Steep wave fronts on extrudates of polymer melts and solutions: lubrication layers and boundary lubrication

Daniel D. Joseph
University of Minnesota
110 Union St.
107 Ackerman Hall
Minneapolis, MN 55455

ABSTRACT: This note is motivated by the observation that in all of the photographs I have seen, the shape of rough and smooth extrudates of polymer melts and solutions is associated with wall slip in a lubricating layer and is such as to steepen the wave at the front. The same type of asymmetric waves with steep fronts appear on heavy oil in pipelines lubricated by water and on abraded rubber samples. I used results known in the theory and practice of lubricated pipelines and ideas borrowed from the theory of hydrodynamic and boundary lubrication to analyze slip and extrudate distortion in polymer melts and solutions.

Lubrication layers and slip

Problems of slip, spurt, fracture and extrudate distortion can be framed in terms of lubrication theory with paradigms arising from the lubrication of heavy oil with water for some problems and concepts from the theory of boundary lubrication for others.

Slipping of extrudates is just one special case of slipping of one material on another, a topic in the well-developed subject of friction, lubrication and wear. In the case of extrudate slip, I divide the subject into two categories, “wet” slip and “dry” slip. In problems of wet slip a lubricating layer of soft material is between the extrudate and the wall; in these problems ideas from theory of hydrodynamic lubrication and lubricated pipelines ought to be important. “Dry” slip is a concept which makes sense when the asperities on the extrudate and the pipe wall make touching contact, and here also there is an excellent theory of boundary lubrication which can be applied (see, for example, Bowden and Tabor [1954] or Roberts [1992]). The concept of “dry slip” should be carefully examined since two bodies which slip either have a substance between or nothing between. “Nothing” would imply a vacuum, which is something nature abhors, or else nothing means that the two materials weld at touching asperities which is actually a credible idea. Even in the case of welded asperities, the two materials are not joined everywhere and one may consider the effects of the substance between. In all cases it is natural to require what and where the substance is and if it is a major player in the dynamics which control the observed phenomena.

Wave core-annular flows

It seems to us (Joseph & Lui [1996]) that the shape of the extrudate of polymers and polymer melts is very much like the wavy shapes one sees in core-annular flows of heavy oils in water. These flows are lubricated by the water and can be said to give rise to slip. Waves are needed to levitate the core when the densities are not matched and to center it when they are. However, the conventional mechanisms of lubrication cannot work. The saw tooth waves shown in Figure 1 are like an array of slipper bearings and the stationary oil core is pushed off the top wall by lubrication forces. If c were reversed, the core would be sucked into the wall, so the slipper bearing picture is obligatory if you want levitation.

Obviously the saw tooth waves are unstable since the pressure is highest just where the gap is smallest, so the wave must steepen where it was gentle, and smooth where it was sharp. This leads us to the cartoon in Figure 2. To get a lift from this kind of wave it appears that we need inertia, as in flying. Liu's [1982] formula for capsule lift-off in a pipeline in which the critical lift off velocity is proportional to the square root of gravity times the density difference is an inertial criterion.

The high and low pressures which are generated in the water as a wave on the oil pushes forward are much more intense when the gap is small; even in a slipper bearing the pressure maximum is proportional to the reciprocal of the square of gap size. In journal bearings the low pressure on the back side are severe enough to produce cavitation even under rather mild conditions. The usual well known effects of lubrication at low Reynolds numbers are greatly intensified and skewed toward the steepening of the wave front at higher Reynolds numbers.

Calculated wave shapes from Bai, Kelkar and Joseph [1996] are shown in figure 3. Photographs of these ubiquitous asymmetric waves in which the sharp fronts advance can be found in many places; for example Oliemans and Ooms [1986], Feng, Huang and Joseph [1995] and figure 5 below. These photographs remind one of the form of waves frequently seen on slipping polymer extrudates.

