STUDIES ON WALL-SLIP IN ENTANGLED POLYMERIC LIQUIDS

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ABSTRACT:
In this work, it is attempted to theoretically understand the phenomenon of wall slip through empirical and molecular models. Initially, we use the framework a transient network theory. We show that the severe disentanglement in the interfacial region can give rise to non-monotonic flow curve locally in that region. Further, we generalize this model into a unified slip model, which predicts wall slip by either disentanglement or by debonding mechanism, depending upon the adhesive energy of the wall-polymer pair. The model predictions of the critical wall shear stress are in good agreement with experiments for various adhesive energies of the wall-polymer pair. The model predicts that the temperature dependence of the critical wall shear stress for debonding is different than that of disentanglement mechanism under certain experimental conditions. To validate the predictions of unified model, we measure the critical stress for sudden slip due to debonding for various temperatures using cone and plate viscometer with fluoroelastomer-coated cone. The temperature dependence of the critical stress for instability (slip) on a coated cone is found out to be inversely dependent on temperature, which expected for the case of debonding. In the final part of this thesis, we develop a parameter-free tube model for predicting the stick-slip phenomenon. The model, which is based on the contour variable model [Mead et al., 1998, Macromolecules, 31, 7895], considers the dynamics of the tethered chains, which are grafted on a high-energy wall and which are entangled with the bulk chains flowing past them. We show that the restricted relaxation modes of the tethered molecule give rise to discontinuous slip instability. More specifically, the slow relaxation of the tethered chain due to the restricted convective constraint release is unable to randomize its flow-induced orientation above a critical shear rate or stress. This decreases the resistance to flow for the bulk chains, which suddenly slip past the oriented tethered chains.

1 INTRODUCTION

Commercial plastic extrusion processes are severely limited by the occurrence of instabilities above a critical production rate, which is determined by the melt properties, the geometry of the die and its material of construction. In the case of polyethylene extrusion, at low flow rates, the extrudate surface is smooth and the extrusion process is steady. Above a critical shear stress, a surface distortion called 'sharkskin' appears on the extrudate though the flow rate and pressure drop in the extrusion is steady. At a still higher stress, the extrusion process becomes unsteady with large fluctuations in flow rate and pressure accompanied by alternating bands of smooth and sharkskin extrudate surfaces. This severe instability is called the 'stick-slip' instability. At still higher flow rates, extrudate shows gross fracture although the flow rate and pressure might remain steady. In this work, we are primarily concerned with the stick-slip instability, which is believed to be caused by the slippage of polymer chains near the wall.

Wall slip in polymer solutions and melts in particular has been a subject of intense investigation for the past several decades and has been recently reviewed by several authors [e.g. 1, 2]. Whenever an entangled polymeric liquid flows over a smooth solid surface, the friction involved is comparable to that in fluids of monomers. However, generally the chains in the flowing bulk are adsorbed on the solid wall forming various lengths of loops and tails. These tethered molecules are entangled with the bulk and resists its flow. The complex dynamics of the tethered chains at higher stresses is the principal cause of the stick-slip flow instability during the shear flow of entangled polymers. Many mechanisms have been proposed to explain this phenomenon but those that have received wider acceptance in recent years are polymer chain disentanglement [3] and the debonding [4] of the tethered chains at the wall-polymer interface.

The physical manifestation of slip shows up in terms of experimental observations of a critical wall-shear stress, flow oscillations in controlled rate extrusion or a sudden increase in shear rate in controlled stress extrusion, extrudate distortion, diameter dependent flow curves, hysteresis and temperature dependence of critical wall-shear stress. However, by merely observing a given manifestation in a given set of experimental data, it has not been possible so far to *a priori* assign a mechanism, be it debonding or disentanglement. Indeed the same set of experimental data on slip for the same polymer has been interpreted in terms of both disentanglement as well as debonding. For example, the experimental data on wall slip for common systems such as polyethylene in steel capillaries has been described by theoretical arguments of debonding [4] as well as disentanglement [12]. It is important to recognize that the physical basis and the mathematical frameworks for debonding and disentanglement are completely different. It is generally believed that the magnitude of the energy of adhesion between the wall and the adsorbed polymer chains will determine the governing mechanism of slip. We believe that a unified model, which can predict slip by both debonding and disentanglement mechanisms and which can distinguish between the two mechanisms on the basis of the relative role of adhesive energy will be helpful in ascribing the correct mechanism to given experimental slip data. In this work, we have proposed such a unified slip model based on the framework of the transient network theory.

