CHAPTER I
INTRODUCTION

Surface smoothness is one of the critical requirements in plastic processing of small-scale products, which require accurate manufacturing. Therefore skin roughness posses a challenging problem for micron-size manufacturing, especially if the products are of mechanical uses.

When polymeric melts are sheared with solid surface, surface roughness will occur when the stresses reach a critical value. Fracture has been observed in all simple shearing flows. The mechanisms for fracture phenomena fall into two categories: wall slip and constitutive instability. The first mechanism proposed that the dispersion forces that promote intimate contact between a polymer with a solid wall are overwhelmed when shearing stresses are high, so that the liquid acts like a solid by sliding as it moves along a solid wall. The critical stress for wall slip ought to be sensitive to the material from which the wall is made. For the constitutive instability, a multivalued flow curve contains a region in which more than one shear rate can exist for a given stress. The instabilities would be solely dependent on the rheological characteristics of the polymer and only occur when both stress and strain are high enough for the rheological properties of the material to be extremely nonlinear.

In a shearing flow of such a fluid, shear gradients would tend to accumulate in thin layers near solid walls, so that the bulk of polymer are lubricated by a thin layer of polymer that has been liquified by the intensity of stress to which it has been subjected. Then instabilities in the flow of the thin layers are responsible for distortions of the surface.

1.1 Brochard and de Gennes Theory

Schematic representation of one surface-anchored N chain and a mobile P chain is shown in Figure 1.1. The N chain has N segments; the P chain has P segments.
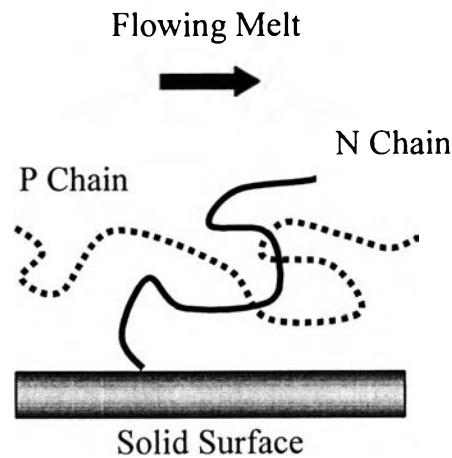
Flowing Melt

N Chain

P Chain

Solid Surface

Figure 1.1 Surface-anchored N chain and a mobile P chain.

Three possible regimes of slip length b were proposed by Brochard-Wyart and de Gennes (1993).

(1) Entanglement regime: a linear low-slip regime, at low shear rates, P chains are weakly elongated.

(2) Marginal regime: as slip velocity increases, the P chains tend to disentangle from N chain resulting in a smaller friction that can no longer balance the elastic force therefore the N chains tend to recoil.

(3) Rouse regime: P chains are completely disentangled state from the N chains.

(1)   (2)   (3)

$\log b$
[μm]
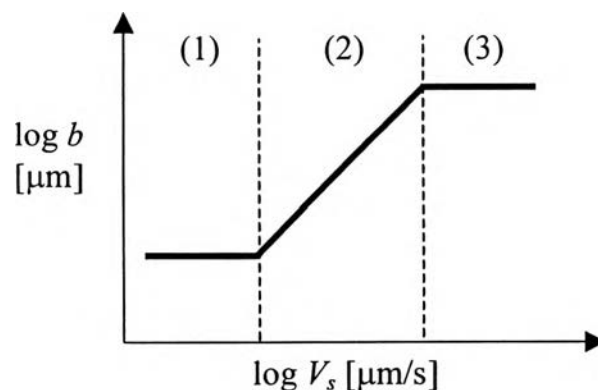
$\log V_s$ [μm/s]

Figure 1.2 Three regimes of Brochard and de Gennes theory.

1.2 Slip Mechanisms

Wall slip can be initiated by 2 mechanisms:

(I) Disentanglement: slippage occurs between the bulk polymer chains and the adsorbed ones. This mechanism can be related with Reptation theory. Because of the presence of entangled polymers, there are many places along the chain where lateral motion is restricted. Doi and Edwards theory (Doi & Edward, 1988) assumes that they are equivalent to placing the molecule of interest in a tube. The relaxation time is given by:

$$\lambda_d \propto \frac{\eta_o M^3}{\rho T} \propto \frac{1}{\omega_d} \qquad \ldots (1)$$

when density is fixed to be the same, this relation can be formed;

$$\omega_d \propto \frac{T}{\eta_o M^3} \qquad \ldots (2)$$

where η_o is the zero shear viscosity, p is degree of polymerization, T is temperature, M is molecular weight, ρ is density, and ω is frequency.
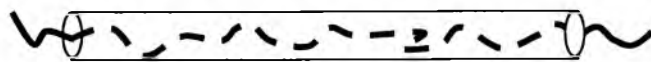

Figure 1.3 Sketch showing the hypothetical tube. assumed by Doi and Edwards.