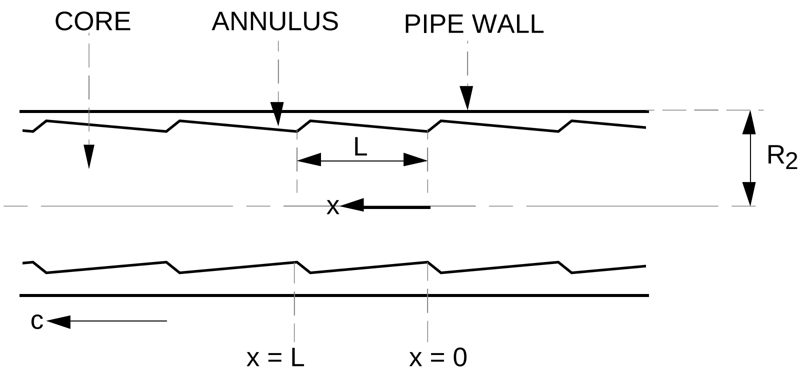

Figure 1. The core is at rest and the pipe wall moves to the left.

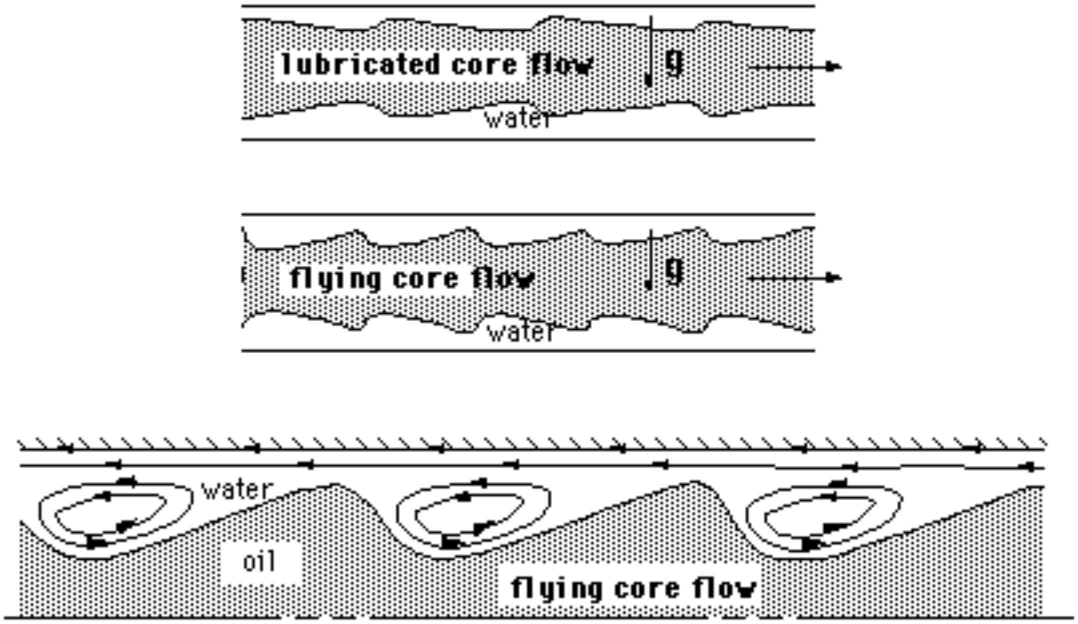

Figure 2. (After Feng et al 1995) (*top*) The interface resembles a slipper bearing with the gentle slope propagating into the water. (*middle*) The high pressure at the front of the wave crest steepens the interface and the low pressure at the back makes the interface less steep. (*bottom*) The pressure distribution in the trough drives one eddy in each trough.

