

## **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 Akerman Hall  
Minneapolis, MN 55455

**ABSTRACT:** Steep wave fronts tend to develop in many regimes of lubricated, slipping flows in which waves appear. 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. In water lubricated pipelines, high pressures are produced at the front side of a wave on the oil when water is forced through the wavecrest and the wall; low pressures develop at the back of the wave where the gap opens. The steep waves which develop on cores of heavy oil lubricated by water are irregular and look like melt fracture. Direct numerical simulation of regular periodic waves give rise to sharkskin solutions in which the wave length decreases with the wave amplitude as the gap size decreases, preserving the steep wave front. Wave steepening seems always to occur in extrusion when the polymers slip, in the abrasion of rubber samples and in Schallamach's waves of detachment.

### **1 Lubrication layers and slip**

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 [7] or Roberts [34]). 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 or else that the two materials weld at touching asperities. Even in the case of welded asperities, the two materials are not joined everywhere and one may consider the effects of the substance between.

## 2 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.

Cohen and Metzner [12], Müller-Mohnssen, Weiss and Tippe [27] and others argue that apparent slip in polymer solutions is due to the reduction of polymer concentration and viscosity in a slip layer of thickness that can be much larger than the hydrodynamic diameter of the macromolecules. This layer of apparent slip is effectively a lubrication layer. Chen and Joseph [11] noted that such lubrication layers exhibiting wet slip could arise by 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. Busse [10] 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 [39], Schreiber et al [40] and Whitlock and Porter [42]. 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 [29], water is released into fractures at high shear forming a self-lubricating layer. Additives in PVC, studied by Funatsu and Sato [16] and Knappe and Krumbock [23], migrate towards the wall forming a lubricating layer between the polymer and the wall. Moynihan et al [26] 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 [13] reported that the flouroelastomer additive in the extrusion flow of PE through capillary tubes was concentrated at the free surface of the extrudate.

Vinogradov, Malkin, Yanovskii, Borisenkova and Berezhnaya [41] 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 [9] 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.

Chen and Joseph [11] suggested that extrudate distortion may arise as an instability of a lubrication layer as it does in core-annular flow. They find an elastic instability to short waves, suggesting sharkskin. Y. Renardy [32] investigated the stability of a lubrication layer in the “spurt flow” associated with the non-monotone response of a Johnson-Segelman model. She finds that in very thin layers the most amplified modes have a very small wave length. In another work Y. Renardy [33] reviews the results of linear stability of lubrication (slip or spurted) layers and discusses so many different mechanisms which have been proposed to explain this phenomenon. The waves which arise in all interfacial instability are symmetric; and evidently unstable to nonlinear mechanisms, like inertia, which lead to asymmetry. Steep wave fronts apparently develop in all lubricated slipping flows in which waves appear.

### 3 Slip transition

In general, at low levels of velocity and stress flows are not lubricated and they do not slip. The extrudate is smooth. Slip occurs as a sudden transition at a certain critical level of stress. We can imagine that the large molecules detach from the wall at a critical stress leaving a lubricated layer behind. The detachment of large molecules is a loss of adhesion and it must depend on the surface energy of adhesion to the solid, consistent with observations.

The sudden appearance of slip or lubrication in pressure controlled flows is marked by a discontinuity in the slope of the curve, giving the pressure drop  $\Delta P$  across the capillary tube as a function of the volume flow rate  $Q$  of the polymeric fluid. If the discontinuity is associated with slip, then the slope will decrease, signalling a decreased frictional resistance as shown in the cartoon in Figure 1. The frictional resistance of the lubricated polymer will depend on how well it is lubricated, or on the coefficient of friction in the case of dry friction.

In the lubricated case, the frictional resistance depends on the viscosity of the soft material in the lubrication layer and the thickness of the layer. For very thin lubrication layers of relatively high viscosity, the change of slope will not be large. For well lubricated flows, the discontinuity will be very large, with a small  $\alpha$  corresponding to small shear stresses on the pipe wall. Large discontinuities will occur

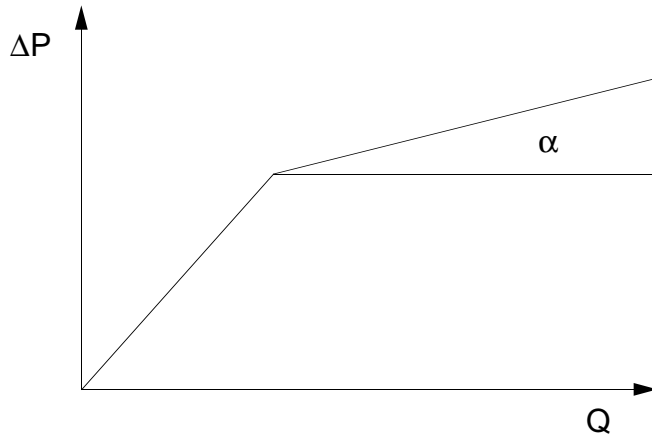


Figure 1: Cartoon of the flux curve given the pressure drop across a capillary versus the volume flux. The frictional resistance decreases at the point of discontinuity, with complete slipping when  $\alpha = 0$

in polymer solutions with watery solvents when the polymers detach, leaving a water layer at the wall. An extreme form of this occurs at the startup of a water lubricated flow of heavy oils at the point when the heavy oil is detached from the pipe wall by flowing water and enters into lubrication. In the lubricated regime, we see the volume flux of water alone, or even a slightly higher volume flux. A graph of  $\Delta P$  vs  $Q$  for this case would look like complete slip with  $\alpha = 0$ .

Discontinuities in four linear or branched silicones through a thin-walled orifice dies are exhibited in Figure 3 of Piau, Kissi and Trembley [31]. They point out that the discontinuity is associated with appearance of melt fracture. There are many examples of the appearance of melt fracture at slip discontinuities in the literature.

