

Using an Electronic Microbalance Technique to Study the Stick–Slip Behavior of Lubricated Polypropylene Fibers

N. Behary, C. Campagne, C. Caze, A. Perwuelz

GEMTEX Research Laboratory, Ecole Nationale Supérieure des Arts et Industries Textiles, 9 Rue de l'Ermitage, BP 30329, F-59070 Roubaix Cedex 1, France

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ABSTRACT: By use of an electronic microbalance, fiber/fiber friction measurements were made on cleaned and lubricated polypropylene (PP) filaments. The filaments were coated with a 0.14- μm -thick layer of one of the five lubricants: two different hydroxylated oils (hydroxylated oleate and hydroxylated stearate) and three different ethoxylated surfactants [(i) ethoxylated 10 OE dioleate; (ii) ethoxylated 15 OE dioleate; and (iii) ethoxylated 20 OE trioleate]. Despite the thick layer of lubricant applied, stick–slip persisted. Theoretical considerations of experimental conditions (load, speed, and viscosity) show that the pressure is very high at the contact point, and this would induce film thinning and thus stick–slips arising from phase transitions. Statistical

evaluations and atomic force microscopy images show that contacts between PP surfaces take place in presence of lubricants because surface asperity heights are larger than the lubricant film thickness. Oils or surfactants having similar surface tensions give different interfiber cohesion. Some explanations correlating the lubricant chemical structure and its spatial conformation, as well as its capacity to form intermolecular bonds and associative organization, to interfiber friction are given. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 645–654, 2003

Key words: polypropylene (PP); lubricants; surfactants; fibers; interfiber cohesion

INTRODUCTION

In the processing of textiles (carding, drafting, and weaving), a lubricant is applied to fibers to provide surface lubricity such that smooth high speed transfer on metallic or ceramic surfaces can take place with a minimum of abrasion and fiber breakage. The lubricants should also bring a certain degree of cohesion between fibers so as to provide strength in textile structures such as yarns and both woven and non-woven fabrics.

In textile applications, the lubricants most generally used are fatty acids, mineral oils, synthetic lubricants such as ethoxylated alcohols and acids, and silicones. Lubricants are in fact contained in finishes, and in the case of polypropylene (PP), finishes are applied during the spinning process of the PP filaments.¹

THEORETICAL BACKGROUND

General frictional behavior of liquid-lubricated textile yarns^{2–5}

Schlatter, Olsen, and Schick all carried out extensive work on fiber lubrication in the 1960s. The frictional

behavior of lubricated textile yarns can be illustrated by Figure 1, which shows the relationship of processing speed, finish viscosity, and pressure to the coefficient of friction. The solid curve, which is the actual coefficient of friction, is the result of two component curves representing forces of boundary friction and hydrodynamic friction. Hydrodynamic friction, represented by the dashed line, results from shear stresses that take place within a thick lubricant film. The friction in this area is governed by the rheological properties of the lubricant (viscosity, temperature, pressure, and speed). The dotted line represents the contribution of the boundary component of friction. Boundary lubrication, the other extreme, results at low speeds of sliding contact, and where high contact pressures exist. This results in a thin film that approaches solid molecular layers between fibers and other contact surfaces. This thin film still gives low friction but repeated contacts readily cause damage and wear. The semiboundary region represents the transition between boundary and hydrodynamic friction and is the area of minimum friction of the system. In the boundary and in the semiboundary area, the phenomenon of stick–slip, as illustrated in Figure 2, occurs between fibers or yarns and guide contact surfaces at low speeds and/or high pressure contacts. In fact, the two sliding surfaces do not slide smoothly, but move by making rapid jumps (slips) separated by longer periods of rest (stick). Friction is the highest in the stick

Correspondence to: A. Perwuelz.

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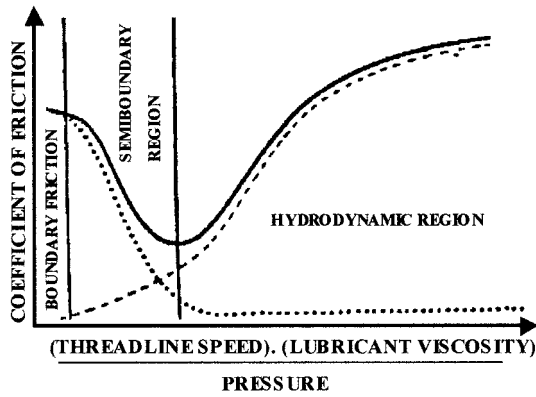


Figure 1 General frictional behavior of liquid-lubricated textile yarns.³

phase (static friction F_s) and the lowest in the slip phase (kinetic or dynamic friction F_k).

Thickness of the lubricant film

The theoretical separation distance between two sliding surfaces in the presence of a lubricant can be calculated by using Persson's equation,⁶ which was derived from Navier–Stokes equations:

$$\frac{1}{h^2(t)} - \frac{1}{h^2(0)} = \frac{4t\sigma_0}{3\eta a^2} \quad (1)$$

where a is the contact surface radius; h is the lubricant thickness [the separation distance $h(t)$ varies with time t and $h(0)$ is the initial film thickness]; η is the lubricant viscosity; and σ_0 is the normal stress, where $\sigma_0 = F_z/\pi a^2$, if a force F_z is applied.