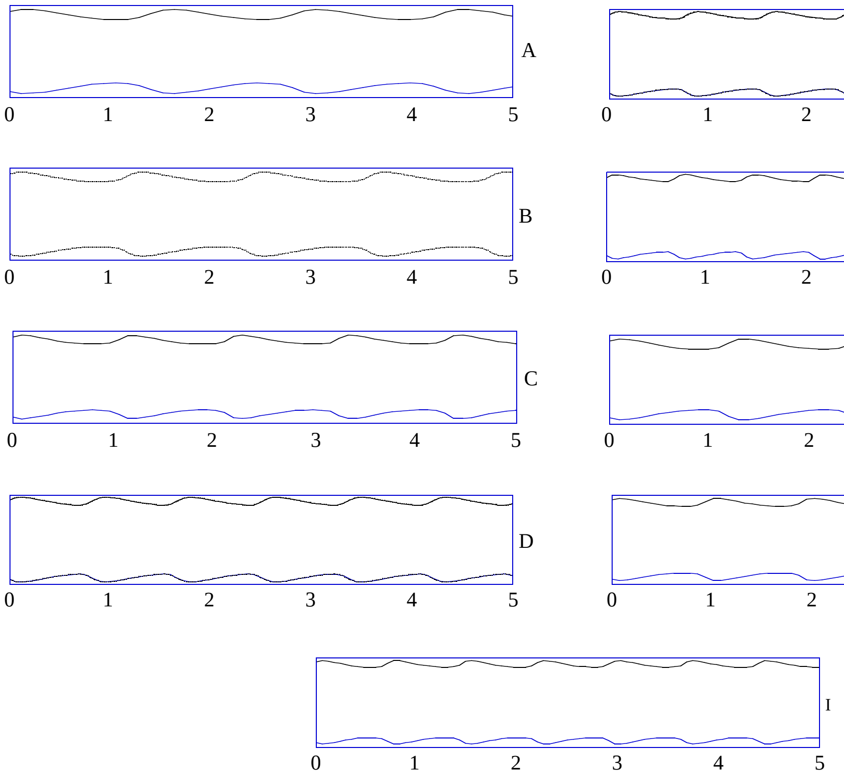

Figure 3. (After Bai et al 1995) Selected wave shapes for water lubricated axisymmetric flow of oil and water with the same density ρ = 1.0 g/cm^3, μ_0 = 0.01 poise and σ = 26 dyne/cm for oil and water. The core is stationary and the wall moves to the right. The pipe diameter is R_2 = 1.0 cm. Q_o and Q_w are in cm^3/sec. The data for each frame is given as a triplet of prescribed dimensional values (R_1, Q_o, Q_w) and as a triplet of prescribed dimensionless values $[\eta,\ h,\ \mathbb{R}]$ where $\eta = R_1/R_2$, h is the holdup ratio and Reynolds number $\mathbb{R}$ is defined by (14). The dimensionless surface tension J = 13 × 10^4 defined in (13) is for all frames. The data for each dimensional and dimensionless triplet is A (0.4, 12.6, 5.05), [0.8, 1.4, 250]; B (0.4, 22.6, 9.09), [0.8, 1.4, 450]; C (0.4, 37.7, 15.2), [0.8, 1.4, 750]; D (0.43, 34.9, 8.8), [0.86, 1.4, 420]; E (0.43, 43.6, 11), [0.86, 1.4, 525]; F (0.43, 69.7, 17.5), [0.86, 1.4, 840]; G (0.39, 26.1, 12), [0.78, 1.4, 600]; H (0.41, 35.2, 12.3), [0.82, 1.4, 600]; I (0.425, 45.4, 12.5), [0.85, 1.4, 600]. Frames A through F show that the wave front steepens and the wavelength decreases for increasing $\mathbb{R}$. Frames G through I show how the wavelength shrinks as the thickness of the water layer decreases. The wave shape does not change much as η is increased for given values of h and $\mathbb{R}$ because the wavelength and amplitude both decrease. This gives rise to a nearly "self similar" wave shape leading to "sharkskin" as $\eta \to 1$ (cf. Figure 10)

