

Temperature dependence of critical stress for wall slip by debonding

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Abstract

The instability in stress-controlled cone and plate viscometry is analysed for a bare cone and for a fluoroelastomer-coated cone. We show that, for the bare cone, the instability is viscoelastic in nature, while for a 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. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

It is generally believed that the strong wall slip observed during melt extrusion occurs either by disentanglement or by debonding processes [1]. However, there are no clear guidelines for discerning the governing mechanism of slip under a given set of experimental conditions. It has been hypothesised that slip occurs by disentanglement for high adhesive energy surfaces and by debonding for low adhesive energy surfaces. The unified model proposed by us provides a quantitative basis for this [2,3]. Furthermore, our model predicts that the temperature dependence of critical stress is an important criterion for discerning the correct mechanism of slip which prevails under a given set of experimental conditions.

The critical shear stress predicted by disentanglement models [3,4] is given by

$$\tau_w^* \propto \nu T, \quad (1)$$

where ν is the number of chains per unit area grafted to the wall (grafting density) and T is the absolute temperature. Eq. (1) indicates that the critical wall shear stress (τ_w^*) increases with temperature. Wang and

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Drda [5] indeed observed a similar dependence for HDPE on steel, and hence, they related the observed slip phenomenon for disentanglement. They ruled out the possibility of debonding and postulated that, since debonding is an activation process, the critical stress for debonding should decrease with increase in temperature. This postulate, which was predicted by our unified model, has not been experimentally confirmed so far.

In this paper, we experimentally determine the critical stress for slip at various temperatures. To ensure that the slip occurs due to a debonding mechanism, we carry out experiments using a low adhesive energy surface. We show that the critical stress indeed decreases with an increase in temperature. We also show that the unified model successfully predicts the observed temperature dependence.

2. Experimental

2.1. Materials

The material used in this study was linear low density polyethylene (Dowlex 2045) from Dow Chemicals having $M_w = 116\,400$ and $M_n = 34\,300$. The molecular weight information was obtained by using 150C Waters GPC fitted with three detectors: light scattering, viscosity and refractive index (RI). The carrier solvent trichlorobenzene was pumped at a flow rate of 1 ml/min at 160°C in the injector and column compartments.

2.2. Apparatus

A Bohlin cone and plate-controlled stress rheometer (CVO 50) was used for the rheological measurements. A 5.4° truncated cone of 15 mm diameter was used. The measurements were carried out by using the bare cone as well as a fluoropolymer-coated cone. The cone was coated by dipping it in a 5% solution in acetone of the fluoroelastomer (SUMMIT, Sumitomo Corporation, Japan) for 2 h. The wetted cone was dried in an open atmosphere till a thin layer of the fluoroelastomer was formed on the cone. The cone was then kept at 60°C for 2 h to remove the acetone and then at 220°C for 12 h to cure the coating. All experiments were carried out under controlled stress conditions at four temperatures, namely, 150, 170, 190 and 210°C.

Extrusion experiments were carried out with a CEAST Rheovis 2100 rate-controlled capillary rheometer at the temperatures mentioned above. LLDPE was extruded through a case-hardened steel die of 1.0 mm diameter, L/D 40 and an entry angle of 60°. Extrusion experiments were also carried out by using a coated die, for which the internal surface was coated with the same fluoroelastomer. Coating was carried out following the procedure recommended by Wang and Drda [6]. A 5% solution of the fluoroelastomer in acetone was made to flow through the capillary for several times followed by drying the capillary at 220°C for 12 h.

3. Results and discussion

Irrespective of the nature of the cone (bare or coated), all the experiments showed a steady and continuous increase in shear rate with shear stress followed by a sudden increase in rpm of the cone at a critical shear stress. The data in Fig. 1 at 150°C shows the observed instabilities for bare and coated fixtures