The coincidence of “melt fracture” with a discontinuity in the slope of the flow curve is a controversial area. This has been a subject of a number of mutually contradictory reports in which some authors (for example, [21]) associate sharkskin with wall slip, while other authors (for example, [31]) look to effects associated with huge stresses at the exit lip. Piau et al [31] note that there is a threshold for the appearance of sharkskin though this threshold is not independent of the material or die. The appearance of sharkskin is not marked by a clear change in the slope of the flow curve and it appears before the sharp break at melt fracture. Here, we pursue the idea that sharkskin also arises as an instability of very thin lubrication layers and document this idea mathematically in section 4 for core-annular flows (see figures 3 and 4) and from observations of abraded rubber samples (see figure

10 and other figures in the cited reference). The analysis of Bai et al [2] shows that sharkskin solutions of core-annular flows, with steep wave fronts maintained, arise only in the limit of surpassingly thin lubrication layers (figure 4). For such thin layers the change in the flow curve would appear as a rounded nose rather than a sharp discontinuity.

#### **4 Wavy core-annular flows and extrudate slip**

It seems to us (Joseph & Liu [19]) 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 at the top of Figure 2 are like an array of slipper bearings and the stationary oil core is pushed off the top wall by lubrication forces. If velocity of core were reversed, it would be sucked into the wall, so the slipper bearing picture is obligatory if you want levitation from lubrication theory.

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 middle and bottom cartoons in Figure 2. To get a lift from this kind of wave it appears that we need inertia, as in flying. Liu's [24] 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 for periodic waves from Bai, Kelkar and Joseph [3] are shown in Figure 3. Photographs of more irregular ubiquitous asymmetric waves in which the sharp fronts advance can be found in many places; for example Olie-mans and Ooms [28], Feng, Huang and Joseph [15] and Figure 5 below. These photographs remind one of the form of waves frequently seen on slipping polymer extrudates.

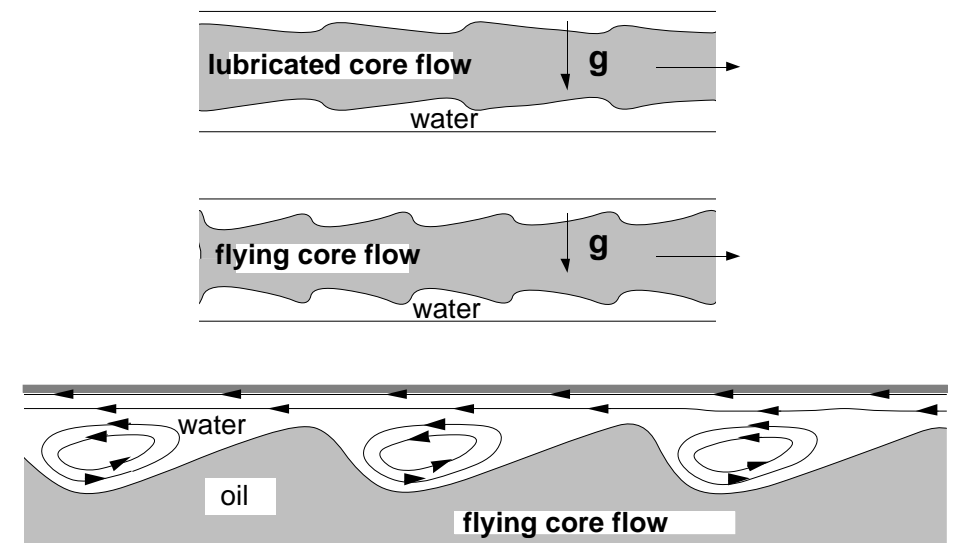


Figure 2: (After Feng et al 1995) (*top*) The interface resembles a slipper bearing with the gentle slope propagating into the water; the shape of these waves is unstable. (*middle*) The high pressure at the front of the wave crest steepens the interface and the low pressure at the back makes the interface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

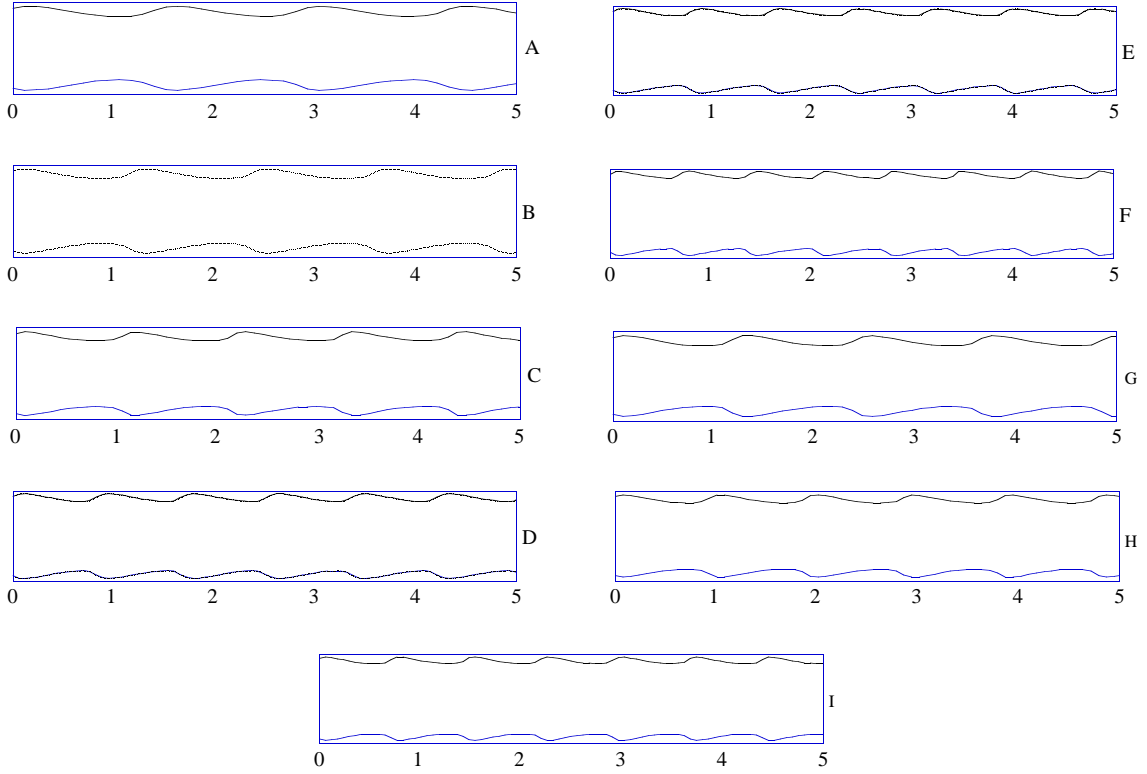


Figure 3: (After Bai et al [1992]) Selected wave shapes for water lubricated axisymmetric flow of oil and water with the same density  $\rho = 1.0\text{g/cm}^3$ ,  $\mu_0 = 0.01$  poise and  $\sigma = 26$  dyne/cm for oil and water. The core is stationary and the wall moves to the right. The pipe diameter is  $R_2 = 1.0\text{cm}$ .  $Q_0$  and  $Q_W$  are in  $\text{cm}^3/\text{sec}$ . The data for each frame is given as a triplet of prescribed dimensional values  $(R_1, Q_0, Q_W)$  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  $J = 13 \times 10^4$  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  $\eta$  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  $\eta \rightarrow 1$ .

