



Molecular interpretation of the “stick–slip” defect of linear polymers

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ABSTRACT

In this paper, we investigate the relationships between stick–slip defect and molecular slip at the wall for linear polymers. By considering Brochard–de Gennes slip model and molecular chain dynamics at the wall, we propose expressions for the critical shear stress and the critical shear rate at the onset of stick–slip. Moreover, we present a criterion of existence for the stick–slip defect, based on the molecular weight distribution. These various expressions are qualitatively validated by experimental data from the literature.

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1. Introduction

1.1. General presentation of the stick–slip defect

The stick–slip defect is well known for linear polymers [1–6]: when imposing the flow rate on a capillary rheometer, one observes that above a critical value (corresponding to a critical shear rate $\dot{\gamma}_c$ or a critical shear stress σ^*), the flow becomes unstable and gives rise to pressure oscillations in the reservoir and flow rate oscillations at the die exit. On the extrudate, this defect is characterized by a regular and periodic succession of zones of different aspects, generally sharkskinned and smooth (Fig. 1). Above a second critical shear rate $\dot{\gamma}_{c2}$, the oscillations disappear and the flow becomes again stable. On a pressure-controlled capillary rheometer, pressure and flow rate oscillations are not observed, but above a critical shear stress σ^* , a sudden jump of the flow rate (spurt) occurs. When the pressure is decreased, the flow rate exhibits a jump for a value lower than σ^* , putting in evidence a hysteresis loop. These different behaviours explain the typical flow curve of linear polymers shown in Fig. 2 with two stable branches (I and II) separated by an unstable zone of flow rate oscillations (or spurt).

The stick–slip defect has been largely studied by numerous authors for more than 30 years. It is commonly admitted that the origin of the stick–slip is not at the die exit, like for sharkskin, but in the die land. The key points to describe the stick–slip defect include

the compressibility of the polymer, its rheological behaviour and the slip conditions at the die wall.

1.2. Influence of molecular and process parameters

Many experimental studies have been carried out in order to understand the stick–slip defect. These studies have been mainly performed using high density polyethylenes (HDPE) and linear low density polyethylenes (LLDPE). It is however difficult to compare the results of these studies because the molecular and experimental parameters often differ and are sometimes not specified. Nevertheless, it is clear that many parameters influence the occurrence of the defect.

1.2.1. Molecular weight and polymolecularity

The study of Wang and Drda on a HDPE [7] shows an influence of the molecular weight on the occurrence of the defect: they note an increase of the critical shear stress when the molecular weight M_w decreases. However, this result can be questioned, as a number of authors find a critical shear stress independent of the molecular weight [6,8–10]. On the other hand, it is well established that the amplitude of the oscillating zone is much more marked when the molecular weight is high: for low molecular weight polymers, the stick–slip defect is not observed.

In 1962, Sabia and Mullier [11] observed on a HDPE that the amplitude of the oscillations decreased when the polymolecularity increased. Similarly, Vinogradov et al. [12] showed that the softness of the transition from branch I to branch II increased with the polymolecularity.

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Fig. 1. Stick-slip defect of a metalocene polyethylene (mPE). Sharkskined zones correspond to branch I, smooth ones to branch II.

1.2.2. Temperature

According to Vinogradov et al. [13], an increase in temperature reduces the flow rate domain of stick-slip defect. Wang and Drda [14], Robert [2], Hatzikiriakos and Dealy [15] have shown that the critical shear stress, at the occurrence of the defect, increases with the temperature. They also proved that time-temperature superposition principle is satisfied on branch I, but not in branch II. It is also important to notice the existence of a temperature window, close to the melting point, for which the stick-slip defect disappears [16,17].

1.2.3. Geometry of the capillary

Many authors showed experimentally that the critical shear stress increases when the ratio L/D of the capillary decreases [1,3]. The stick-slip defect totally disappears with an orifice die ($L/D \approx 0$).

1.2.4. Nature of the surface

Ramamurthy [18] was among the firsts to note an influence of the nature of the die surface on the critical shear stress of appearance of the stick-slip defect. Perez-Gonzalez and de Vargas [19] noticed that the critical shear rate was lower with a stainless steel die than with a brass die. They also pointed out, like Ramamurthy [18] or Ghanta et al. [20], the existence of an induction time before the defect vanishing. Finally, it is well known that the use of PTFE coatings or fluorinated additives makes it possible to eliminate completely the stick-slip defect [21,22].