However, this equation does not hold for very thin films (a layer of just a few molecules thick), because on the one hand the last monolayers of liquid form an adsorbed layer during wetting, which is often difficult to squeeze out, and on the other hand nucleation of molecules may occur, leading to a varying lubricant viscosity such that the Navier–Stokes equations may no longer be applied.⁶

Recent theories on boundary lubrication

During the past two decades, extensive research has been conducted to understand the different mechanisms of boundary lubrication and stick–slip phenomena.

Recent investigations in the field of tribology, with a surface force apparatus (SFA)^{7–10} and by atomic force microscopy (AFM)^{11,12} as well as computer simulations,¹³ aim at understanding molecular configurations of very thin lubricant films at contacting surfaces and changes that occur during sliding.

Computer simulations show that lubricant molecules can be arranged either parallel or perpendicular to a surface, depending on the chemical and physical nature of the contacting surfaces.¹³ Investigations with AFM have shown the configuration of grafted lubricants at contacting surfaces.^{11,12}

The studies that focused on films of simple straight and branched alkyl silicones confined between two mica surfaces⁸ and on grafted monolayers of surfactants⁹ show that that stick–slip movement is generated when the confined thin film undergoes phase transitions between solidlike and liquidlike states. The stick–slip behavior may vary with the molecular shape of a lubricant (spherical, linear, or branched).⁸

Further research on thin films of straight chain alcohols, octanol and undecanol, has shown that, although the first monolayer of lubricant is adsorbed at the substrate surface, additional liquid confined between the two can undergo layering at the solid interface. Such layers of molecular thickness are parallel to the substrate surface and they undergo continuous layering transition, passing from a liquid bulk behavior to a solidlike behavior, thus generating a stick–slip behavior.¹⁰

Other theories on stick–slip behavior

The two classical models known before these recent investigations, and which explained stick–slip behavior, are (1) the rough surface model and (2) the velocity-dependent model.

Rough surface model¹⁴

In this model rapid slips can occur whenever an asperity on one surface goes over the top of an asperity on the opposing surface. The extent of the slip will depend on asperity heights, slopes, sliding speed, and on the elasticity of the system.

Velocity-dependent model⁹

This was the most studied mechanism of stick–slip. In this model, two sliding surfaces move in a periodic

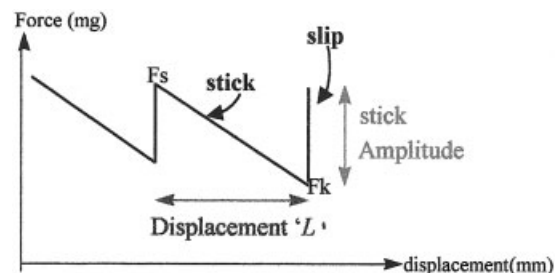


Figure 2 Stick–slip curve profile during fiber/fiber friction. The maxima and minima are called static (F_s) and dynamic (F_k) friction force, respectively.

TABLE I
General Characteristics of Lubricants Used to Coat Polypropylene Filaments^a

Lubricant	Viscosity, η (mPa.s)	Surface tension, γ_L (mN/m)	Extraction speed, V ($\mu\text{m/s}$)	Thickness deposited, e (μm)
Hydroxylated alkyl stearate	16	30.5	520	0.14
Hydroxylated alkyl oleate	12	31	720	0.14
Ethoxylated 10 OE dioleate	84	34.7	95	0.13
Ethoxylated 15 OE dioleate	109	34.8	128	0.18
Ethoxylated 20 OE trioleate	277	36	30	0.14

^a Measured at room temperature and ambient pressure.

fashion punctuated by abrupt stops and starts whose frequency and amplitude depend on the velocity, and on the mechanical coupling between two surfaces as well as on the applied load. To understand the origin of the phenomenon, it is useful to consider a solid block on a plane surface to which a pulling mechanism is attached by a spring. If the free end of the spring is pulled at a constant velocity V , then, initially, the block remains stationary and the pulling force on the block gradually increases as the spring extends. Eventually, this spring force exceeds the static frictional force and the block will slip. The relative motion between the block and the plane surface corresponds to the slip phase, whereas the initial extension of the spring defines the stick phase.¹⁵

In this model, stick-slip continues at all speeds but in the phase-transition model of lubricants, stick-slip will disappear at a critical velocity V_c . Indeed, if $V > V_c$, then molecules do not have enough time to make the transition to a solidlike state, and the two contacting surfaces will slide in a continuous manner.⁷

In the case of industrially produced, finished fibers, one or several of the three stick-slip mechanisms may intervene, because of the well-known surface roughness of fibers,¹⁶ the presence of lubricants in the finish, and velocity effects during sliding of fibers.

Recent friction studies on fiber friction with an electronic microbalance^{17,18}

We shall recall some of the conclusions on the work on the fiber/fiber friction and "pull-off" experiments carried out on glass fibers in past studies.^{17,18}

Static friction forces and the stick amplitudes are related to cohesive forces between fibers. These inter-fiber cohesive forces can be evaluated, on the one hand, from the mean decohesion work done calculated from stick signals of friction experiments and, on the other hand, from adhesion force F_{ad} values measured during the "pull-off" experiments [see Fig. 4(i) and (ii)]. Thus, for n number of sticks, the mean decohesion work done W can be expressed by the following equation:

$$\bar{W} = \frac{\sum_{i=1}^n W_i}{n} = \frac{1}{2} \sum_{i=1}^n \alpha L_i^2 \quad (2)$$

where α is the gradient of stick slope and is always constant, given that each stick amplitude is proportional to its duration when the applied load and the sliding speed are constant¹⁸; and L is the displacement of the horizontal fiber during the stick phase.