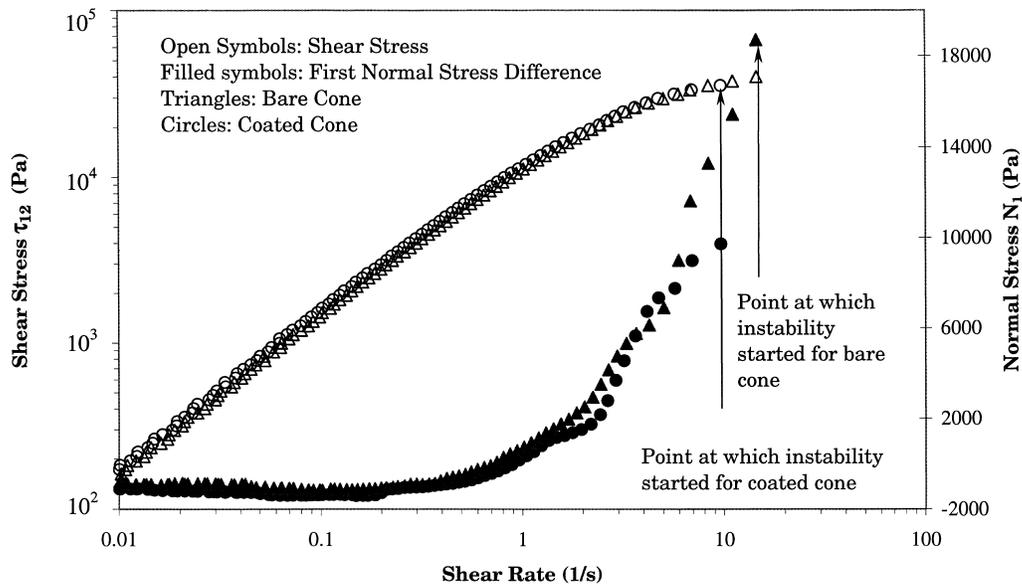


Fig. 1. Shear stress and first normal stress difference plotted against shear rate. It can be seen that, at the onset of instability, N_1 increases more rapidly for the bare cone. $T = 150^\circ\text{C}$.

(cones). Such instabilities in curvilinear viscometric flows are known to arise due to any of the failure mechanisms, namely, cracking, centrifugal expulsion, elasticity-driven meniscus distortion or slip at the interface [7,8].

It was consistently observed during our experiments that, at all temperatures, the sudden increase in shear rate in the case of bare cone occurred at higher stresses than that for the coated cone. It was also observed that the first normal stress difference at the onset of instability increased much more rapidly for the bare cone than that for the coated cone. Fig. 1 shows the shear stress and normal stress data at 150°C .

Fig. 2 shows photographs of the samples on the plate after a sudden increase in the shear rate in experiments using both coated and uncoated cones at 170°C . It can be seen that, when the bare cone was used, the sample cracked and was partly thrown out of the gap, while in the case of experiments with a coated cone, the sample was almost devoid of any distortions. Although the material in the bare cone has been seen to be expelled out from the gap, the possibility for the centrifugal expulsion is ruled out, since the Reynolds number is much lower than the critical Reynolds number for expulsion [7]. In Fig. 3, the ratio of first normal stress difference (N_1) and shear stress (τ_{12}) is plotted against the shear stress (τ_{12}). It can be seen that, at the onset of distortion for the bare cone, N_1/τ_{12} increases sharply as compared to that for the coated cone. Such sharp increase in the slope for the bare cone can be related to the surface distortion phenomena (elasticity-driven meniscus distortion) [7]. We believe that the instability in bare cone is initiated by meniscus distortion resulting finally in expulsion and/or cracking at very high speeds. For the case of the coated cone, the slope of N_1/τ_{12} curve at the point of instability is much smaller than that of bare fixtures and also the instability occurred at lower shear stress (or shear rate). Hence, we believe that the instability in the coated cone case is most probably driven by slip. Based on the combined observations of higher critical shear stresses, a sudden rise in the value of N_1/τ_{12} and the visual state of the sample after a sudden increase in cone rpm for the case of bare cone, we believe that instability was



Fig. 2. The photograph of the plate immediately after the instability has occurred in the cone and plate rheometer. The left picture (a) is from the plate where the coated cone was used, while the right picture (b) corresponds to a bare cone. The sample with the coated cone is almost free from distortions relative to the bare cone case.

initiated due to an elasticity-driven meniscus distortion. On the other hand, in the case of the coated cone, the sudden increase in rpm is due to the adhesive failure between cone and the material.