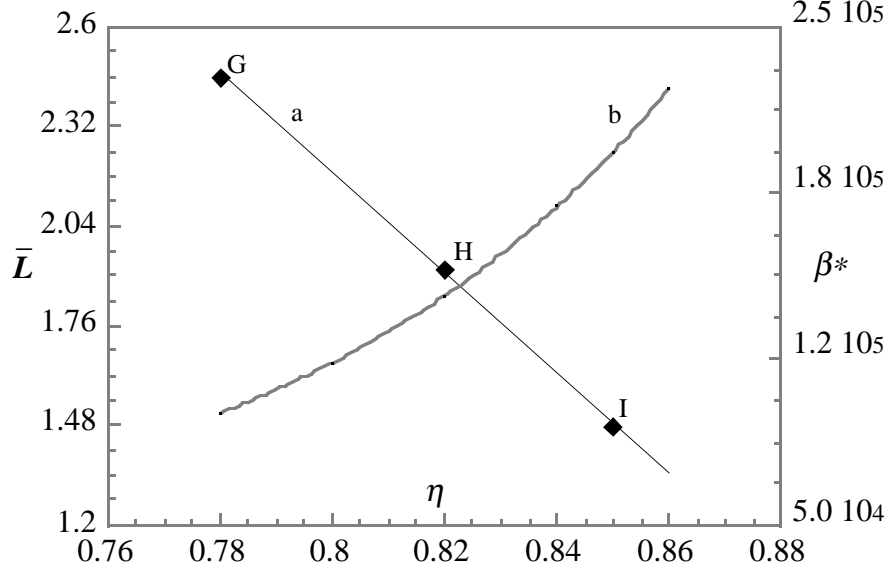


Figure 4: (After Bai et al [1995]) Curve  $a$  represents the wavelength  $\bar{L}(\eta) \approx 13.463 - 14.087\eta$  for  $[\mathbb{R}, h, J] = [600, 1.4, 13 \times 10^4]$ ; Curve  $b$  represents the pressure gradient  $\beta^*$  vs.  $\eta$  under the same conditions. The wave shapes for the points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

## 5 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 [3] 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 [2]. 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,  $\eta \rightarrow 1$ , the





Figure 5: The saw-tooth waves on the oil core in a horizontal pipeline. The flow is from left to right.

wavelength  $\bar{L}(\eta)$  decreases linearly with  $\eta$  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.

## 6 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].

Beautiful scanning electron microscope photographs<sup>1</sup> of oblique waves with steep wave fronts on film blown and extruded LLDPE are exhibited in figures 6,

<sup>1</sup>The photographs were generated as part of the Ph.D. research of R.P.G. Rutgers on polymer melt rheology and melt flow instabilities under the supervision of M.R. Mackley in the Department of Chemical Engineering at the University of Cambridge, and they have not been published previously. Thanks are due to the Materials Laboratory of the Department of Engineering for the use of their Leica Scanning Electron Microscope. The photographs are of an industrial grade LLDPE provided by BP chemicals.

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

7, 8 and 9. By a wave front we understand the part of the oblique wave which is perpendicular or nearly perpendicular to the flow. The waves shown vary from perpendicular to parallel and the parallel parts are symmetric without fronts. Preliminary indications from stylus surface profile measurements on extruded tapes, are that the waves are sharp at the front, confirming visual impressions. Parallel waves arise frequently as an instability on extrudates. The instability which leads to parallel waves can be called a rubbing or striping instability; they seem to have been first noticed by Giesekus [17], but they are also in evidence in nearly all of the cases of extrusion documented in Piau et al [31] and elsewhere. In some cases the development of melt fracture appears to arise as instability of the ribs.

## **7 Steep wave fronts generated by rubber abrasion**

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 [36], [35]) and “waves of detachment” ([37]), Barquins and Courtel [4], Briggs and Briscoe [8], Barquins and Roberts [6] and Roberts [34]). 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 10 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 11. 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