The aim of this work was to study boundary friction of polypropylene fibers at the fiber/fiber interface by analysis of variations of static friction coefficients, stick amplitudes, and decohesion work done during friction experiments and correlating these values to the adhesion values obtained during "pull-off" experiments.

EXPERIMENTAL

The work reported here consisted essentially in applying various lubricants to cleaned PP yarns and recording the stick-slip data during fiber/fiber friction.

Industrially finished polypropylene filaments (diameters between 46 and 54 μm) were first cleaned by an extraction procedure, after which they were treated three times in a bath of heptane for 15 min to eliminate all hydrophobic species in the finish and then they were subjected to a similar rinsing in bidistilled water to dissolve all amphiphilic species.

The measured receding surface energy γ_s^D of the cleaned PP fibers was found to be 33.5 mN/m.

Lubricants

Pure lubricants were used as finishes to coat cleaned polypropylene filaments. Two different oils [(i) hydroxylated alkyl stearate and (ii) hydroxylated alkyl oleate] and three different ethoxylated surfactants [(i) ethoxylated 10 OE dioleate, (ii) ethoxylated 15 OE dioleate, and (iii) ethoxylated 20 OE trioleate] were used.

Table I gives the different characteristics (density,

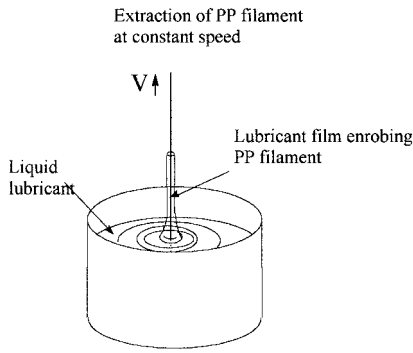


Figure 3 Coating of a polypropylene filament at constant speed.

viscosity, and surface tension) of the lubricants measured at room temperature and ambient pressure.

Coating of PP fibers

Pure lubricants were deposited on a polypropylene filament by immersing it vertically in the liquid lubricant and then by extracting it at a constant speed by using the Cahn microbalance (see Fig. 3). The thickness e of the deposited lubricant can be calculated by using the Landau equation¹⁹:

$$e = 1.34r \left(\frac{\eta V}{\gamma} \right)^{2/3} \quad (3)$$

where V is the extracting speed of the filament, r is the radius of a PP filament, η is the liquid lubricant viscosity, and γ is the liquid lubricant surface tension.

Table I summarizes the speed V used and the thickness e of each lubricant deposited.

Friction force measurements

The experimental setup for friction force measurements has already been described in the study concerning the tribology of glass fibers.¹⁷

Briefly, the friction force was measured between two crossed fibers [see Fig. 4(i)]. A horizontal fiber acted as a stationary rod, and a vertical one linked to a microbalance, passed over it at a wrap angle of 2.3° . Force variations were recorded when the horizontal fiber moved upward (because the microbalance platform is constrained to move upward). The experimental friction force curves, which resembled an irregular waveform [see Fig. 4(iii)], were treated by computer; detailed statistical analysis was performed on a large amount of data. In particular, the amplitude and frequency of the stick phase were studied; the amplitude was obtained by the difference between the maximum and minimum friction force values. During friction force measurements, the computer gave force values as a function of the vertical displacement L of the

horizontal fiber (in μm) and of time t (in s), given that speed V of the horizontal fiber was always constant ($L = Vt$). Thus, the frequency of stick events could be characterized by the duration of a stick phase or by the vertical displacement of the horizontal fiber during the stick phase.

"Pull-off" force measurements

Cohesive forces between two monofilaments placed in an orthogonal position were measured as follows. The vertical fiber, in the form of a loop, was connected to a microbalance [Fig. 4(ii)] at the weighing position. The horizontal fiber was fixed to a platform whose vertical movement was motorized (as in the friction force measurement experiment). To measure the "pull-off" force, the platform was raised to bring the horizontal fiber into contact with the loop, at the position where its curvature was the strongest. Then by making the platform move in the downward direction, the force necessary to separate the two fibers, that is the "pull-off" force, was measured [see Fig. 4(iv)].

This "pull-off" force is linked to the receding surface energy by DMT (Derjaguin, Muller, Toporov) theory:

$$F_{ad}(\text{"pull-off" force}) = 4\pi R\gamma \quad (4)$$

where R is the radius of curvature of contacting surfaces, such that for two crossed cylinders of radius r_1 and r_2 , $1/R = 1/r_1 + 1/r_2$.

All experiments were carried out at a constant speed of $5 \mu\text{m/s}$ and a constant relative humidity of 45%. A load of 200 mg was applied to the free end of the vertical filament. For all types of filaments (coated and uncoated), we determined that the number of measurements (stick-slip cycles) was sufficient for statistical analysis at 95% confidence level.

RESULTS AND DISCUSSION

Static friction coefficients

Static friction coefficients were evaluated from the static friction forces of stick-slip curves as described in a previous study.¹⁷ In our particular case, minima of the curve gave static friction force, given that the platform with the horizontal filament was constrained to move upward during friction experiments.