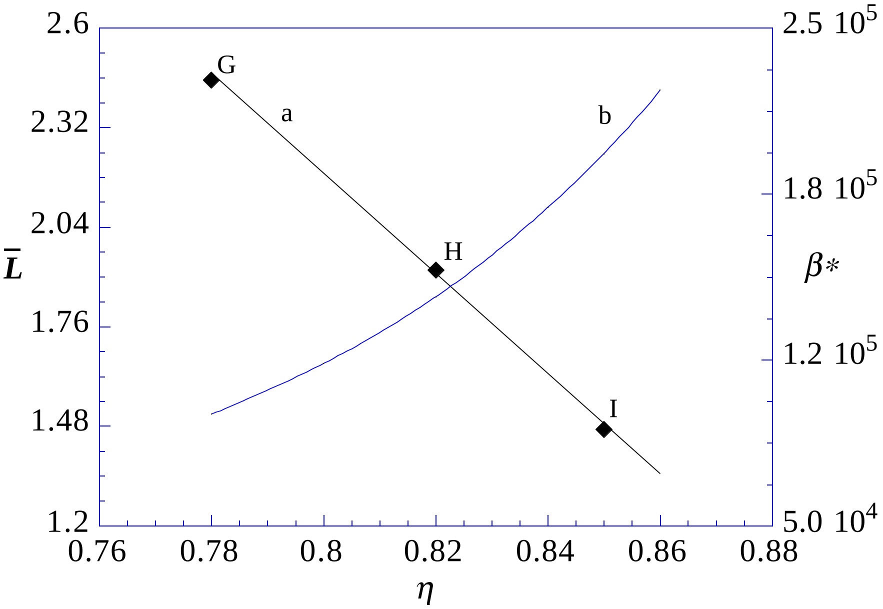

Figure 4. (After Bai et al 1995) Curve *a* represents the wavelength $\bar{L}(\eta) \approx 13.463 - 14.087\eta$ for $[\mathbb{R}, h, J] = [600, 1.4, 13 \times 10^4]$; Curve *b* represents the pressure gradient β^* vs. η under the same conditions. The wave shapes for the points *G*, *H*, and *I* are shown in Figure 2. Curve *a* extrapolates to zero $\bar{L}$ with a finite η. We could not get convergent results for η very close to 1. The extrapolation suggests a limiting zero value of wavelength and amplitude leading to "sharkskin."

Sharkskin solutions for core-annular flows

Sharkskin is a form of extrudate distortion in which very short waves with sharp crests appear on the surface of the extrudate. I have inspected photographs of sharkskins and it appears to me that these waves have steep fronts, like saw tooth waves where the steep part of the saw-tooth advances in the cutting stroke. These waves have not been calculated; they have in fact not even been characterized in mathematical terms. Such waves may thought to be self-similar, saw-tooth like waves in which the wave form and the ratio of the wave amplitude to wave length are unchanged and the wave length tends to zero with the mean gap size. In fact such waves arise in the direct numerical simulation of core-annular flow of an infinitely viscous but deformable core lubricated by water. Bai et al [1995] did a direct simulation of steady axisymmetric, axially periodic CAF, assuming that the core viscosity was so large that secondary motions could be neglected in the core. They found that wave shapes with steep fronts always arise from the simulation. A selection of such shapes is shown in Figure 3. The wave front steepens as the speed increases. The wave shapes are in good agreement with the shapes of bamboo waves in up-flows studied by Bai et al [1992].

A new and important feature revealed by the simulation is that long waves do not arise when the gap size tends to zero as is usually assumed in long wave theories. As the gap size decreases, $\eta \to 1$, the wavelength $\bar{L}(\eta)$ decreases linearly with η as shown in Figure 4. This means that the wave shape hardly changes and a steep wave will stay steep in this limit. It is the first solution ever to show how "sharkskin" waves arise as a natural consequence of the dynamics of lubricated flows without the special assumptions sometimes made in the rheology literature to explain such wave shapes in extrudate flows.