(II) Desorption: slippage occurs directly between a bulk polymer and the surface and is governed by the bare friction between the polymer segments and the surface. This mechanism is cooperated with the roughness on the solid surface. Desorption between adsorbed polymer chains and solid wall is related with modified Rouse theory. This theory can be applied for low molecular weight molten polymers. This modified theory predicts that the relaxation modulus is given by:

$$\lambda_R = \frac{6\eta_o M}{\pi^2 p^2 \rho RT} \qquad \qquad \dots (3)$$

$$\lambda_R \propto \frac{\eta_o M}{\rho T} \propto \frac{1}{\omega_R} \qquad \qquad \dots (4)$$

when density is fixed to be the same, this relation can be formed;

$$\omega_R \propto \frac{T}{\eta_o M} \qquad \qquad \dots (5)$$

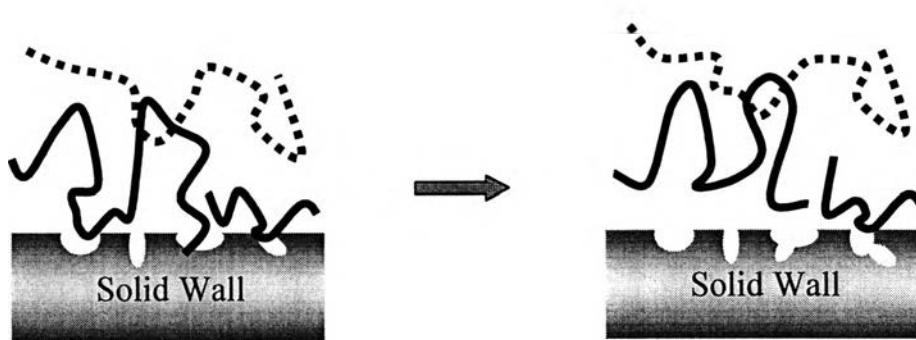Picture of physical desorption is shown in Figure 1.4.

Figure 1.4 Desorption of polymer chain to solid surface.

1.3 Literature Survey

The critical regimes of shear in polybutadiene have been carried out by Vinogradov and Insarova (1972). The method of visualization of the flow in a flat slit with the aid of circular-polarized light has been used. The results of polarization-optical investigation were compared with the results of capillary viscometry and dynamic measurements at small amplitudes. It was shown, in accordance with theoretical prediction, that when a polymer passed from the fluid to the high elastic state with an increased in the shear rate, it ceased to behave as a fluid under shear. This was accompanied by various forms of flow perturbation at the duct exit and entrance and inside the duct. Perturbations at the duct entrance and exit are due to stress concentration in these zones. The transition of a polymer to the high elastic state near the walls inside the duct

gives rise to the stick-slip process or to continuous slippage along the duct walls, depending on the velocity of polymer movement. This could be clearly traced by the changed in the interference band pattern. Still higher velocities result in an intensive process of continuity break in the polymer and in its chaotic movement in the duct as an aggregate of irregularly shaped lumps, which, relaxing, may form a continuous body again. Attention was drawn to the significance of these observations for a quantitative description of the viscosity anomaly of polymer systems and of the relationship between the viscosity anomaly with various flow irregularities and perturbations in such systems.

The effect of the nature of the polymer-wall interface on extrudate appearance was emphasized by Ramamurthy (1986), in his work with capillaries made from different metals. This results indicated that the assumption of "no-slip at the rigid boundary" was not valid for polyethylenes above a critical shear stress of approximately 0.1-0.14 Mpa. He also found the breakdown of adhesion at the polymer/metal interface in the die land region at the critical stress appearing to be responsible for the initiation of slip and the observed extrudate irregularities.

Recently, Kalika and Denn (1987) successfully measured a slip velocity of linear low density polyethylene melts in regimes before and after the load fluctuation regime by using a capillary rheometer. The slip velocity, normalized by the average velocity and collapsed well for many diameters, was a strong function of the wall shear stress. At a first critical stress, they observed small-amplitude, large-frequency distortion on the surface of the extrudate, which was called sharkskin. At higher stresses the pressure at the die inlet and the extrudate throughput were observed to go through periodic oscillations. At the same time, the extrudate showed alternating regions of sharkskin and smoothness, which was called slip-stick region. When higher

stresses were applied the extrudate was found to be grossly distorted which are commonly termed melt fracture.

Hill, Hasegawa, and Denn (1990) reported relation between adhesive failure and melt fracture. The fundamental reasons for the onset of instabilities were constitutive instabilities, and failure of adhesion or slip of the polymeric liquid at the confining interface. The results showed that melt fracture was a consequence of an adhesive failure between the melt and the metal or oxide surface of the die. Both the onset of extrudate surface distortions and the functional form and magnitude of the melt slip velocity could be obtained solely from peel tests on the polymer below the melt processing temperature and a knowledge of the temperature and pressure dependence of the viscoelastic shift factor.