Cleaned polypropylene filaments

Figure 4(iii) shows a typical friction stick-slip curve obtained when cleaned PP filaments rub against each other. Like glass fibers studied in previous investigations,^{17,18} the static friction value varies over many stick-slip cycles. Figure 7(i) shows a frequency distribution of the static friction coeffi-

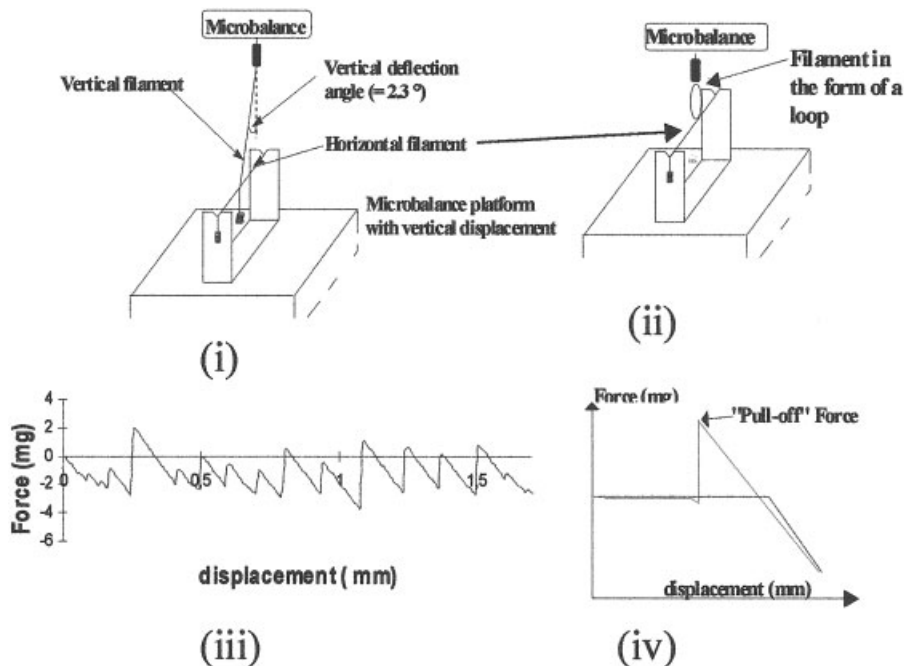


Figure 4 Experimental setup and force variations observed, respectively, during fiber/fiber friction measurement [(i) and (iii)] and during “pull-off” force measurements [(ii) and (iv)] of the cleaned PP filaments. [In (iii) minima give static friction coefficients as the platform with the horizontal fiber is constrained to move upward.]

cient μ_s . The μ_s values follow a bimodal distribution that can be attributed to the physical heterogeneity of the cleaned PP filaments. Topographic AFM images, like the one shown in Figure 5(i), confirm that the PP surface is rough, with randomly distributed bumps. Thus, the second distribution having a

higher μ_s value may be attributable to contact between these rough surfaces (bumps), whereas the first one may be related to contacts between smoother surfaces. Indeed, when the different lubricants are applied, the first distribution disappears, as discussed in the next section.

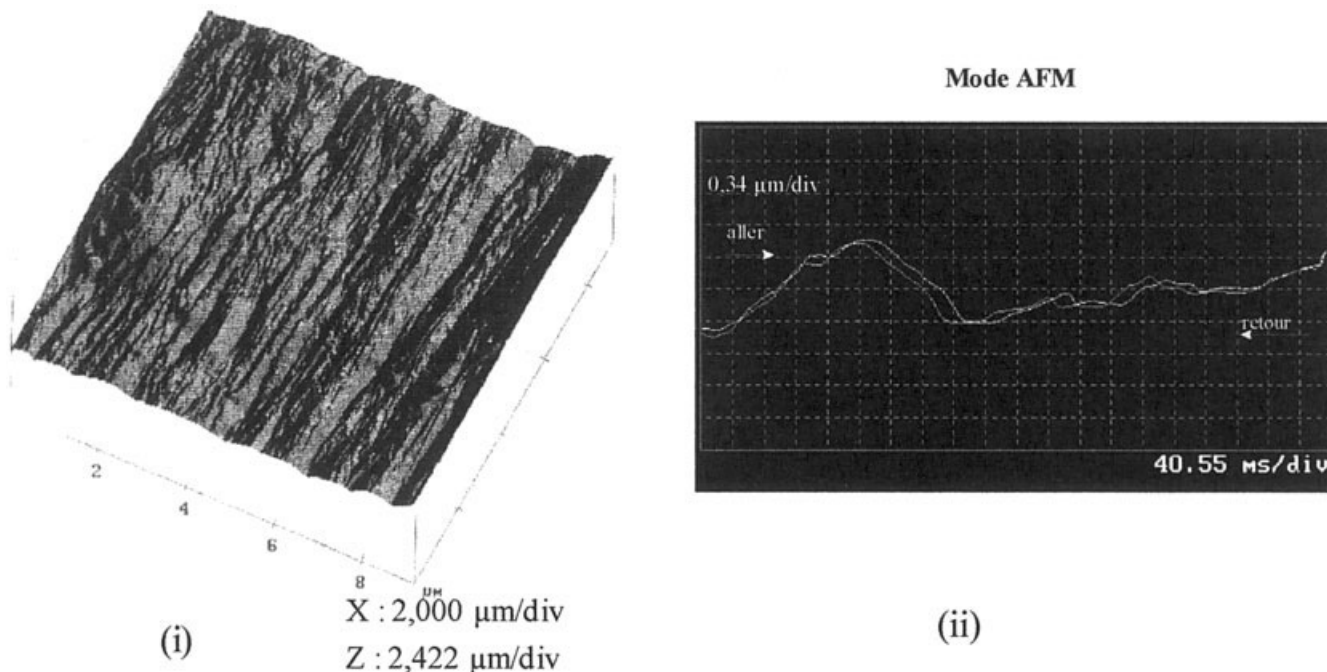


Figure 5 Typical topographic image of cleaned PP surface (i) and AFM signals showing the dimensions of a large asperity of height $\sim 1 \mu\text{m}$ at the fiber surface (ii).