To confirm this hypothesis, we performed similar experiments on the capillary rheometer. Fig. 4 shows the data at 170°C obtained from a capillary rheometer (using coated and bare dies) and from cone and

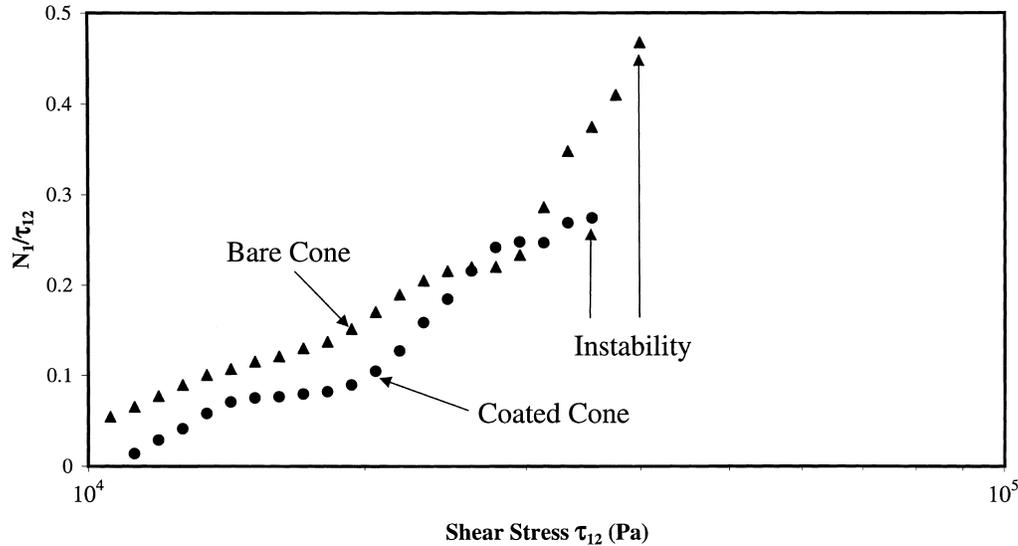


Fig. 3. N_1/τ_{12} vs. shear stress (τ_{12}), plotted for the data shown in Fig. 1. It can be seen that, at the onset of instability, N_1/τ_{12} increases more rapidly for the bare cone than that for the coated cone.

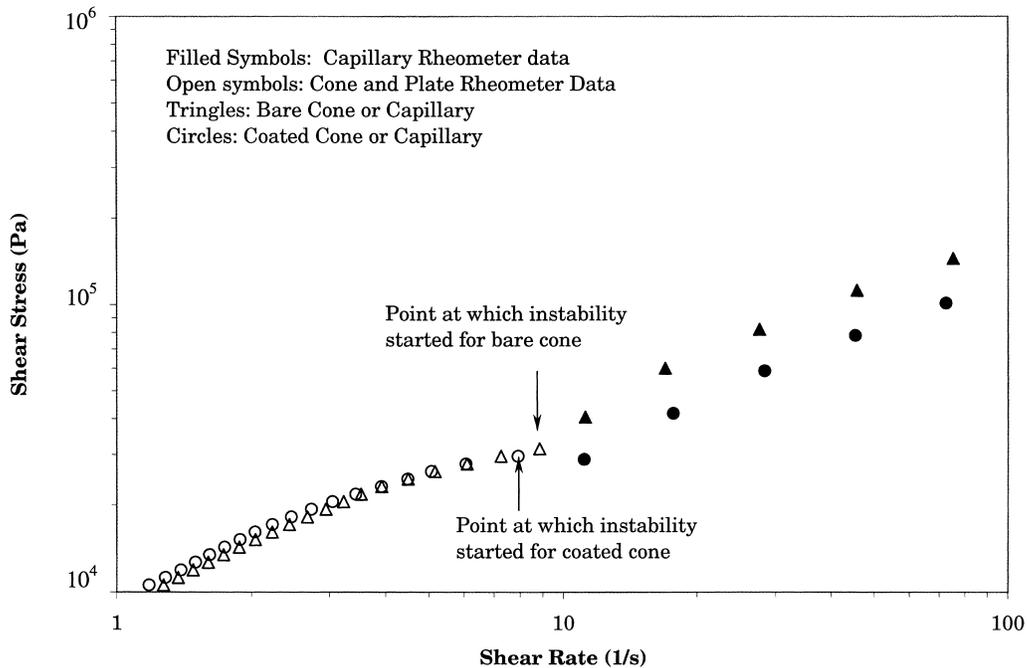


Fig. 4. Flow curves for coated and uncoated surfaces (cone and capillary die) at 170°C. The flow curves obtained from an uncoated cone smoothly merge with those obtained from an uncoated capillary die. The flow curve for a coated cone overlaps with that for the uncoated cone up to the point of slip, after which the flow curve in the coated die is always below that for the uncoated die.

plate rheometer (using coated and bare cones). It can be seen that the stress at which the slip occurred on the coated cone is the same at which the flow curve for the coated extrusion die separated from the flow curve of the bare extrusion die. A similar separation of flow curves for coated and bare surfaces has been observed by Xing and Schreiber [9] and by Koran and Dealy [10].