Hatzikiriakos and Dealy (1991) studied the wall slip of high density polyethylene using sliding plate rheometer. The sliding plate geometry could be used effectively to study melt slip phenomena, because it generated a uniform stream rate field with no pressure gradient. Another advantage over capillary rheometer is that it enables convenient modification and control of the polymer-wall interface. From steady shear experiments, slip occurred above a critical shear stress of 0.09 Mpa. The slip velocity was determined as a function of shear stress and was found to follow a power law. In addition, they also studied the wall slip of molten high density polyethylenes (1992) by using a capillary rheometer. They found that all high density polyethylene melts slipped when the wall shear stress exceeded a critical value. This critical value was found to be a function of the average molecular weight of the resin. While the critical shear stress for the onset of slip was found to be independent of temperature, temperature was found to have a strong effect on the slip velocity of these polymers. A modified Mooney technique was developed in order to be able to detect such effects and to calculate the slip velocity as a function of both wall shear stress and wall normal stress.

Brochard and de Gennes (1992) considered shear flows of a polymer melt near a solid surface in which a few chains have been grafted. The slip velocity and the slippage length were sensitive functions of the shear stress imposed. They proposed that there existed chain disentanglements from the bulk polymer, resulting in a transition from the weak slip to the strong slip.

Larson et al. (1994) studied shear fracture of polystyrene melts and solutions using cone-and-plate rheometer. They found that symptoms of polymer melt fracture could be induced by oscillatory torsional shearing flow of polystyrene melts and solutions, even when the polymer molecular weight was below the entanglement threshold, and the strain amplitude was as low as 3%. They also found that melt fracture was not always caused by "constitutive instabilities" which required the viscoelastic properties to be highly nonlinear while their observations of melt fracture in unentangled polymers at shearing strains were well within the linear viscoelastic range. Three possible explanations for the waveform changes were viscous heating, constitutive instability, and cohesive and/or adhesive failure. Anyway, the mechanisms of decay in complex modulus were still not clear.

In 1995, Drda and Wang carried out a detailed analysis of stick-slip transition on capillary flow of linear polyethylene melts. For highly entangled polymer melts, significant deviation from the law of the stick hydrodynamic boundary condition could occur. The action of extremely high interfacial shear stress produced massive disentanglement between adsorbed and free chains at a melt-solid interface. Their experimental results suggested that at the stick-slip transition, the increase of slip velocity with temperature indicated that the friction coefficient decreased rapidly with increasing temperature. The extrapolation length remained constant at the stick-slip transition with respect to temperature. Furthermore, stress increased linearly with temperature, and the transition obeyed the time-temperature superposition principle. Interfacial

transition was arisen from chain disentanglement and extrapolation length was solely a material property of the melt-solid interface.

Leger, Hervet, and Massey (1997) studied the role of attached polymer molecules in wall slip. Experiments have been conducted on one model system, polymethylsiloxane (PDMS) and a silica surface. PDMS strongly adsorbs on clean silica, developing hydrogen bonds with the silanol sites of the surface. Extrapolation length was directly related to the friction between the fluid and the surface. Three slip regimes were observed. At low shear rates, a linear friction regime was characterized by a small extrapolation length ($b<1$ m). Above a critical slip velocity, a nonlinear friction regime appeared, characterized by a power law dependence for extrapolation length as a function of slip velocity. At large shear rates, a transition towards another linear friction regime was apparent, with an extrapolation length much larger than the size of the surface-anchored polymer molecules, and the flow became almost plug flow.

Mhetar and Archer (1998) carried out the experiments on apparent violations of the no-slip boundary condition using a series of narrow molecular weight distribution polybutadiene melts, subjected to plane-Couette shearing over clean silica glass surfaces. Log- log plots of slip velocity versus shear stress displayed three distinct power-law regimes: (I) A weak slip regime at low shear stresses that was characterized by extrapolation/slip lengths of the order of a few micrometers, (II) A stick-slip regime at intermediate shear stresses marked by periodic oscillations in slip velocity and shear stress, (III) A strong slip regime beyond a defined critical shear stress. Slip violations in this last regime were characterized by large slip velocities and massive extrapolation lengths. For all polymers studied the critical stress for the weak-to-strong slip transition was found to be proportional to the plateau modulus of the bulk polymer. These experimental observations were found to be in good agreement with a recently proposed scaling theory (P. A.

Drda and S.-Q.-Wang, 1995) for friction and slip in entangled polymers, which assumes noninteracting surface chains. This last result was rationalized in terms of a polymer adsorption model in which a single macromolecule spontaneously attaches to numerous surface sites, yet offers a sufficiently long tail to resist relative motion of a chemically identical bulk polymer that attempts to slide over it.

1.4 Objectives

To determine the mechanisms for the slip between polymer melts and solid surface in oscillatory shear mode

1.5 Scope of Work

1. Effects of temperature, strain, and molecular weight on critical conditions and the asymptotic transient angular slip
2. Slip velocity and slip length analysis
3. Morphology of polymers at interface
4. The analysis of the anomalous data at 200°C