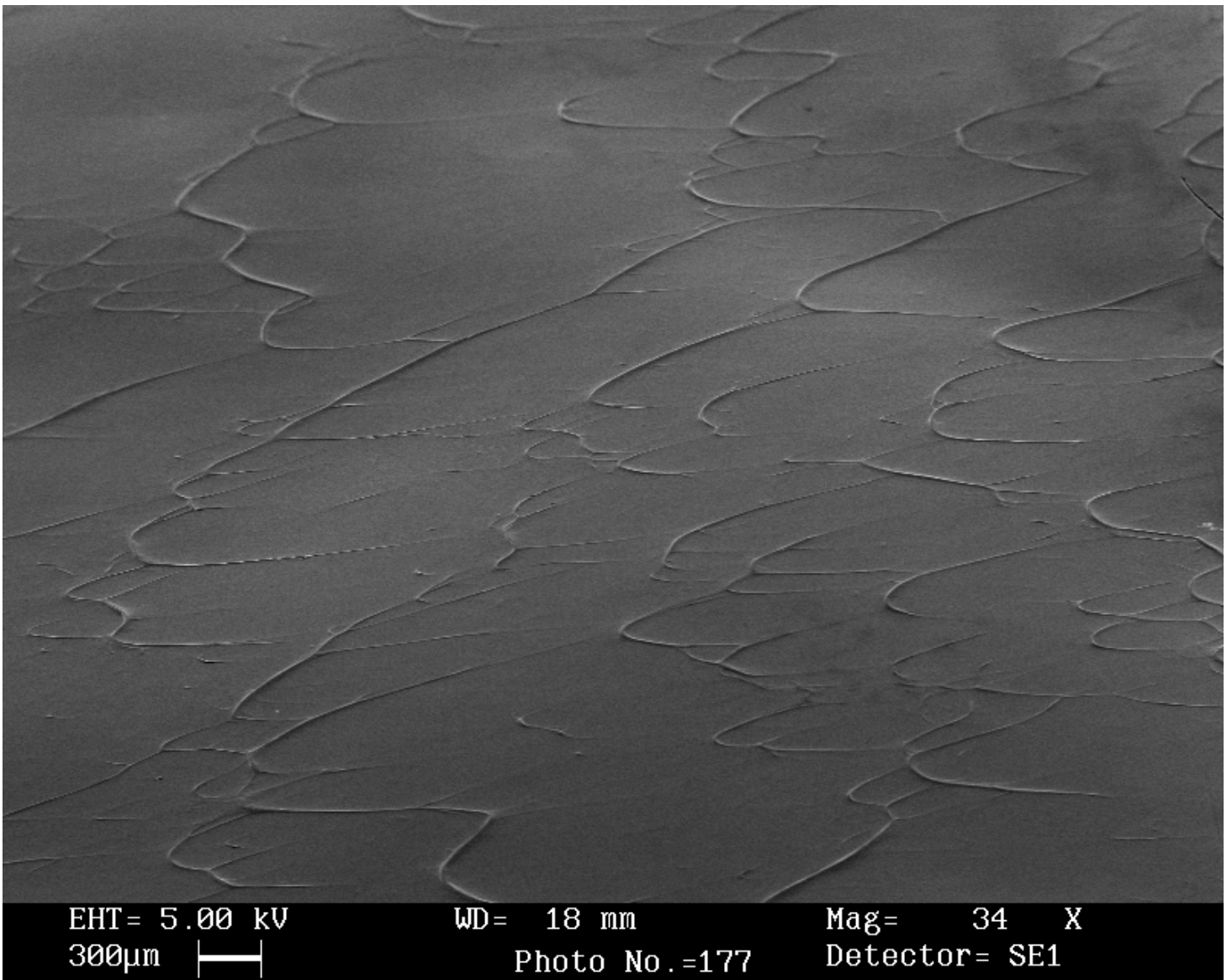


Figure 6: (Courtesy of R.P.G. Rutgers) Film blown of a 40 mm Kiefel extruder with a 0.8 mm die gap width. Haul off ratio of 3:1, blow up ratio of 2.5:1, melt temperature of 205°C, wall shear rate =  $277s^{-1}$ . Direction of melt flow from right to left. Surface profile characteristics parallel to the flow direction, obtained with a stylus apparatus (Talysurf+) at a 2.5 mm cut off: average roughness  $R_a = 1.8\mu$ , average of 5 highest peaks  $Rz_{din} = 29\mu$ , average distance between peaks  $Rsm = 0.65$  mm. Scale as indicated on the photograph.

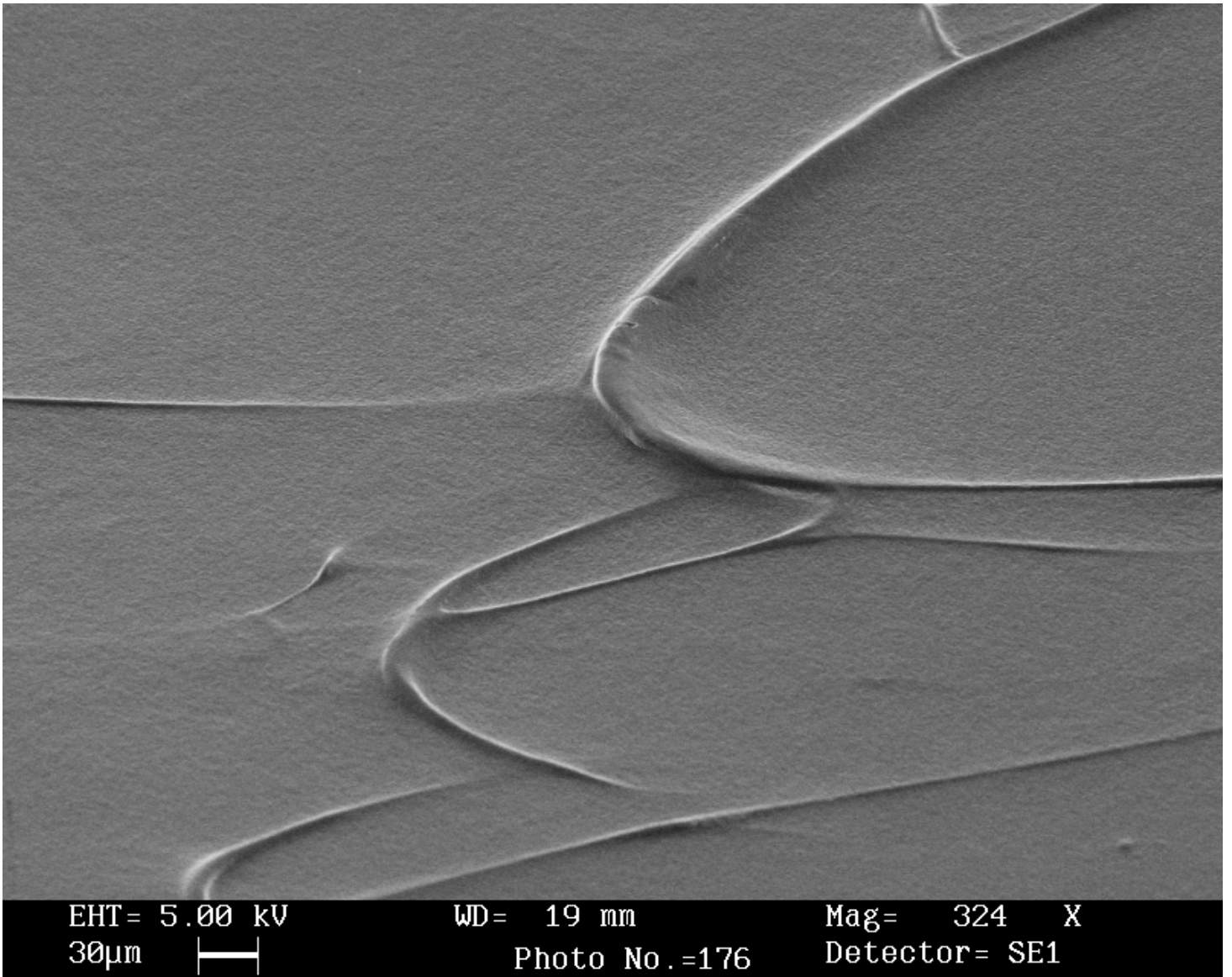


Figure 7: (Courtesy of R.P.G. Rutgers) As figure 6, but larger scale, as indicated on the photograph. Direction of melt flow from right to left.