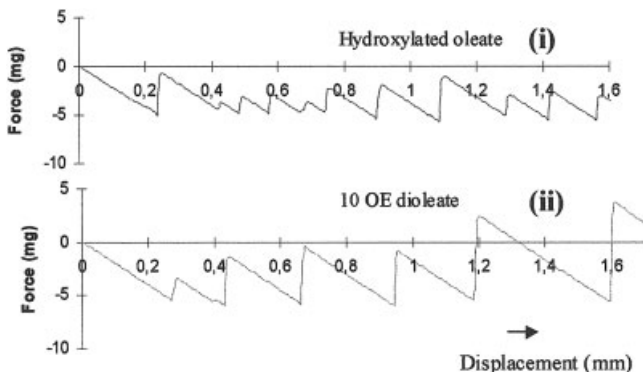


Figure 6 Stick-slip curves recorded during fiber/fiber friction of PP filaments coated (i) with an oil (hydroxylated oleate) and (ii) with a surfactant (ethoxylated 10 OE dioleate).

Nevertheless, for the cleaned PP fibers, the two modal values are close and the overall mean μ_s value is estimated to be 0.28, with a standard deviation of 0.13.

Effect of oil and surfactant lubricants

In the experimental conditions chosen (speed, $5 \mu\text{m/s}$; load, 200 mg; relative humidity, 45%), stick-slip phenomenon persists despite the thick layer of lubricant at the fibers' interface in the case of both oil- and surfactant-coated filaments. Figure 6 shows the friction curve profiles of filaments coated with hydroxylated oleate oil and with the 10 OE dioleate surfactant. The range of μ_s values of each type of lubricated filament is given in Table II.

A close analysis of the frequency distribution curves of μ_s values of all lubricated PP filaments provides evidence of a bimodal distribution of the μ_s values in each case. The solid-line curves in Figure 7(ii) and (iii) show the actual μ_s frequency distribution for hydroxylated oleate oil and 10 OE dioleate surfactant, respectively. The dotted lines show the striking bimodal

distribution of μ_s values in both cases. Statistical analysis allows us to evaluate the mean static friction coefficient of both distributions: μ_{s1} for the first and μ_{s2} for the second. Table II shows that the mean value of the first distribution for all lubricated filaments approaches that of the second distribution of cleaned PP filaments. These results would mean that, despite the application of a thick layer of oil onto the filaments' surfaces, contact between PP surfaces occurs during sliding of lubricated filaments. However, the mean μ_{s2} varies with the nature of the lubricant used. Thus, this value is greater in the case of hydroxylated oleate (0.56) than that of the hydroxylated stearate (0.49) and dioleates have a greater μ_{s2} value (~ 0.60) than that of the trioleate surfactant (0.47).

Stick phase amplitudes

Like static friction coefficient values, amplitude values also vary over stick-slip cycles for both cleaned and lubricated PP filaments [see Figs. 4(iii) and 6(i) and (ii)].

Statistical distribution of stick amplitudes shows that the range of amplitude values for the lubricated filaments (0–8.25 mg) is greater than that of cleaned PP filaments (0–4.25 mg; see Table II). This means that in the presence of a lubricant, a greater force is required to separate two contacting filaments. All lubricants used (except for 20 OE trioleate) imparted better interfilament cohesion between polypropylene filaments.

The average decohesion work done W has been evaluated [from the amplitudes and durations of sticks as in eq. (2)] and Table II shows that, like stick amplitude values, the decohesion work done is greater for all the lubricated filaments (except for 20 OE trioleate). The W values of both oils are nearly the same, and twice that of cleaned PP filament; and both dioleates have greater W values than those of the two oil

TABLE II
Summary of Results Obtained During Fiber-to-Fiber Friction and "Pull-Off" Experiments for Cleaned and Lubricated PP Filaments

Parameter	Cleaned PP	PP coated with hydroxylated oils		PP coated with ethoxylated surfactants			
		Oleate OH	Stearate OH	10 OE dioleate	15 OE dioleate	20 OE trioleate	
Range of μ_s values	0–0.73	0.02–0.73	0.17–0.73	0.12–0.83	0.32–0.98	0.27–0.88	
Mean μ_{s1}	0.28	0.33	0.32	0.32	0.34	0.32	
Mean μ_{s2}	—	0.56	0.49	0.60	0.59	0.47	
Range of stick amplitude values (mg)	0–4.5	0–6.5	0–7	0–7.5	0–12	0–5	
Mean decohesion work done, W (10^{-9} /J)	1.1	2.4	2.4	3.3	4.9	1.1	
Mean F_{ad} ("pull-off" force in mg)	0.44	0.65	0.51	0.71	0.81	0.65	
γ (mN/m)		$\gamma_s^A = 28^a$ $\gamma_s^D = 33.5^a$	31	30.5	34.7	34.8	36

^a γ_s^A and γ_s^D are the advancing and receding surface energies of the cleaned PP, respectively.