Lubrication Layers and Extrudate Slip

I ask the reader to take an indulgent view of how a lubrication layer of soft material next to the wall might form when a polymer melt or solution is extruded from a die. In this view we allow that apparent slipping may take place in the soft material next to the wall and that origins of soft material could possibly occur by different mechanisms in solutions and melts. The slip that occurs through the loss of adhesion or by cohesive fracture falls more properly into the domain of boundary lubrication in which the fluidity of a soft layer is not a determining factor.

Some of the ways in which lubricating layers of soft materials arise are discussed just below.

Chen and Joseph [1992] argued for a sort of wet slip with segregation or fractionation of small molecules on the wall and large molecules inside. Intuitively, large molecules cannot get as close to a capillary wall as small molecules. Cohen and Metzner [1985] suggested that the apparent slip is due to the reduction of polymer concentration in a slip layer of thickness that can be much larger than the hydrodynamic diameter of the macromolecules. Busse [1964] argued that there is a thermodynamic force that tends to increase the concentration of very small molecules at the wall, and of the large molecules near the center. Indirect experimental evidence has been given by Schreiber and Story [1965], Schreiber et al [1966] and Whitlock and Porter [1972]. This small molecule layer could be just the solvent or could be additives. In the flow of colloidal aqueous silica dispersions as studied by Persello et al [1994], water is released into fractures at high shear forming a self-lubricating layer. Additives in PVC, studied by Funatsu and Sato [1984] and Knappe and Krumbock [1984], migrate towards the wall forming a lubricating layer between the polymer and the wall. Moynihan et al [1990] have suggested that 3M's Dynamar additive, which is known to promote slip in LLDPE, forms an LLDPE/flouroelastomer blend at the surface of the melt. De Smedt and Nam [1987] reported that the flouroelastomer additive in the extrusion flow of PE through capillary was concentrated at the free surface of the extrudate.

Vinogradov, Malkin, Yanovskii, Borisenkova and Berezhnaya [1972] reported that there is an accumulation of electric charge on the extrudate surface when wall slip occurs beyond a critical shear rate. In this case, it can be expected that the forces acting on the interface between the electrically charged thin layer and the solid wall is such that less drag is promoted. Therefore, such an electrically charged thin layer may function as a lubricating layer.

Brochard and de Gennes [1992] studied shear flows of a polymer melt near a solid surface. Chains which are chemically identical to the melt were grafted on the wall. It was found that when the shear stress exceeds a critical value these grafted chains are stretched by the flow and therefore disentangled from the bulk polymer molecules. These disentangled polymer strands near wall were thought to lubricate the flow of the bulk polymer. Another idea is that a thin layer of polymer softens as a consequence of instability associated with a non-monotone response in the constitutive equation. This also gives rise to a lubricating layer on which the polymer may slip.

Many mechanisms have been proposed for slip and they all lead to some form of lubrication.

Steep wave fronts on extrudates

I do not know what produces the steep wave fronts which appear on extrudates and in experiments on friction and abrasion of rubber; in the case of lubrication layers the high pressure at the front of a wave and the low pressure at the back give an intuitively appealing and readily understood interpretation. Assuming, for the moment, the presence of a lubricating layer and a dynamic effect similar to the one which steepens wave fronts in core-annular flows, exacerbated by the surpassingly small gaps for slipping polymers, we may consider the idea that every wavy extrudate will have a steep wave front and a flatter rear. This idea seems to work well in all of the cases in which the direction of flow could be ascertained from photographs or the associated text. In fact, researchers in this subject do not say much about the direction of flow, and they do not look at the asymmetry of the wave as a window for understanding. We were able to know the direction of the extrudate only in the cases in which the die exit is shown. In all these cases the steep part of the wave advances [see Table 1].

