CHAPTER I
INTRODUCTION

Melt flow instability refers to a change in flow behavior from being a steady state to another steady state or to uncertain behaviors, such as an oscillating or intermittent flow (Leonov and Prokunin, 1994). The adhesion of flowing liquids to solid boundaries, the so-called no-slip condition, is a classic assumption made by fluid mechanicians dating back at least to Stokes. Several recent experiments (Petrie and Denn, 1976; Ramamurthy, 1986) suggest that at high shear stresses this no-slip assumption may not be valid for entangled polymer fluids. To investigate slip between a polymer and a surface, we follow Brochard and de Gennes (1992) and define the extrapolation slip length b as the distance at which the extrapolated velocity profile vanishes. Thus the slip length b is V_s / γ where V_s is the slip velocity and γ is the shear rate corrected for slip. For simple molecules, b is typically of the order of the molecular size irrespective of the stress imposed. For entangled polymers, however, b can become several orders of magnitude larger than the molecular size when stress exceeds a critical value of the order of the plateau modulus of the polymer (Mhetar and Archer, 1998).

Much of the recent interests in polymer slip originate from the speculation that slip is at least partially responsible for surface instability commonly observed in polymer melt extrusion processes (Drda and Wang, 1995). These instabilities produced extrudate surface defects which provide a technical motive for such studies. Polymer surface instabilities in extrusion are also fascinating for three other reasons. First, the instabilities are found at vanishing *Reynolds numbers, Re,* which eliminates the usual inertia-based instability mechanisms, often found in bulk Newtonian fluids. Second, the

instabilities begin at the polymer-wall interface, indicating that the details of *configuration, friction* and *dynamics of macromolecules* near solid surfaces may play a major role. Third, the instabilities are governed by the important dimensionless parameter, the so-called *Weissenberg number, Wi,* which represents the effects of viscoelastic and normal stress difference.

1.1 Wall Slip Phenomena

For all simple-shear rheometers, there are solid boundaries against which fluid is intended to adhere, while neighboring fluid is moving by drag or pressure gradients. For simple small molecule liquid, such as water, wall slip is usually negligible, that is the classic no-slip boundary condition holds. In contrast for a macromolecule, it can behave as a liquid at low shear rate but when the shear rate is sufficiently higher, the solid-like behavior is predominant where the fluid dynamic can possibly undergo the no-slip violation at the boundary condition. That is the fundamental appearance of the slip phenomena. Both direct and indirect measurements have been developed to observe this slip existence (Larson, 1999)

1.1.1 Gap-Dependent Apparent Shear Rate

Indirect measurement of slip can be extracted from the flow curve (shear stress versus shear strain rate) measured at different die diameters (Mooney, 1931). If slip occurs, one expects the slip velocity $V_s(\sigma)$ to depend on the shear stress, σ. Thus, if a fluid is sheared in a Capillary rheometer with a capillary diameter, d_C, there will be a velocity jump of magnitude $V_s(\sigma)$ at the interface between the fluid and solid capillary wall. The apparent shear strain rate will therefore be

$$\dot{\gamma}_{app} = \dot{\gamma}_{app,s} + \frac{8V_s}{d_C}. \qquad (1.1)$$

A plot of γ_{app} against $1/d_c$ will then be a straight line with slope $8V_s$. This method has been used to measure the slip velocity indirectly (Wang and Drda, 1996; Rosenbaum and Hatzikiriakos, 1997).

1.1.2 Effect of Surface Treatment

Some role of the solid boundary in slip is implicated in cases where one can show that changes in the wall material or surface treatments of it (such as Teflon coating) influence the magnitude of the apparent slip velocity (Hatzikiriakos and Dealy, 1991; Wang and Drda, 1996).

1.1.3 Particle Tracers

Small amounts of micron-size particles are used to visualize slip near the solid surface. The motion of these particles will be detected with an optical microscope and hence can infer the existence of slip at the wall, or within a fluid layer whose thickness is no greater than the diameter of the particles (Mhetar and Archer, 1998).

1.1.4 Evanescent Waves

The most sophisticated method to measure slip velocities is a technique developed by Migler *et al.* (1993) that uses *evanescent-wave spectroscopy*. When a beam of monochromatic light is reflected from a surface or interface, the electric field associated with the light penetrates the interface, with the field strength decaying exponentially as a function of distance into the reflecting material. The decay constant of this exponential is a fraction of the wavelength of light: thus the penetration distance is around 0.1 μ m. the intensity of the reflected light depends on the optical properties of the material in this fraction-of-a-micron-thick layer. In this method, they used two interfering laser beams to bleach a sinusoidal "grating" into a dye-

containing poly(dimethylsiloxane) melt confined between glass surfaces. When the sample was sheared by translating the top plate, motion of the grating in the layer of fluid near the bottom stationary plate could be detected by analyzing the time-dependent intensity of a beam reflected from the interface between the fluid an the bottom plate. Movement of the grating implied the existence of slip within the 0.1-μm layer and allowed the slip velocity to be measured.