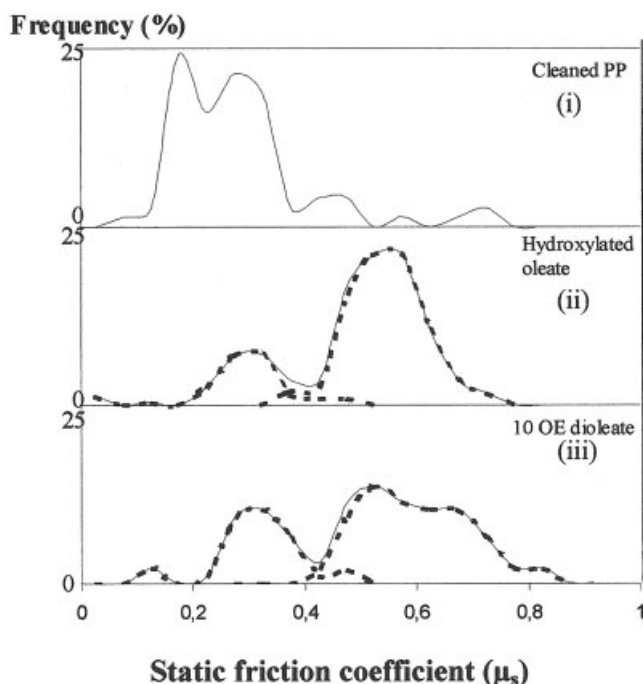


Figure 7 Frequency distribution curves of the static friction coefficient μ_s (i) of cleaned PP, (ii) of an oil (hydroxylated oleate)-coated PP filament, and (iii) of a surfactant (10 OE dioleate)-coated PP filament. The solid dark line illustrates the real frequency curve, whereas the dotted curve separates the bimodal distribution into two distinct distributions.

lubricants, which are three to five times that of cleaned PP filaments.

Values of the decohesion work done were then compared to F_{ad} values measured by “pull-off” experiments. Like the W values, F_{ad} values of both dioleates are higher than those of the two oils. Nevertheless, a high F_{ad} value does not necessarily mean a greater decohesion work done; for example, the 20 OE trioleate, which has an F_{ad} value similar to those of the two oils, has a mean decohesion work done value that is the same as that of cleaned PP filaments.

In addition, the F_{ad} values, measured when two filaments are separated, are not directly related to the surface tension of the liquid (see Table II) at the interface of fibers. Thus, the two oils as well as the three surfactants have similar surface tensions but give different F_{ad} values. The oleate oil imparts a greater F_{ad} mean value than does the stearate; and the two dioleates have greater F_{ad} values than that of the trioleate. In general, the F_{ad} values during “pull-off” experiments seem to be linked more closely to static friction coefficients of the second distribution obtained during fiber/fiber friction.

The most important question that arises out of this work is concerned with the origin of the distributions of static friction coefficients and stick amplitudes during fiber/fiber friction, and how these vary on the application of a lubricant.

The results obtained with cleaned PP filaments, particularly the wide distribution of μ_s values, can be attributed to the physical heterogeneity of the cleaned PP filament. Topographic AFM images like the one in Figure 5(i) confirm that the PP surface is rough, with randomly distributed bumps. Thus, it can be said that in the absence of a lubricant, the formation of adhesive junctions and/or geometric engagements would generate stick phases and their rupture would generate the slip phases. Sliding of imperfect PP surfaces leads to a different contact area each time a PP surface is in contact with another one and this would generate irregular stick-slip as described by Rabinowicz.¹⁴

The second question is why the stick-slip phenomenon persists despite the thick layer of lubricant at the fibers’ interface. Very thin films (two- to three-molecule-thick layers) confined between two smooth surfaces can exhibit stick-slip friction by phase transitions between solidlike and liquidlike states, as Israelachvili has shown.^{7,9} In the present case, the average thickness of the lubricant layer at the fibers’ interface is $2 \times 0.14 \mu\text{m}$ ($0.28 \mu\text{m}$), which would be equivalent to about 80-molecule-thick layers in the case of oil lubricants (we assume that the oil lubricant molecules are positioned perpendicularly to the fiber surfaces and that the oil molecules contain 24 carbon-carbon single bonds of 1.5 \AA each).

Using Persson’s eq. (1) we can evaluate the average film thickness at the contact point, under the experimental conditions, during fiber/fiber friction experiments. In the case of two orthogonally positioned filaments, with a load of 200 mg applied to the vertical filament, and a wrap angle of 2.3° , $F_z = 2 \times 10^{-3} \text{ N}/\sin 2.3^\circ$, and the surface of contact was calculated by using the DMT theory²⁰ for two crossed cylinders (see method used in Behary et al.¹⁷) $A = 2.83 \times 10^{-11} \text{ m}^2$; the pressure calculated at the point of contact was $1.76 \times 10^9 \text{ N/m}^2$, a notably high value.

Under these conditions, we can calculate the time taken for the initial thickness of lubricant [$h(0) \sim 0.28 \mu\text{m}$] to be reduced to 100 \AA (equivalent to approximately three-molecule-thick layers of oil lubricant) and to 10 \AA , respectively (see Table III).

Thus, theoretically the 0.28- to $0.36\text{-}\mu\text{m}$ -thick lubricant films are almost instantaneously reduced to 100 or 10 \AA . The thinning of film under the experimental conditions (high pressure, low viscosity, and low speed) would be instantaneous. Thus the stick-slip by phase transitions of the confined lubricant film (as described by Israelachvili⁹) may be a predominant phenomenon during fiber/fiber friction.