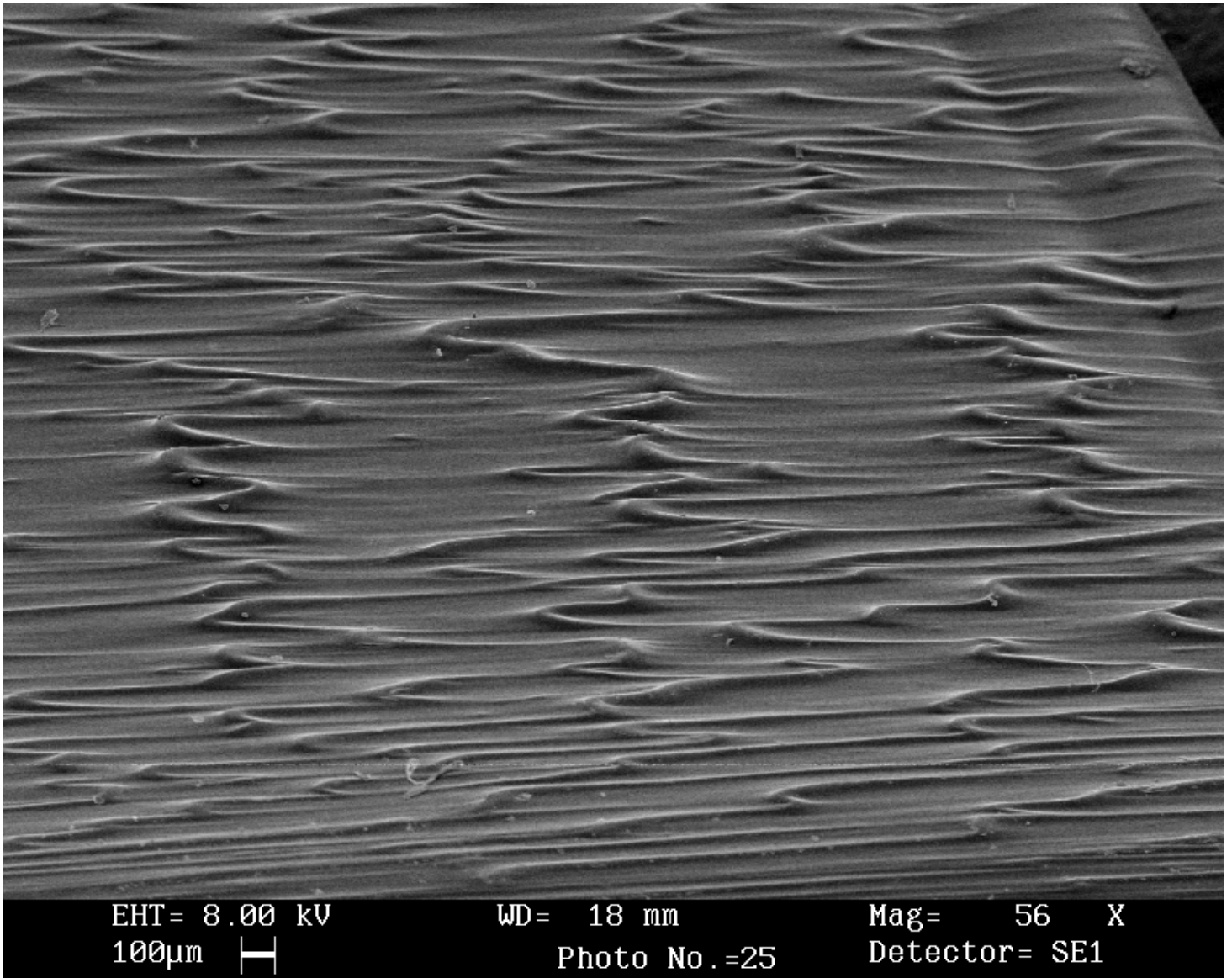


Figure 8: (Courtesy of R.P.G. Rutgers) Extruded tape from a 25 mm Betol single screw extruder with a 15:1 abrupt entry slit die of 1 mm gap width (x), and 8 mm length (z). Haul off ratio of 7.3:1, melt temperature of 178°C, wall shear rate = 163 s<sup>-1</sup>. The extrudate surface shown is the y-z plane. Direction of flow from right to left. Scale as indicated on the photograph.