1.1.5 Laser-Doppler Velocimetry

Muller-Mohnssen *et al.* (1990) used laser-Doppler velocimetry to measure the velocities of small (0.15-μm diameter) tracer particles in flowing of polyacrylamide solutions at various radial positions across a tube, as close as 1 μm from the wall. The measured velocity profiles showed an apparent finite slip velocity at the tube wall. Using total-reflection-microscope anemometry (a form of evanescent wave spectroscopy), the velocities as close a 0.15 μm from the tube wall were measured. These high-resolution measurements showed that the apparent slip at a resolution of 1 μm was caused by a thin wall layer of fluid in which the velocity gradient was much higher than in the bulk. Because of this thin high-shear layer, the bulk velocity gradient, when extrapolated to the wall, appeared to reach a nonzero value. The polymer was a polyelectrolyte whose charges were apparently repelled by the wall, leading to a near-wall layer denuded of polymer and therefore having a low viscosity. This low-viscosity layer could support a higher velocity gradient than the bulk and therefore acted as a lubricant, creating apparent wall slip. The existence of a polymer-depleted layer as a cause of slip had been proposed earlier by Cohen and Metzner (1985).

1.1.6 Rheo-NMR

Velocities near a wall, and indeed throughout the fluid can be measured without tracer particles, and in opaque samples, by using nuclear magnetic resonance velocity imaging (Abbott *et al.*, 1991; Rofe *et al.*, 1996), as can the presence of yield surfaces and shear banding within the sample (Britton and Callaghan, 1997). It is especially useful for soft solids, including foods, where the assumption of uniform shear can fail drastically. In such cases, uncritical analysis of ordinary rheology data, without the aid of velocity imaging, can lead to serious misinterpretations.

1.2 The Extrapolation Length

Beyond the solid surface, an imaginary distance that can describe to the severity after slippage taking place is called the extrapolation slip length *b* (de Gennes, 1979) as shown in Figure 1.1
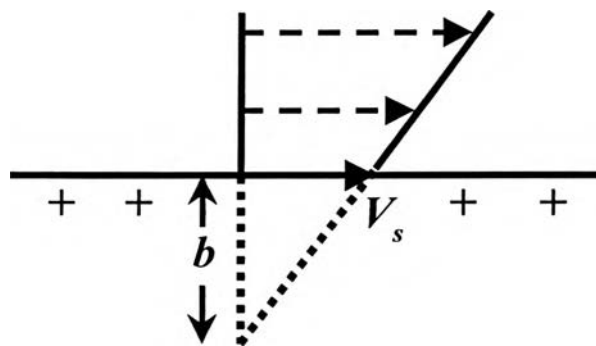

Figure 1.1 Schematic of the extrapolation length

$$b \equiv \frac{V_s}{\dot{\gamma}}.$$ (1.2)

where V_s is the slip velocity and $\dot{\gamma}$ is the true shear strain rate at the surface. The relationship between the extrapolation length and the slip velocity was originally proposed in the *Disentanglement model* (Brochard and de Gennes,

1992). This model assumes that a few chains are bound onto a solid surface and form the elastically spherical-coil conformation which entangle with the bulk chains. They suggested that the wall shear stress is expressed by the combination between elastic force of the adsorbed coils and frictional force of the bulk chain motion. When the shear stress is greater than a critical value, slippage will undergo the different possible regimes as illustrated by Figure 1.2. Three observable regimes are possible:
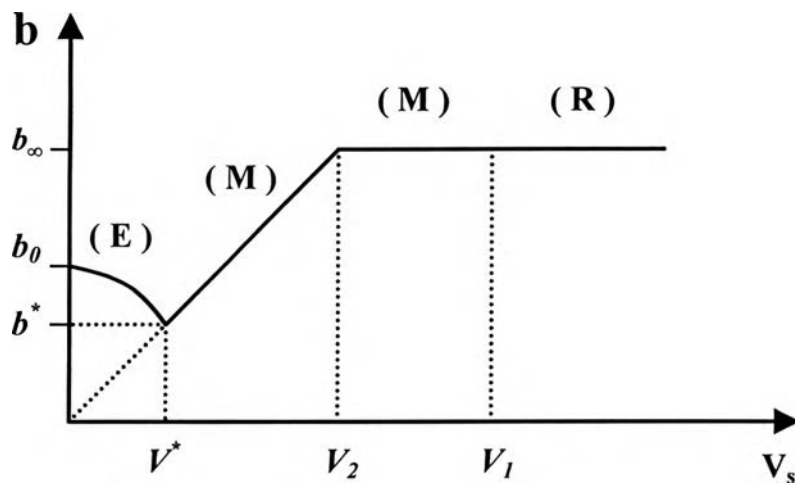