While the unified model provides an “engineering model” that can be useful for predicting slipping flows, it is mainly a phenomenological model consisting of several model parameters that have to be determined through independent rheological experiments. It is desirable to develop a truly molecular model that can predict slip based on only molecular parameters and no other adjustable parameters.

The molecular models available so far on slip phenomena are at scaling level, which, while providing a molecular understanding for wall slip, cannot quantitatively predict the slip data [3, 5]. In this work, we have proposed a parameter-free molecular constitutive equation based on the tube model for predicting slip on a high-energy wall. Our motivation is to develop an understanding of the molecular mechanisms that are responsible for slip on a high-energy wall and to quantitatively predict various characteristic features of wall-slip.

2 DETAILS OF THE MODEL DEVELOPMENT

The main work in this thesis is divided into four chapters, which are summarized below. Much of the work in this thesis is theoretical in nature, although we have also undertaken some critical experimental investigations as outlined in subsection 3. The primary objectives of the work are *a)* to propose a unified model that will predict wall slip by disentanglement or debonding mechanisms using the mathematical framework of the transient network theory, and *b)* to develop a parameter free molecular model based on tube theory to quantitatively predict the experimental results.

2.1 DISENTANGLEMENT MODEL

As a first step towards proposing a unified model, we propose a disentanglement model. We look at the wall slip phenomenon from the point of view of a transient network model, which is suitable for describing both entangled solutions and melts. We assume that the surface is of very high energy and the dynamics of chain entanglement and disentanglement at the wall are different from those in the bulk. We show that severe disentanglement in the annular wall region of one radius of gyration thickness can give rise to nonmonotonic flow curve locally in that region. By proposing suitable empirical functions for the chain dynamics so as to capture the right physics, we show that the model can predict all features of wall slip. These include flow enhancement, diameter dependent flow curves, discontinuous increase in flow rate at a critical stress, hysteresis in flow curves, the possibility of pressure oscillations in extrusion and a second critical wall shear stress at which another jump in flow rate can occur. In Fig. 1, we show that how model successfully predicts diameter dependence of flow curves [6].

2.2 UNIFIED MODEL

The disentanglement model is upgraded into a unified slip model, which predicts wall slip by disentanglement mechanism or by a debonding mechanism depending upon the adhesive energy of the wall-polymer pair. The model is based

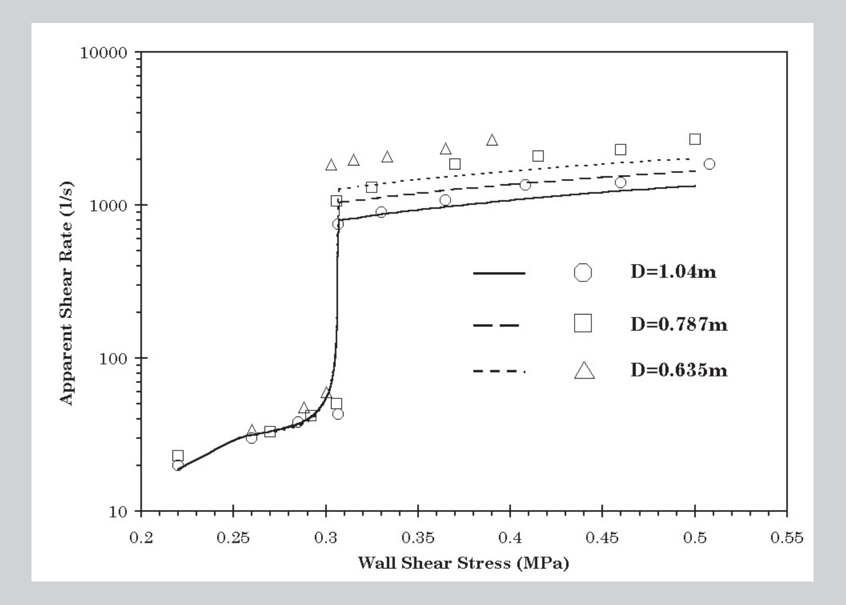


Figure 1: Comparison of model prediction for apparent shear rate vs. wall shear stress with polyethylene melt experimental data [12]. Flow curve for D = 1.04 mm is fitted using model parameters while the flow curves for other diameters are predictions. Points represent experimental data and line represents model fit.

on the transient network theory, in which the activation processes of adsorption and desorption are considered to occur at the wall in parallel to the stretching of the adsorbed chains. It is shown that the stick-slip transition occurs due to the local non-monotonic flow behavior near the wall irrespective of the mechanism of slip. The model predictions of the critical wall shear stress are in good agreement with experimentally observed values of the critical stress for various adhesive energies of wall polymer pair. Another important prediction of the model is that the temperature dependence of the critical wall shear stress for debonding is different from that of disentanglement mechanism under certain experimental conditions. We believe that this may be useful for discerning the correct mechanism of slip. The unified model encompasses different systems (viz. entangled solutions and melts) and diverse mechanisms (viz. disentanglement and debonding) in a common mathematical framework [7].