Another question that arises concerns the bimodal distribution of static friction coefficient μ_s values of the lubricated filaments with the first distribution mean value corresponding to that of contacts between cleaned PP surfaces.

TABLE III
Theoretical Thinning Time for the Film Lubricants Calculated Using Persson's Eq. (1)^a

Lubricant	Initial lubricant film thickness, $h(0)$ (μm)	Time taken for film thickness to reach 100 Å (s)	Time taken for film thickness to reach 10 Å (s)
Hydroxylated oleate	0.28	6.0×10^{-7}	6.2×10^{-5}
Hydroxylated stearate	0.28	4.6×10^{-7}	4.6×10^{-5}
10 OE dioleate	0.26	3.2×10^{-6}	3.2×10^{-4}
15 OE dioleate	0.36	4.2×10^{-6}	4.2×10^{-4}
20 OE trioleate	0.28	1.1×10^{-5}	1.1×10^{-3}

^a Ref. 6.

Two assumptions have been proposed to explain contacts between PP surfaces in lubricated filaments:

1. Under high pressure, the thinning of the lubricant may be followed by its rupture, resulting in contacts between PP surfaces.
2. The lubricant may be distributed in a heterogeneous manner at the surface of PP filaments.

As for the first assumption, we can wonder about the effect of the pressure on the layer of lubricant. Theoretically, the thinning of film is instantaneous, but is the pressure high enough to squeeze out the remaining thin layer of lubricant? In fact, Persson's eq. (1), which is based on Navier–Stokes for constant bulk viscosity (continuum theory), is no longer valid for molecularly thin lubricated films. Indeed, it is not possible to squeeze out the last one or two layers of trapped molecules. The reason for this is related to wetting (de Gennes²¹), to the solid nature of the adsorbed layers, and to the fact that these are pinned by the substrate potential.⁶ Repeated sliding and a large enough stress may fluidize or shear-melt the adsorbed layer; in this case it may be possible to squeeze out this adsorbed layer. During the fiber/fiber experiments, repeated sliding is avoided because a new contact is made for each stick–slip cycle, and therefore it is not likely that rupture of the lubricant film may occur.

The second assumption seems to be the most probable. Indeed, because the surface energies of both cleaned PP surfaces and each of the lubricants are nearly the same, dewetting of the lubricant at the PP surface may occur such that some regions of the polypropylene may not be covered with the lubricant. Furthermore, topographic images of cleaned PP surfaces like the one in Figure 5(i), show asperities whose heights exceed the lubricant thickness (0.14 μm); the R_{max} (difference between the highest peak and the deepest hollow) of the PP surface was measured to be 0.96 μm and signals in AFM (topographic) mode shown in Figure 5(ii) show an asperity that is approximately 1 μm high. Thus, it is most likely that dewetting would occur more rapidly on asperities whose heights exceed the lubricant film thickness; thus, there

would be places on the PP filament where no lubricant is present. Recently, Cheng et al.²² showed that for a small ratio of film thickness to surface roughness, contacts of the asperities are significant.

The last question that is posed is related to the variations of the friction and adhesion parameters (μ_{s2} , W , and F_{ad}) with the change in the nature of lubricants having similar surface tensions.

Molecular arrangements and interactions of the lubricant at the fiber/fiber interface in both a confined form or in a bulk liquid, and physical changes that may occur when subjected to different modes of solicitations, may explain these differences. During fiber/fiber friction, given that thinning out of the lubricant is quasi-instantaneous, sliding takes place in the presence of a confined film: this is called boundary or semiboundary lubrication. Thus, the greater the interaction between the PP surface and the lubricant, the more solidly will the boundary layer be pinned to the PP surface, and the better the fiber/fiber sliding (i.e., a smaller friction coefficient μ_s value). However, the more intermolecular bonds there are between lubricant molecules coming from adjacent fiber surfaces, the greater will be the decohesion work done W , and sliding will be difficult.

The main difference between interfiber cohesion measured by friction and by “pull-off” experiments is that in the latter case, no load is applied; squeezing out of the lubricant film is therefore less likely to occur so that contacts between PP surfaces are rare. During “pull-off” the two filaments are most probably separated by a thicker layer of lubricant than during friction experiments, such that a continuous film may be formed at the point of contact, and thus capillary force would predominate over separation forces.²⁵

We next consider each of the lubricant types and propose possible explanations for the results obtained.

Hydroxylated oils

As far as the hydroxylated oils are concerned, we can compare their arrangement to that of undecanol molecules confined between two surfaces and extensively studied by Salmeron et al. using SFA, RMN, and AFM

techniques to determine the conformation of these alcohol molecules at a mica interface.^{10,23} The first layer of undecanol was found to be very strongly bound to the mica, whereas additional liquid organized into compressible bilayers (with hydrogen bonds between two -OH groups), which could be expelled by applying high pressure. The authors concluded that there is phase transition between a phase of more or less vertically oriented bilayers and a phase with double layers of flat lying molecules.

As far as the polypropylene is concerned, it does not have any site or any chemical group capable of reacting with oils: however, it is hydrophobic, with a receding surface energy of 33.5 mJ/m². The lubricant molecules may lie horizontally at the fiber surface like liquid polymers at surfaces,²⁴ with the hydrocarbon chain directing toward polypropylene and the hydroxyl (-OH) in the opposite direction.