Authors	Photographs	Predicted direction by present authors	Indicted direction by original authors
Benbow and Lamb [1963]	Figures 1.3 & 1.4	Left to right	No
	Figures 10.1, 10.2 & 10.3	Left to right	
De Smedt and Nam [1987]	Figure 1(b)	Left to right	No
Kalika and Denn [1987]	Figures 3(a) & (b)	Right to left	No
	Figure 8	Right to left	No
Denn [1990]	Figures 1(a) & (b)	Right to left	No
Piau, Kissi and Tremblay [1990]	Figures 6(d) &(e)	Downward	Downward
	Figures 7(b), (c) & (d)	Downward	Downward
	Figure 8(f) & (g)	Downward	Downward
	Figures 9(e)	Downward	Downward
Kissi and Piau [1990]	Figure 4(g)	Downward	Downward
	Figure 5(d) & (e)	Downward	Downward
	Figures 11(a)-(e)	Downward	Downward
Piau, Kissi and Mezghani [1995]	Figure 4(b)	Downward	Downward

Table 1. Identification of directions of extrusion flow from the photographs published in literature. The direction is such that the steep front of the wave advances. Unpublished photographs of S. Kurtz and W.R. Schowalter also show the steep part of the wave at the front.

Steep Wave Fronts Generated by Rubber Friction

The study of the friction of rubber is important for the tire industry. Concentrated solutions and melts are thought to be rubber like when deformed rapidly. Two types of wave systems in which steep fronts develop can be observed in experiments: abrasion patterns (Schallamach [1952], [1963]) and “waves of detachment” (Schallamach [1971], Barquins and Courtel [1975], Briggs and Briscoe [1978], Barquins and Roberts [1986] and Roberts [1992]). The mechanics responsible for the waves are not the same as those which produce steep waves on heavy oils lubricated by water but “waves of detachment” could conceivably occur in systems of extruded polymers. The rubber friction systems share the property that severe deformations occur at the wave front when the relative motion between the wall and slipping substrate forces material through the converging part of the gap between the wavy substrate and the wall.

When rubber is abraded without change of direction, sets of parallel ridges are often found on the surface of the samples at right angles to the direction of motion; these have been called “abrasion patterns”. The four examples shown in figure 6 were obtained in experiments carried out on actual road surfaces. The intensity of the waves increases with coarseness of the track, and with decreasing stiffness of the rubber compound. The waves increase the rate of abrasion by mechanisms suggested by the comparison of the cross sections of abrasion patterns in a laboratory experiment and a tire surface shown in figure 7. The saw teeth seen in both profiles point against the direction of abrasion. When moving over track or road they are bent backwards, thus exposing their underside to scouring and protecting part of the surface in their rear. The scouring motion is probably like the secondary eddies in the trough of a wavy core shown in figure 2. The teeth wear progressively thinner until the crests are bodily torn off leaving blunt edges. In the meantime the ridges continue to grow out of the underlying bulk material and the pattern is to a certain degree self perpetuating. When keeping the pattern under observation during an abrasion experiment it is found that it maintains its general configuration for a short time but moves as a whole across the surface in the direction of abrasion. The reason is that the attack of the abrasive on the rubber has a forward component. The abrasion patterns shown in figure 6 look like some of the forms of melt fracture; in particular, figure 6 (a) suggests “sharkskin”.

Schallamach’s “waves of detachment” are another special domain of rubber friction in which rubber does not slide over a hard surface in the accepted sense; instead moving folds in the rubber cross the contact area in the sliding direction of the rubber at speeds greatly exceeding the imposed sliding velocity. The fronts of these waves are very sharp. Adhesion seems complete between the waves (see figures 7-10 in Schallamach [1971]). Schallamach [1971] thought that folds were produced by buckling induced by compression in the presence of a tangential stress gradient. Additional mechanisms have been proposed by Barquins and Courtel [1975] and an interesting mathematical analyses was given by Briggs and Briscoe [1978]. An excellent review of the subject of rubber friction can be found in Roberts [1986].