The above experimental observations lead us to believe that it is possible to measure the critical stress for slip due to adhesive failure by conducting controlled stress experiments on a fluoropolymer-coated cone. We have measured the critical stress for slip as a function of temperature. Fig. 5 shows the measured critical stress plotted against temperature. It can be seen that the critical stress for adhesive failure (slip) clearly decreases with an increase in temperature. The observed temperature dependence of critical stress for coated surfaces is opposite to that observed by Wang and Drda [5] for uncoated steel dies. We believe that the results presented here are the first observations of temperature dependence of slip occurring due to debonding, providing further evidence that the temperature dependence of critical stress can indeed be used to discern the true mechanism of slip.

This behaviour is predicted by our unified slip model [3], which is based on a transient network formalism. The model assumes that the network dynamics of tethered molecules at the interface is different from that of the bulk molecules. The stress in the interfacial region (i.e. wall shear stress) is given by

$$\tau_{12} = \phi \frac{G_0 \gamma_e f}{g} = (\phi n_0 k T) n \gamma_e, \quad (2)$$

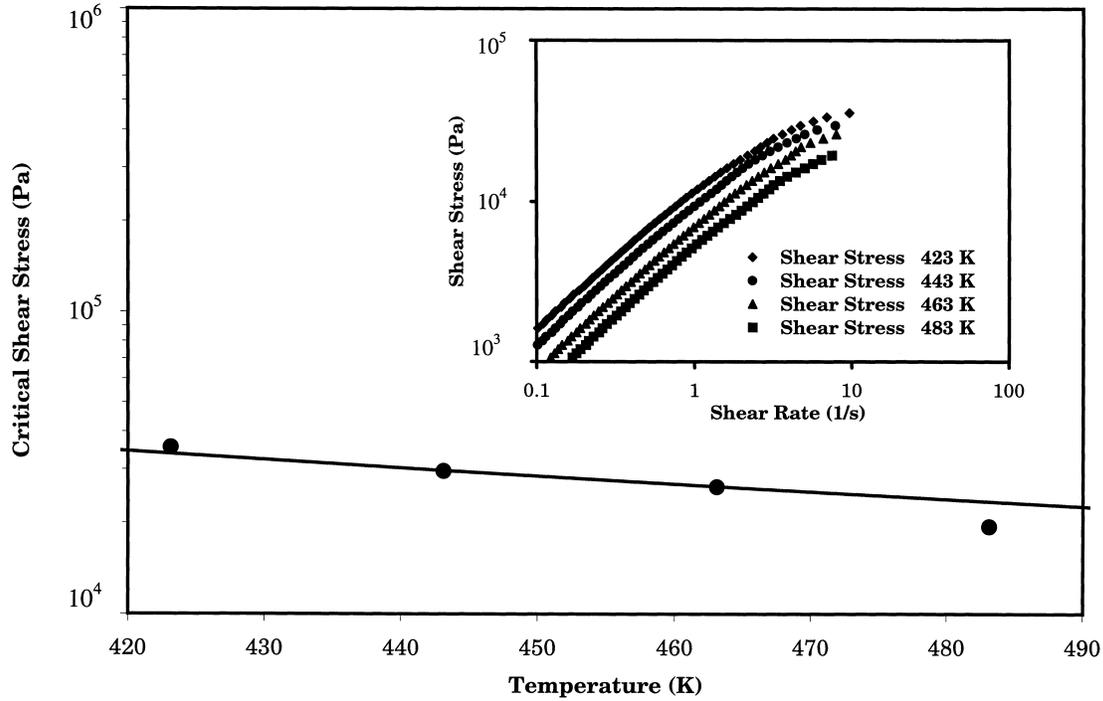


Fig. 5. The critical stress for debonding is plotted against temperature. The points show experimental data, while the line shows the model prediction. The model parameters are $A = 0.0025$, $\Delta E_{\text{adh}} = 2.921\text{E}-20$ J per molecule, $n_0 = 2.057\text{E}+26$. In the interfacial region, $a = 8.0$, $b = 11.25$. The plot inserted within the figure shows shear stress plotted against shear rate for the coated cone up to the point of instability (slip).