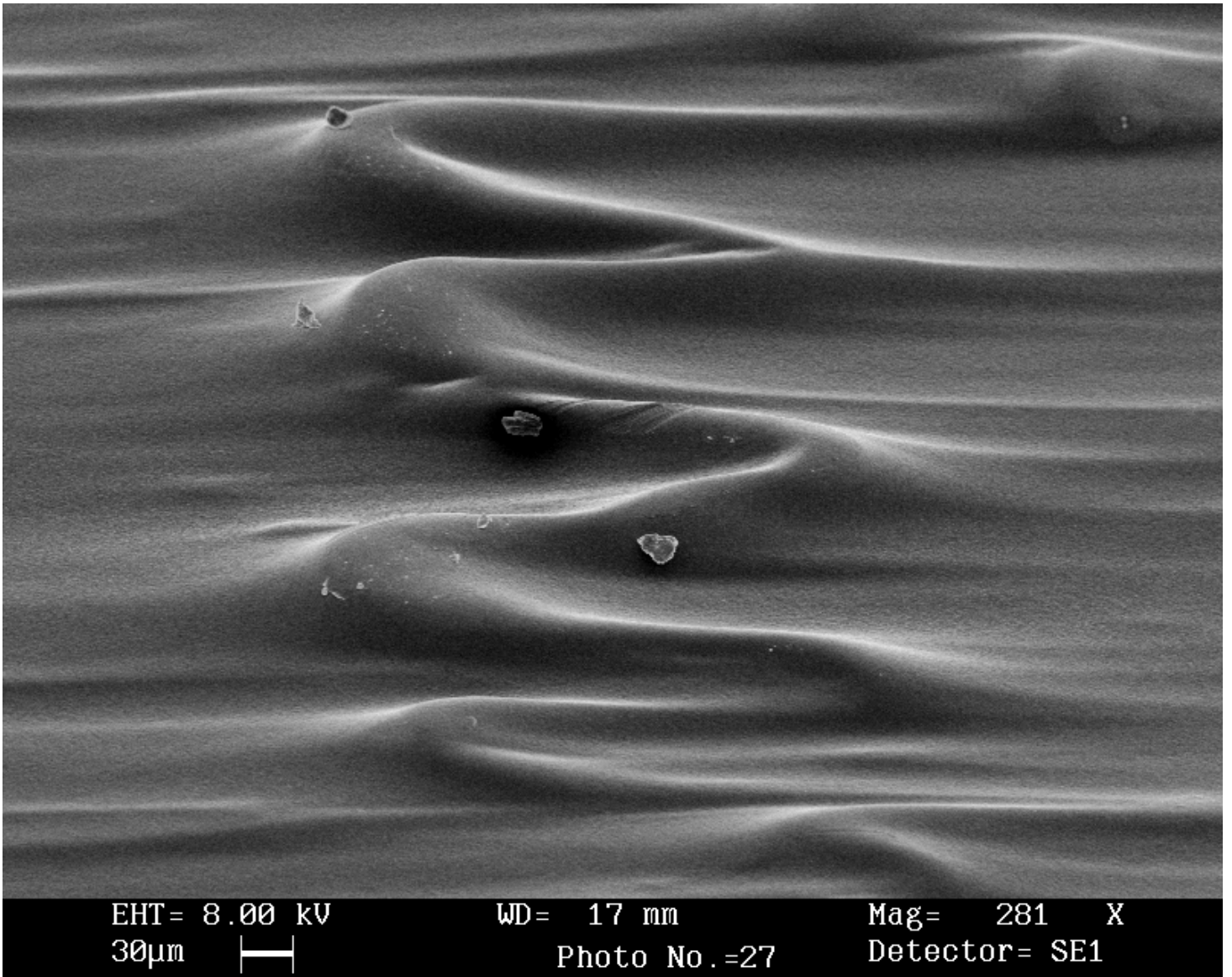


Figure 9: (Courtesy of R.P.G. Rutgers) As figure 8, but larger scale as indicated on photograph. Direction of flow from right to left.

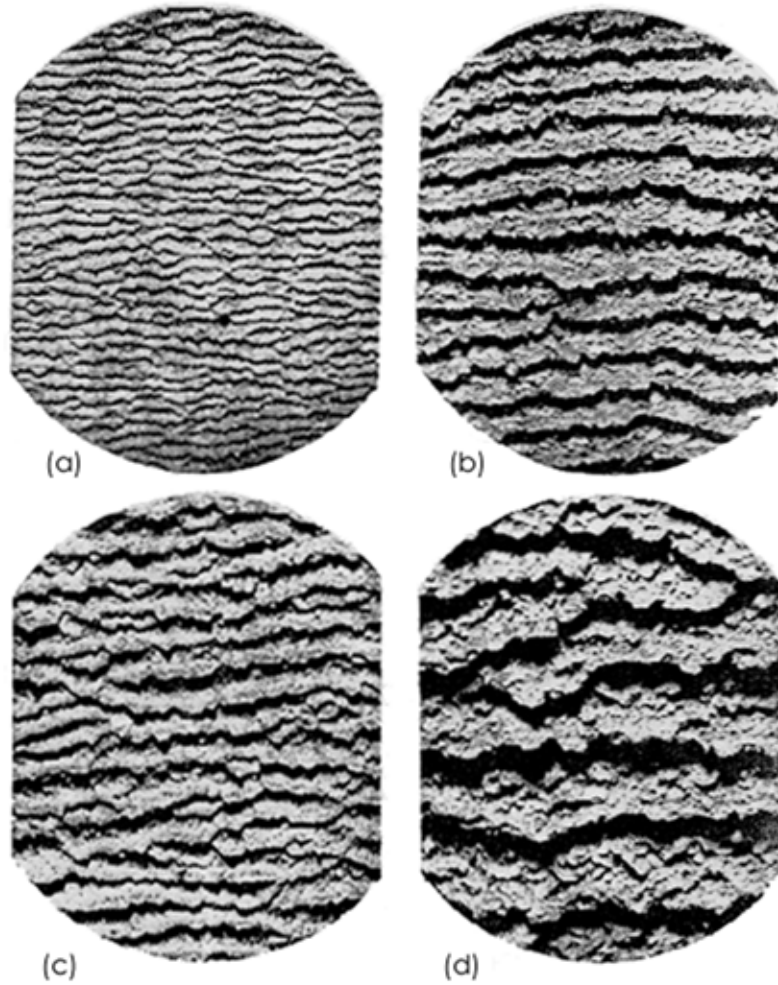


Figure 10: Abrasion patterns on two black-filled NR vulcanizates: (a) and (c) 45 pph HAF; (b) and (d) 25 pph HAF. Tracks: (a) and (b) fine tarmac; (c) and (d) coarse concrete. Direction of abrasion upwards. Magn.  $14 \times$ . *Wear*, 1958, **1**, 406, Fig. 17



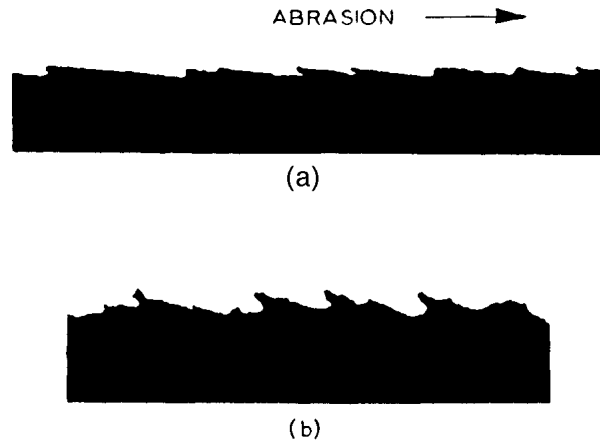


Figure 11: Profiles of abrasion patterns: (a) gum vulcanizate of NR abraded under  $1.6 \text{ kg/cm}^2$  on silicon-carbide cloth,  $5\times$ ; (b) worn NR tyre surface, horizontal magn.  $30\times$ , vertical magn.  $42.5\times$ . *Trans. IRI*, 1952, **28**, 259, Fig. 3

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 10 look like some of the forms of melt fracture; in particular, figure 10(a) suggests “sharkskin”.