Figure 1.2 Extrapolation length versus slip velocity for a weakly grafted surface expose to a polymer melt (chemically identical to the grafted chains); (E) = entangled slip regime; (M) = Marginal regime; (R) = Rouse regime.

(I) Entangled Slip Regime: the adsorbed chains are stretched out from a spherical coil conformation to an elliptical coil conformation but the bulk chains are still entangled with these grafted chains due to a huge friction in the low velocity regime which gives *b* values which are extremely small. The corresponding slip length is

$$b_0 \cong \frac{1}{vR_0} \qquad (1.3)$$

where ν is the grafting density of the adsorbed chains, and R_0 is the radius of coil conformation

(II) Marginal Regime: above the critical slip velocity V^*, the expansion of elliptical coil was stationary whilst the bulk chains begin to reptate or disentangle out from this elliptical coil. In this regime the extrapolation length increases linearly with the slip velocity

$$b(V) = \frac{\eta V}{\sigma^*} \tag{1.4}$$

and

$$\sigma = \sigma^* = \frac{\nu k T}{N_e a}. \tag{1.5}$$

where a is monomer bead size and N_e is the number of monomer between the entanglement. Until $V_s = V_2$, the extrapolation length b crosses over continuously from the marginal form to the ideal surface value at b_∞, and at this condition the dissipation due to the grafted chains becomes negligible.

(III) Rouse Regime: ultimately, at $V_s > V_1$ we should go into a disentangled state after the bulk chains completely reptate from the adsorbed chains. In this regime the extrapolation length is now independent of the slip velocity but strongly depends on the bulk viscosity of the fluid as given by

$$b_\infty = a\left[\frac{\eta}{\eta_1}\right]. \tag{1.6}$$

where η_1 is the viscosity of the monomer liquid and η is the bulk viscosity of the polymer fluid.

1.3 Deborah Number and Weissenberg Number

It is well known that for a non-Newtonian fluid, a so-called viscoelastic property is normally observed, unlike a Newtonian fluid. For example, the climbing up of polymer melt on the rotating rod, or the Weissenberg effect, in Couette flow obviously exhibits the viscoelastic effect for non-Newtonian system (Tadmor and Gogos, 1979). The dimensionless parameters called the Deborah number (De) and Weissenberg number (Wi) are often used to attribute the elasticity of material flow. In the oscillatory shearing, the Deborah number is defined as the ratio of a characteristic relaxation time (λ) and a characteristic deformation time of the liquid flow (t) as given by

$$De = \frac{\lambda}{t}. \qquad (1.7)$$

If De $\gg$ 1, the polymer behavior is almost that of a purely elastic body. But if De $\ll$ 1, the elasticity plays an insignificant role. On the other hand, for steady shearing flow, Weissenberg number is often used as the parameter. For polymer melt flow through process equipment, such as capillary die extrusion, an obvious choice of a characteristic process time is the inverse of the rate at the wall ($t = 1/\dot{\gamma}$). Thus we have

$$Wi = \lambda\dot{\gamma}. \qquad (1.8)$$

Alternatively, Weissenberg number is defined as the ratio of the elastic forces over the viscous forces for Maxwell model,

$$Wi = \frac{\text{elastic force}}{\text{viscous force}} = \frac{\tau_{11} - \tau_{22}}{2\tau_{12}} = \frac{N_1}{2\tau_{12}}, \qquad (1.9)$$

where τ_{12} is the wall shear stress and N_1 is the first normal stress. The above dimensionless quantities are identical in representing the elasticity of material depending on the flow type. The most common dimensionless grouping in viscoelastic simulations is the Weissenberg number. In such simulation, the characteristic material time is chosen as one of the relaxation times included

in a viscoelastic constitutive equation. Viscoelastic calculations are typically reported for Weissenberg number values ranging from unity to several thousands (Dealy and Wissbrun, 1990).

1.4 Research Objectives

- To study slip phenomena and find the relationship between wall slip velocity and extrapolation length as a function of shear stress on the effects of molecular weight, polydispersity and temperature.

- To construct the normalized flow curve of polymer melts which is a plot of shear stress/crossover modulus versus the Weissenberg number.