1.3. Explanation of defect origin: slip at the wall

To explain the stick-slip defect, the majority of the authors, according to direct experimental measurements [3,23,24], privilege a mechanism of wall slip: the defect would be due to a transition between weak slip and strong slip. Two possible

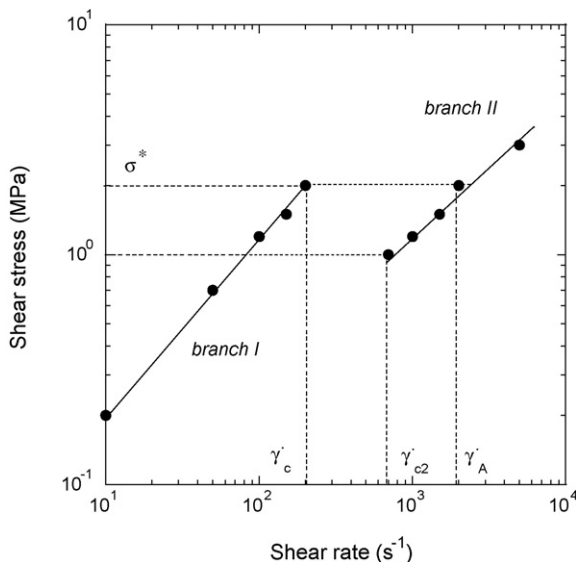


Fig. 2. Typical flow curve of a linear polymer.

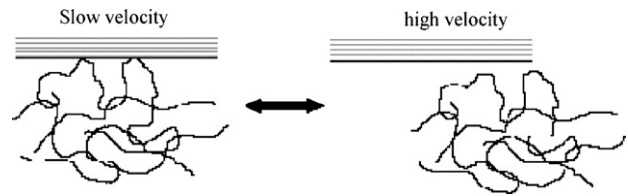


Fig. 3. Desorption of an adsorbed molecule.

origins of slip have been proposed: adsorption-desorption or entanglement-disentanglement. For the first one, when the shear stress at the wall overtakes a critical value, the molecules adsorbed at the wall can be desorbed. Such model has been proposed, for example, by Adewale and Leonov [25] (Fig. 3). However, it is well known that the temperature decreases the surface tension (surface energy) and, by consequence, is favourable to desorption. At the same time, when the temperature increases, the critical shear stress also increases [2,14,15]. Consequently, we think that this mechanism is not the most plausible.

The second mechanism involves entanglement-disentanglement between the free molecules of the bulk and the molecules adsorbed at the wall [7]. According to Brochard and de Gennes [26], the chains adsorbed at the wall can undergo, at a critical shear stress, a coil-stretch transition (Fig. 4). Then, the molecules adsorbed and stretched are no more entangled with those of the bulk and the molecules of the bulk slip on the stretched chains adsorbed at the die wall.

Even if theoretical models have been proposed for unifying both mechanisms of desorption and disentanglement [27–29], we will focus in this paper on this last mechanism to propose expressions of the critical shear stress and the critical shear rate at the onset of stick-slip. We will consider the molecular weight effect to propose a physical mechanism at the origin of this defect and a criterion of existence, based on the molecular weight distribution, as we already did for the sharkskin defect [30].

2. Expressions of the critical shear stress and the critical shear rate and criterion of existence of the defect

2.1. The different regimes of slip

Let us consider more precisely the physical mechanisms at the origin of the slip at the wall and the relationships between shear stress σ and wall slip velocity V_s . We will use the work of Mhetar and Archer [31,32] who developed the initial results of Brochard and de Gennes [26]. Working on polybutadienes of high molecular weight, they were able to define slip regimes which were not observed previously. More precisely, Mhetar and Archer [31] identified five regimes of slip for an entangled polymer (Fig. 5):

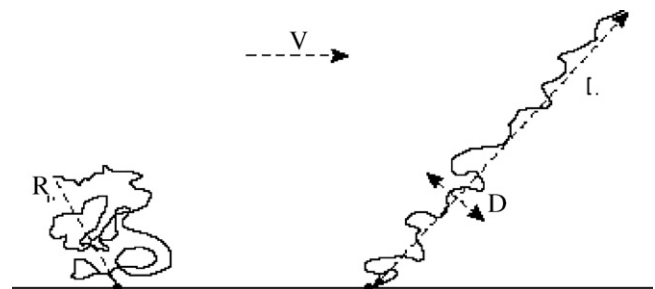


Fig. 4. Molecular conformation at the wall according to Brochard-de Gennes model.

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