where

$$\phi = \frac{A \exp([\Delta E_{\text{adh}}]/kT)}{A \exp([\Delta E_{\text{adh}}]/kT) + \exp((3/2)\gamma_e^2)} \quad (3)$$

is the fractional surface coverage, ΔE_{adh} is the adhesive energy, $\gamma_e = (\tau_{11} - \tau_{22})/2\tau_{12}$ is the effective strain, $n (=f/g)$ stands for the number of entanglements per unit volume under flow normalised with respect to the equilibrium number of entanglements n_0 , and where f and g are the rates of creation and the loss of entanglements given by

$$f = \exp(a\gamma_e), \quad g = \exp(b\gamma_e). \quad (4)$$

Here, A , a and b are adjustable model parameters. The effective strain γ_e is directly proportional to shear rate. We have shown that the stress–effective strain curve shows a non-monotonic behaviour due to a sudden decrease in ϕ (i.e. debonding) or due to sudden decrease in n (i.e. disentanglement) [3]. The critical stress for slip can be calculated from the non-monotonic stress curve as the value of the maximum stress before it begins to decrease.

The important model parameter in the unified model is the adhesive energy. The adhesive energy for the LLDPE–Teflon[®] system (the difference between polymer–metal work of adhesion and polymer–polymer work of cohesion) is known to be 0.93 Pa [11]. This adhesive energy is converted into (energy)/(adsorption

junction) or (energy)/(adsorbed molecule) for model calculations. The maximum shear stress is calculated using Eq. (2) for various temperatures. Fig. 5 shows a quantitative fit for the temperature dependence that was observed experimentally in the case of coated surfaces. We had earlier shown that the same unified model also predicts an increase in critical stress with temperature for slip occurring by disentanglement on high-energy surfaces (polyethylene on bare steel walls) [3]. Thus, the unified model provides the first successful prediction of the correct temperature dependence of critical stress for slip occurring due to disentanglement and due to debonding.

4. Conclusion

We have presented an experimental verification of the temperature dependence of critical shear stress for slip when the operative mechanism is debonding. The critical stress for polyethylene slipping on fluoropolymer surfaces was found to decrease with increase in temperature, which is opposite to the increase in critical stress with temperature observed for polyethylene slipping on uncoated steel surfaces [5]. The unified slip model predicts both the trends correctly by simply using the correct adhesive energy values for the two surface–polymer pairs. We have shown correctly for the first time that the temperature dependence of critical stress can be used to discern the true mechanism of wall slip for any polymer–wall pair.

References

- [1] S.-Q. Wang, Molecular transitions and dynamics at polymer/wall interfaces: origins of flow instabilities and wall slip, *Adv. Polym. Sci.* 138 (1999) 227–275.
- [2] Y.M. Joshi, A.K. Lele, R.A. Mashelkar, Slipping fluids: a unified transient network model, *J. Non-Newtonian Fluid Mech.* 89 (2000) 303–335.
- [3] Y.M. Joshi, A.K. Lele, R.A. Mashelkar, A unified wall slip model, *J. Non-Newtonian Fluid Mech.*, in press.
- [4] F. Brochard, P.G. de Gennes, Shear-dependent slippage at a polymer/solid interface, *Langmuir* 8 (1992) 3033–3037.
- [5] S.-Q. Wang, P.A. Drda, Super fluid like stick-slip transition in capillary flow of linear polyethylene melt. 1. General features, *Macromolecules* 29 (1996) 2627–2632.
- [6] S.-Q. Wang, P.A. Drda, Super fluid like stick-slip transition in capillary flow of linear polyethylene melt. 3. Surface condition, *Rheol. Acta* 36 (1997) 128–134.
- [7] R.G. Larson, Instabilities in viscoelastic flows, *Rheol. Acta* 31 (1992) 213–263.
- [8] R.L. Powell, in: A.A. Collyer, D.W. Clegg (Eds.), *Rheological Measurements*, Chapman & Hall, London, 1998, pp. 260–296.
- [9] K.C. Xing, H.P. Schreiber, Fluoropolymers and their effect on processing linear low-density polyethylene, *Polym. Eng. Sci.* 36 (1996) 387–393.
- [10] F. Koran, J.M. Dealy, Wall slip of polyisobutylene: interfacial and pressure effects, *J. Rheol.* 43 (1999) 1291–1307.
- [11] S.H. Anastasiadis, S.G. Hatzikiriakos, The work of adhesion of polymer/wall interfaces and its association with the onset of wall slip, *J. Rheol.* 42 (1998) 795–812.