The Schallamach waves detach the rubber from the hard surface and relative motion between the two surfaces occurs only in the regions where contact has temporarily been lost. The effect is similar to a caterpillar moving over a leaf. Schallamach waves do not appear below a critical value of the sliding speed and above this value the frictional stress is almost independent of the sliding speed, load and temperature, properties which are characteristic of spurt transitions to lubrication. Barquins and Roberts [1986] note that “...It appears that whenever the waves are present, their speed and number adjust within the contact so that the resultant frictional stress, surprisingly, is always about the same.” Another possibility is that the wave speed and amplitude adjust to keep the local shear rate constant, U/L = const where U is the speed and L is the amplitude.

Boundary Lubrication and Slip

Not all cases of slip fall in the domain of wet slip in which a soft fluid is generated at the wall. We can imagine that in the case when polymers suddenly detach from the wall, that a dry slip involving rubbing friction after adhesive failure is at issue.

Atwood and Schowalter [1989] and Lim and Schowalter [1989] assumed that loss of adhesion was the case of slip in the material they studied, but they did not identify the mechanisms responsible for the loss of adhesion. Hatzikiriakos and Dealy [1991] studied the slip of a polydisperse polyethylene in a sliding plate rheometer; they increased the slip by coating the steel plates with Dynamar 9613 and they reduced slip by coating the steel plate with “DFL” (dry film lube) suggesting that coatings produce slip in a lubricating layer and suppress slip in an adhesive layer.

These features of dry “slip” appear to be related to properties which are well known and partly understood in theory of boundary lubrication. That subject teaches that the reduction of friction is related to a property, called oiliness in the old literature, which does not correlate with viscosity but instead is a property of a monomolecular film, or surpassingly thin layer of surfactant molecules absorbed on the surface on one of the slipping bodies. The classical realization of this effect is the great reduction in the coefficient of static friction when small amounts of oleic acit (or other fatty acids) are added to mineral oils lubricating metals. These acids can be less than a percent by weight in the solution; even in trace amounts they are selectivey absorbed onto the metal where they act as a lubricant unrelated to lubricity. It is useful, if not common, to think of surfactants on solid surfaces rather than at fluid-fluid interfaces. A good example are soaps or even standard anionic surfactants like SDS in trace amounts in water which are absorbed on lipids of the skin. Such absorbed layers increase the slippery sensations between the thumb and forefinger dramatically. In fact the presence of very thin layers of water will increase the friction over its dry value as is well known to persons turning the pages of a book or counting money, but the wet friction of soap solutions remains even when the layer of water has dried.

Roberts [1992] has given a description of how rubber friction varies with rubbing speed and other parameters. His discussion treats static friction, kinetic friction, the appearance of Schallamach waves at a critical speed and the effects of changing the rigid material of the track on which the rubber slides. Of special interest is his discussion of the effects of lubricants. He used Newton’s colors in white light and fringe patterns to determine the film thickness in the presence of lubricating layers. For the case of a rubber hemisphere against a water lubricated glass turntable, he found that when the sliding speed is less than 10 mm/s, the appearance of black streaks in the water film indicates film breakdown and the friction increases as the speed decreases. At low speeds of 0.1 to $10\ \text{m/sec}$ or less, wet Schallamach waves are seen, particularly at the start of sliding. At speeds $0.1-10\ \text{mm/sec}$, the wet waves appear more like undulating ripples in the rubber interface -- the so-called regime of mixed lubrication (boundary / elastohydrodynamics). Figure 8 is taken from Roberts [1992] paper. It shows how waves may be entirely eliminated and the friction greatly reduced by the selective absorption of small amounts of SDS (a well known anionic surfactant) in water. It is possible that additives for polymers which enhance slip work like aqueous SDS in the boundary lubrication regime of rubber friction.

References

Bai, R., Kelkar K., Joseph D.D., Direct simulation of interfacial waves in a high viscosity ratio and axisymmetric core annular flow. *Supercomp. Inst. Res. Rep # UMSI 95/107*, University of MN, (1995).

Barquins, M., and Courtel, R., Rubber friction and the rheology of viscoelastic contact. *Wear*, **32** (1975), 133-150.