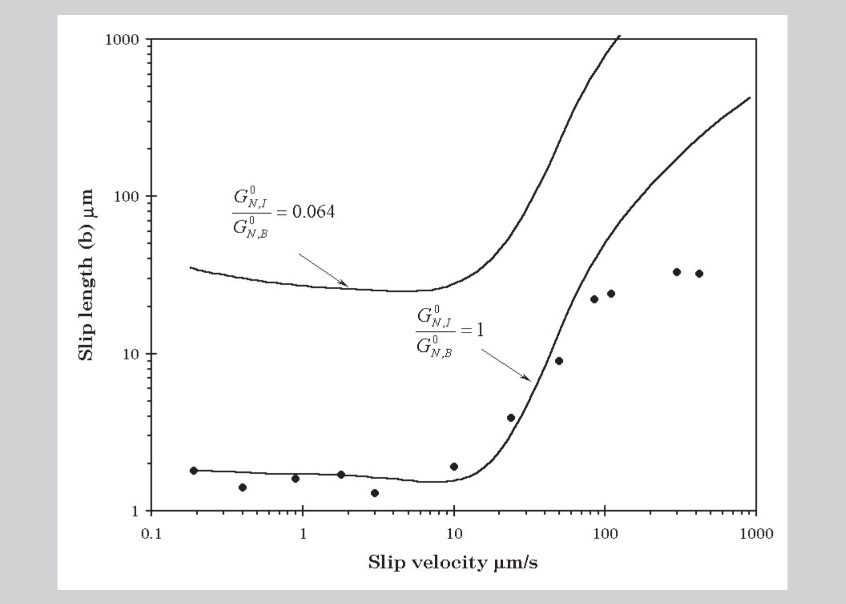
2.3 TEMPERATURE DEPENDENCE OF CRITICAL STRESS FOR SLIP DUE TO DEBONDING

In this subsection, we experimentally probe the instability at high shear stress in a controlled stress cone and plate rheometer for a steel cone and for a fluoroelastomer-coated cone. We show that for the steel cone, the instability is viscoelastic in nature probably driven by edge fracture, while for the fluoroelastomer-coated cone the instability is driven by slip. We measure the temperature dependence of the critical stress for instability (slip) on a coated cone and find it to be inversely dependent on temperature. This is expected for the case of debonding, which is known to be an activation process. We also show that the unified slip model successfully predicts the observed temperature dependence quantitatively [8].

2.4 A TUBE MODEL FOR WALL SLIP

In this subsection, we develop a molecular model for wall slip. In particular, a tube model is proposed for predicting the wall slip phenomenon driven by the interfacial 'disentanglement' mechanism. The model, which is based on the contour variable model [9], considers the dynamics of the tethered chains, which are grafted on a high-energy wall and which are entangled with the bulk chains flowing past them. We show that the restricted relaxation modes of the tethered molecule give rise to discontinuous slip instability. More specifically, the slow relaxation of the tethered chains due to the subdued constraint release by the convecting bulk chains (CCR) [10] plays a crucial role in determining the nature of the flow curve near the wall. The restricted CCR experienced by a tethered chain is unable to randomize its flow-induced orientation above a critical shear rate or stress. This decreases the resistance to flow for the bulk chains, which suddenly slip past the oriented tethered chains. The model correctly predicts the molecular weight dependence of the slip length, critical slip velocity and critical wall shear stress. It also quantitatively predicts the slip length and the critical slip velocity for a PDMS melt (Fig. 2) [11].

Figure 2: Comparison of experimental data of slip length vs. slip velocity with model prediction. The experimental data is by Durliat et al. [13] and is for PDMS melt. The upper curve is corresponds to the lower value of interfacial modulus than that of the bulk modulus. For both interfacial and bulk modulus equal to each other the model predicts the experimental data quantitatively.



We hope that the new molecular insights proposed in this work will stimulate further theoretical and experimental work to understand this phenomenon in complicated systems.

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