## 8 Schallamach waves

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 [37]). Schallamach [37] 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 [4] and an interesting mathematical analyses was given by Briggs and Briscoe [8]. An excellent review of the subject of rubber friction can be found in Roberts [34].

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 [4] 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,  $U/L = \text{const}$  where  $U$  is the speed and  $L$  is the amplitude. Roberts [34] 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 mm/sec or less, wet Schallamach waves are seen, particularly at the start of sliding. At speeds 0.1–10 mm/sec, the wet waves appear more like undulating ripples in the rubber interface – the so-called regime of mixed lubrication (boundary / elastohydrodynamics). Figure 12 is taken from Roberts [34] 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.

## 9 Boundary lubrication and surfactants

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 [1] and Lim and Schowalter [18] 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 [20] 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

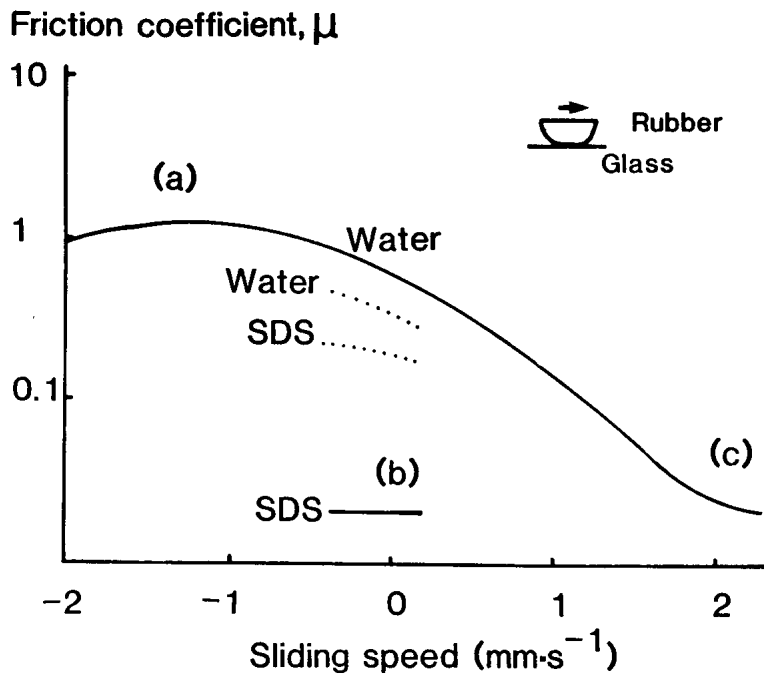
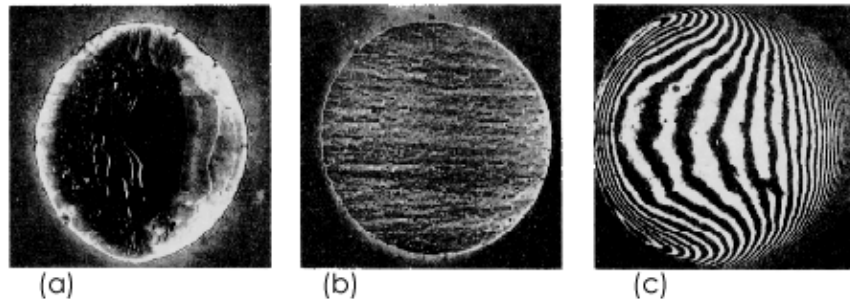


Figure 12: (*RC&T*, **65**, pg. 680, Fig. 6) The effect of velocity (log scale) on friction of isoprene rubber hemispheres (cured to 45 IRHD with 2presence of lubricants, water or SDS solution; —, smooth rubber; ···, roughened rubber. The insert shows the appearance of the contact area at the indicated conditions for smooth rubber; (a), “wet” Schallamach waves seen for low sliding speeds in water; (b), thin stable film of SDS solution at intermediate sliding speeds; (c), interference fringes for a thick elastohydrodynamic fluid film at high sliding speeds in water.

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 acid (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 selectively 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 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 had dried.

## 10 Conclusion

The shape of waves which develop on extrudates of polymer melts and solutions are such as to steepen the waves at the front. Similar steep waves appear on heavy oil lubricated by water, on abraded rubber samples and on Schallamach's waves of detachment. The mechanism of wave steepening in core-annular flows of oil in water are well understood and are associated with the high pressures which are produced at the front side of a wave when water is forced through the gap between the wave crest and the wall. Low pressures must develop at the back of the wave where the gap opens. Direct simulation of these waves gives rise to sharkskin in which the wave length decreases with the wave amplitude as the gap size decreases, preserving the steep front. Long waves are unstable to stagnation pressures which steepen the wave at its front.

The sharp wave fronts on polymer melt extrudates are not so well understood and the fluid rheology and detachment mechanisms enter the picture in as yet unknown way. However, wave steepening by pressures associated inertia as in core-annular flows of heavy oil may also be important. We have already argued that the appearance of sharp waves is associated with the formation of lubrication layers, whatever of the many mechanisms proposed for slip may be, and in these layers we may have mobile liquid, which work like water in coreflow. The extrudate itself is usually very viscous and so is advected in the lubricated flow as a rigid but deformable material as in the calculation of smooth, periodic and axially symmetric waves shown in figure 4. It is however noteworthy that the waves which do develop on the surface of lubricated flows of heavy oils (figure 5) are closer to melt fracture

than to the smooth surfaces one might expect from mathematical analysis.

