polymer melt at the exit region of the die.

Drda and Wang (1995) investigated the stick-slip transition of HDPE by using a controlled-pressure capillary rheometer and found that the extrapolation length (b) was independent of temperature but strongly dependent on molecular weight.

Hatzikiriakos, Hong, Ho and Stewart (1995) used two LLDPE resins to determine the critical conditions for the occurrence of wall slip an melt fracture in capillary extrusion. They found that the polymer-metal interface failed at a critical value of the wall shear stress of about 0.1 Mpa as slip occurred at 0.18 Mpa. The extrudate surface appeared to be matte, while sharkskin appeared above 0.25 MPa. On Teflon® coated slit die, slip was promoted, thus decreasing in power requirement and, most importantly, eliminated sharkskin at high extrusion rates.

Wang, Drda and Inn (1996) found that the time dependent molecular entanglement-disentanglement fluctuation produced sharkskin like the extrudate in the regime where the slope change took place. And the sharkskin periodicity was found to be of the same magnitude as the characteristic molecular relaxation time $\tau^* \approx 1/\omega_c$.

Brochard-Wyart, Gay and de Gennes (1996) studied the slippage of highly viscous polymer melt on a solid substrate grafted as a function of grafting density, ν. At low grafting density, the low-velocity became independent of ν. Above a certain threshold slippage velocity the N chains were strongly stretched and reached a marginal state. For $\nu > \nu_C$, $V^*(\nu)$ increased linearly, the trapped chains may be stretched and progressively disentangled from N chains.

Black and Graham (1996) presented a slip model that takes into account the unsteady-state kinetics of the wall-polymer interactions. In this model, both the shear and normal stress were incorporated, showing that slip can lead to an instability in viscoelastic shear flow.

Shore, Ronis, Piche and Grant (1997) numerically modeled the instability flow of polymer melts using the Maxwell model. In various regimes, their model exhibited steady flow, periodic oscillations, and more complicated spatiotemporal structures, which can explain to the sharkskin defect observed.

Leger, Hervet and Massey (1997) used a direct measurement of slip velocity by technique of evanescent-wave induced fluorescence and fringe-pattern fluorescence recovery after photobleaching. They found that PDMS on a silica surface plane shear flow displayed three distinct friction regimes. (I) A linear friction regime, small constants slip length $(b_0 < 1\mu m)$. (II) Above a critical slip velocity, the slip length showed power law dependence on the slip velocity with the exponent of 0.88 ± 0.02. (III) A strong slip regime presented a b_∞ value much larger than the size of the surface-anchored polymer molecules.

Rosenbaum and Hatzikiriakos (1997) developed a classic Mooney technique for nonisothermal capillary flow to determine the slip velocity at high shear rates corrected for the effect of viscous heating and several polymers, including PS, PP, HDPE and LLDPE.

Mhetar and Archer (1998) studied slip in entangled polymer solutions using a plane-Couette shear flow cell. Slip behavior was observed to be a strong function of the chemical nature of the surface. On a low-energy surface, the slip velocity was found to be essentially proportional to the shear stress to the first power up to a moderate stress. At higher stresses, the evidence of enhanced concentration fluctuations was observed to be strongly influenced by the interaction between the polymer and the surface. A scaling model was developed to estimate the frictional drag on a probe polymer chain (*N-mer*) pulled by one of its ends through an entangled polymer (*P-mers*). This model takes into account changes in the probe chain conformation and relaxation processes of the probe and the surrounding chains. This model was extended to study slip of an entangled polymer over a weakly grafted solid surface.

Yarin and Graham (1998) derived a steady-state dependence of slip velocity on shear stress at polymer/solid surface from a molecular mode that include effect of drag, disentanglement, detachment and reattachment of chains from solid surface.

Anastasiadis and Hatzikiriakos (1998) calculated work of adhesion of various polymer/wall interfaces. A linear correlation was found between the critical shear stress for the onset of slip and the work of adhesion, indicated that the wall slip was possibly a result of an adhesive failure of the interface.

Kumar and Graham (1998) studied the effect of the pressure dependence on flow curve multiplicity using a simple multivalued slip model to relate the phenomena of hysteresis and spurt flow as the pressure drop and the L/D ratio were changed. Results showed that, despite the multivalued nature of the slip model, multiplicity was absent at high L/D ratio. For a constant piston speed case, these simulations showed the oscillating behavior took place only if the system was operated in the multiplicity region of steady stage flow curve.

Mhetar and Archer [part I] (1998) used simultaneous measurement of slip velocity by technique of tracer particles to study the slip velocity as a function of shear stress for several molecular weights of polybutadiene melts. The results displayed three distinct power law regimes. (I) A weak slip regime ($b_0 \approx 2-120\mu m$). (II) A stick-slip transition regime at intermediate shear stress marked by periodic oscillation in slip velocity and shear stress. (III) A strong slip regime ($\sigma > \sigma^*$), b_∞ was in the range between $100-1500\mu m$. These results were consistent with a shear-induced polymer disentanglement mechanism.

Mhetar and Archer [part II] (1998) investigated the influences of various physical and chemical characteristics of solid substrates on apparent slip violation: (I) On uncleaned (heterogeneous), smooth surface, extensive void/shear fracture occurred near the polymer interface when $\sigma > \sigma^{*}$. (II) On cleaned (homogeneous), roughened surface, no evidence of stick-slip instability was found due to the differences in the surface relaxation dynamics of polymer chains. (III) On low-energy, smooth surface, very large slip velocities were found over the entire range of shear stress. (IV) On polymer-grafted surface, the experimental result was consistent with the phenomenon of clean smooth surface, which are reasonably approximated of entangled, end-grafted polymer model.

Haupt, Ennis and Sevick (1999) took an atomic force microscope (AFM) to investigate the detachment of single polymer chains from a weakly adsorbing surface. They proposed a sawtooth force profiles with detachment force in small extension, but found a featureless force profile at large extension.

Black and Graham (1999) studied an increasing dependence of the slip velocity on the elastic normal stress in the flow direction leading to short wavelength flow instability at sufficiently high Weissenberg number (>10), indicating that slip velocity was not solely dependent on the shear stress. They found that the scaling of the critical shear stress for instability with modulus and molecular weight and of the distortion period with polymer relaxation time were qualitatively consistent with experimental observations of the sharkskin instability in linear polyethylenes.