Benbow, J.J. and Lamb, P., New aspects of melt fracture, *SPE Transactions*, **3** (1963), 7-17.

Barquins, M., and Roberts, A.D., Rubber variation with rate and temperature: some new observations. *Journal of Physics D: Applied Physics,* **19** (1986), 547-563.

Bowden F.P., and Tabor, D., Friction and lubrication of solids. *Oxford University Press*. (1954).

Briggs, GAD., and Briscoe B.J., How rubber grips and slips: Schallamach waves and the friction of elastomers., *Philosophical Magazine,* **38 (4)** (1978), 387-399.

Chen, K.P. and Joseph, D.D. 1992 Elastic short wave instability in extension flows of viscoelastic liquids, *J. Non-Newtonian Fluid Mech.*, **42**, 189-211.

De Smedt, C. and Nam.S., The processing benefits of fluorelastomer application in LLDPE, *Plastics and Rubber Processing and Applications*, **8** (1987), 11-16.

Denn, M.M., Issues in viscoelastic fluid mechanics, *Annu. Rev. Fluid Mech*., **23** 1990), 13-34.

Feng, J., Huang, P.Y., Joseph D.D., Dynamic simulation of the motion of capsules in pipelines, *J. Fluid Mech.,* **286** (1995), 201-207.

Joseph D.D., Liu J.Y., Steep wave fronts on extrudates of polymer melts and solutions. *J. Rheol*, (1996).

Hatzikiriakos, S.G. and Dealy, T.M., Wall slip of molten high density polyethylene. I. Sliding plate rheometer studies, *J.Rheol.*, **35** (1991), 497-537.

Kalika, D.S. and Denn M.M., Wall slip and extrudate distortion in linear low-density polyethylene, *J. Rheol.,* **31** (1987), 815-834.

Kissi, N. El and Piau, J.M., The different capillary flow regimes of entangled polydimethylsiloxane polymers: macroscopic slip at the wall, hysteresis and cork flow, *J. Non-Newtonian Fluid Mech.,* **37** (1990), 55-94.

Migler, K.B., Hervet, H., and Leger, L., Slip transition of a polymer melt under shear stress, *Physical Review Letters,* **70** (1993), 287-290.

Oliemans RVA, Ooms G., Core-annular flow of oil and water through a pipeline, *Multiple Science & Technology,* ed. GF Hewitt, JM Delhaye, and N Zuber, Vol 2, Hemisphere Publishing Company, (1986).

Persello, J., Magnin, A., Chang, J., Piau, J.M. and Cabane, B., Flow of colloidal aqueous silica dispersions, *J. Rheol.,* **38** (1994), 1845-1870.

Piau, J.M., Kissi, N.E. and Mezghani, A., Slip flow of polybutadiene through fluorinated dies, *J. Non-Newtonian Fluid Mech.,* **59** (1995), 11-30.

Piau, J.M., Kissi, N.E. and Tremblay, B., Influence of upstream instabilities and wall slip on melt fracture and sharkskin phenomena during silicones extrusion through orifice dies, *J. Non-Newtonian Fluid Mech.,* **34** (1990), 145-180.

Roberts A.D., A guide to estimating the friction of rubber. *Rubb. Chem. Technol.,* **65** (1992), 673-686.

Schallamach, A., Abrasion and Tyre Wear, in *The Chemistry and Physics of Rubber-Like Substances,* ed. L. Bateman, Maclaren London (1963).

Schallamach, A., Abrasion and Tyre Wear, *Wear,* **1** (1958): 406.

Schallamach, A., How does rubber slide, *Wear,* **17** (1971), 301-312.

Schowalter, W.R., The behavior of complex fluids at solid boundaries, *J. Non-Newtonian Fluid Mech.*, **29** (1988), 25-36.

Schreiber, H.P., Storey, S.H. and Bagley, E.B., Molecular fractionation in the flow of polymeric fluids, *Trans. Soc. Rheol.*, **10** (1966), 275-296.