## References

- [1] Atwood, B.T. and Schowalter, W.R., Measurement of slip at the wall during flow of high density polyethylene through a rectangular conduit, *Rheol. Acta*, **28** (1989), 134–136.
- [2] Bai, R., Chen, K., & Joseph, D.D., Lubricated pipelining: stability of core-annular flow. Part V. Experiments and comparison with theory. *J. Fluid Mech*, **240** (1992), 97–132.
- [3] Bai, R., Kelkar K., Joseph D.D., Direct simulation of interfacial waves in a high viscosity ratio and axisymmetric core annular flow. *J. Fluid Mech*, **327** (1996), 1–34.
- [4] Barquins, M., and Courtel, R., Rubber friction and the rheology of viscoelastic contact. *Wear*, **32** (1975), 133-150.
- [5] Benbow, J.J. and Lamb, P., New aspects of melt fracture, *SPE Transactions*, **3** (1963), 7-17.
- [6] 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.
- [7] Bowden F.P., and Tabor, D., Friction and lubrication of solids. *Oxford University Press*. (1954).
- [8] 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.
- [9] Brochard, F., and P.G. de Gennes, Shear-dependent slippage at a polymer/solid interface, *Langmuir* **8** (1992), 3033–3037.
- [10] Busse, W.F., Two decades of high-polymer physics: a survey and forecast, *Physics Today*, **9** (1964), 32–41.
- [11] Chen, K.P. and Joseph, D.D., Elastic short wave instability in extension flows of viscoelastic liquids, *J. Non-Newtonian Fluid Mech.*, **42**, (1992) 189-211.
- [12] Cohen, Y., and Metzner, A.B., Apparent slip flow of polymer solutions, *J. Rheol.* **29**(1) (1985) 67–102.

- [13] De Smedt, C. and Nam.S., The processing benefits of fluorelastomer application in LLDPE, *Plastics and Rubber Processing and Applications*, **8** (1987), 11-16.
- [14] Denn, M.M., Issues in viscoelastic fluid mechanics, *Annu. Rev. Fluid Mech.*, **23** (1990), 13-34.
- [15] Feng, J., Huang, P.Y., Joseph D.D., Dynamic simulation of the motion of capsules in pipelines, *J. Fluid Mech.*, **286** (1995), 201-207.
- [16] Funatsu, K. and Sato, M., *Adv. Rheol.*, B. Mena, A. Garcia-Rejon and C. Rangel-Nafaile (Eds.), (Mexico), **4** (1984), 465.
- [17] Giesekus, H., On instabilities in Poiseuille and Couette flow of viscoelastic fluids in *Progress in Heat and Mass Transfer*, V, Eds: W.R. Schowalter, A.V. Luikov, W.J. Minkowycz and N.H. Afgan. Pergamon (1972), 95.
- [18] Lim, F.J. and Schowalter, W.R., Wall slip of narrow molecular weight distribution polybutadienes, *J. Rheol.*, **33** (1989), 1359.
- [19] Joseph D.D., Liu J.Y., Steep wave fronts on extrudates of polymer melts and solutions. *J. Rheol.*, (1996).
- [20] 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.
- [21] Kalika, D.S. and Denn M.M., Wall slip and extrudate distortion in linear low-density polyethylene, *J. Rheol.*, **31** (1987), 815-834.
- [22] 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.
- [23] Knappe, W. and Krumbock, E., in *Advances in Rheology*, B. Mena, A. Garcia-Rejon and C. Rangel-Nafaile (Eds.), (Mexico), **3** (1984), 417.
- [24] Liu, H. A theory of capsule lift-off in pipeline, *J. Pipelines* **2**, (1982) 23–33.
- [25] Migler, K.B., Hervet, H., and Leger, L., Slip transition of a polymer melt under shear stress, *Physical Review Letters*, **70** (1993), 287-290.
- [26] Moynihan, R.H., Bird, D.G. and Ramanathan, R.R., *J. Non-Newtonian Fluid Mechanics* **36** (1990), 256–263.

- [27] H. Müller-Mohnssen, D. Weiss, and A. Tippe, Concentration dependent changes of apparent slip in polymer solution flow, *J. Rheol.*, **34**(2) (1990), 223.
- [28] Oliemans RVA, Ooms G., Core-annular flow of oil and water through a pipeline, Multiple Science & Technology, ed. GF Hewitt, JM Delhay, and N Zuber, Vol 2, Hemisphere Publishing Company, (1986).
- [29] Persello, J., Magnin, A., Chang, J., Piau, J.M. and Cabane, B., Flow of colloidal aqueous silica dispersions, *J. Rheol.*, **38** (1994), 1845-1870.
- [30] 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.
- [31] 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.
- [32] Renardy, Y., Spurt and instability in a two-layer Johnson-Segalman liquid, *Theoretical and Computational Fluid Dynamics*, **7**, 463-475.
- [33] Renardy, Y., An instability of plane Couette flow of the Johnson-Segalman liquid, in "Advances in Multi-Fluid Flows", Eds. Y. Renardy, A.V. Coward, D. Papageorgiou, S.M. Sun. The Society for Industrial and Applied Mathematics, Philadelphia, pp. 199-210.
- [34] Roberts A.D., A guide to estimating the friction of rubber. *Rubb. Chem. Technol.*, **65** (1992), 673-686.
- [35] Schallamach, A., Abrasion and Tyre Wear, in *The Chemistry and Physics of Rubber-Like Substances*, ed. L. Bateman, Maclaren London (1963).
- [36] Schallamach, A., Abrasion and Tyre Wear, *Wear*, **1** (1958): 406.
- [37] Schallamach, A., How does rubber slide, *Wear*, **17** (1971), 301-312.
- [38] Schowalter, W.R., The behavior of complex fluids at solid boundaries, *J. Non-Newtonian Fluid Mech.*, **29** (1988), 25-36.
- [39] Schreiber, H.P., and Storey, S.H., Molecular fractionation in capillary flow of polymer fluids, *Polym. Lett.*, **3** (1965), 723-727.
- [40] 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.

- [41] Vinogradov, G.V., Malkin, A.Ya., Yanovskii, E.K., Borisenkova, B.V. and Berezhnaya, G.V., *J. Polym. Sci. Part A-2*, **10** (1972), 1061–1084.
- [42] Whitelock, L.R. and Porter, R.S., Experimental investigation of the concept of molecular migration within sheared polystyrene, *J. Polym. Sci.* 10 (1972), 877–886.