Interaction between the cleaned PP surface and the oil molecules will depend on the organization of the hydroxylated oil molecules at the PP surface, whereas interfiber cohesion will be related to hydrogen-type intermolecular bonds, which can take place between the hydroxyl groups of oil molecules from adjacent fibers. Because the hydrophobic part of the stearate is less rigid than that of the oleate, which has a carbon-carbon double bond C=C in its chemical structure, the stearate can take a coil conformation more easily. It is thus probable that there are many more interactions between the stearate and the cleaned PP surfaces as well as more intermolecular bonds (through the -OH bonds) between two molecules on the same fiber surface, rather than between two molecules from two adjacent fiber surfaces. The rigidity of the oleate reduces the probability of the oil molecule of lying flat on the PP surface, and thence of intermolecular bonds between molecules on a same fiber surface; however, on the other hand, it increases the probability of intermolecular bonds between two molecules from two adjacent fibers. Sliding is thus more easily facilitated in the presence of stearate during fiber/fiber friction ($\mu_s = 0.49$; with oleate, $\mu_{s2} = 0.56$) because there is better interaction between the lubricant layer and the PP surface.

The mean decohesion work done W (during friction to friction experiment) happens to be of the same value in the case of both hydroxylated oils. Indeed, in evaluating W , all the contacting surfaces were involved, that is, stick parameters of both contacts between PP surfaces and between lubricated fibers. That is perhaps the reason that both lubricant oils give the same W value. The F_{ad} values measured by "pull-off" show that interfiber cohesion is better in the case of the more rigid hydroxylated oleate ($F_{ad} = 0.65$ mg; with the hydroxylated stearate, $F_{ad} = 0.51$ mg) because of the greater probability of hydrogen bond formation between two molecules from two adjacent fibers.

The ethoxylated dioleates

In the case of the dioleates, associative organization can occur with the hydrophobic parts directed toward the nonpolar PP surface, and cohesion would depend on polar interaction between the hydrophilic (OE) groups coming from adjacent fibers. Because both dioleates have the same hydrophobic part, interaction between the thinned lubricant layer of both surfactants and the PP surface would be the same. That is the reason that during fiber/fiber friction, the friction coefficient μ_{s2} is nearly the same for both dioleates. However, given that the 15 OE dioleate has a greater HLB (hydrophile lipophile balance) value than that of the 10 OE dioleate (for the same hydrophobic part) the polar/polar interaction is higher in the former case. Thus, in the presence of 15 OE dioleate, a higher shearing force is needed to separate two fibers, and so there is a higher mean decohesion work done W (see Table II).

Compared to the hydroxylated oils, intermolecular interactions are far greater in the case of dioleates, and these induce a considerable effect on the W and F_{ad} values that are greater in the latter case.

The ethoxylated trioleate

The trioleate surfactant is very peculiar and yields results that differ from that of dioleates, although it has nearly the same surface tension. Because it has three hydrophobic chains in each of its molecules, the associative organization of its molecules at the PP surface would be more difficult because of the steric obstruction. In the presence of the trioleate, sliding is the easiest (lowest friction coefficient): $\mu_{s2} = 0.47$, and fiber/fiber decohesion occurs more readily ($W \approx 1.1 \times 10^{-9}$ J) than with the other lubricants. However, the adhesion force F_{ad} measured by the "pull-off" experiment is quite significant and approaches that of the hydroxylated oleate. It is most probable that the trioleate surfactant molecules behave differently when subjected to different modes of sollicitation: *shearing* in the case of fiber/fiber friction and *elongation* in the case of "pull-off." During "pull-off," the trioleate surfactant, which has a high viscosity (277 m Pa·s), would act like an adhesive between two fibers, but then shearing would induce a decrease of its viscosity and thus a bad cohesion and a good sliding during fiber/fiber friction.

CONCLUSIONS

The tribological study undertaken on polypropylene (PP) fibers with or without lubricants (oils or surfactants) and recent research on boundary lubrication have been used to explain lubrication of PP fibers at

low speed. In particular, the stick–slip amplitudes and frequencies vary with the type of lubricant used.

The great irregularities in the stick–slip parameters are attributed to the roughness of the surface of the PP filament and to the heterogeneous distribution of the lubricant applied. The stick–slip phenomenon persists in spite of the application of the lubricants because experimental conditions (raised pressure, low speed, and viscosity) are sufficient to induce an almost instantaneous thinning of lubricant, and consequently a stick–slip motion.

The lubricants (oils or surfactants) do not cover the entire surface of the PP because the friction coefficients corresponding to that of cleaned PP appear during fiber/fiber friction. AFM images showing asperity heights of cleaned PP larger than the thickness of the lubricant also explain the results.

Interfilament cohesion between filaments does not depend on the surface tension of the lubricant at the interface. Hypotheses are made to explain the different behaviors of lubricants at the PP interface [the spatial conformation of lubricant molecules and their interaction with the PP surface and with molecules on the adjacent fiber surface as well as the physical behavior (e.g., rheology of the lubricant)].

The major goal of this study aimed at classifying lubricants according to their frictional behavior at low speed at the fiber/fiber interface. Such study would help to optimize textile finishes that should be formulated to give good fiber cohesion in a textile structure.

Only further investigations like those carried out by Salmeron et al.¹⁰ by using SFA would allow prediction of more precise models for the structure of lubricant molecules confined at polypropylene interfaces.

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