# The Effect of Grafted Polymeric Lubricant Molecular Weight on the Frictional Characteristics of Nylon 6,6 Fibers

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Received 31 August 1998; accepted 3 December 1998

**ABSTRACT:** Boundary friction between two crossed nylon 6,6 fibers has been reduced up to  $6 \times$  by grafting polymeric lubricants to the surface. A modified adhesion model of friction, accommodating multiple materials on the surface, explains the variation in the friction coefficient with the molecular weight of the lubricant. The friction coefficient is proportional to the fraction of the surface covered by the grafted chain, represented by  $\pi R_G^2/A$ , where A is the surface area per graft site, and  $R_G$  is the radius of gyration of the lubricant. It is also shown that for larger the grafted chains, the appropriate surface area fraction depends on  $\pi R_G^2/3A$ . It is argued that if  $R_G$  of the grafted lubricant is larger than half the distance between graft sites, the next nearest graft site is used due to steric blocking of the nearest graft site. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 129–136, 1999

Key words: nylon; friction; lubricant; surface modification; fiber

## **INTRODUCTION**

Due to the extremely high ratios of surface area to volume in fibers, the surface properties play a dominant role in many of their applications. The surface properties affect both the processing conditions and end-use properties. It is not surprising then that there have been many attempts to modify the surface properties, starting in prehistoric times and continuing to the present. The most common method of modifying the surface properties is via topical treatment of the fibers with lubricants, antistatic agents, and size. Most of these are lost in subsequent processing, especially during cleaning. Since the surface properties are so important and since most of the topical treatments are lost, there have been many attempts to make durable surface treatments.

These treatments have largely been limited to three types, that is, plasma treatment, addition of the surface modifier to the polymer melt or solution before extrusion, and chemically modifying the surface with small molecules. Plasma treatment is generally slow and expensive and has found only limited use in fiber applications. Addition of the surface modifier to the polymer melt or solution before spinning provides good durability in some cases, but the surface modifier is generally lost each time the fabric is cleaned, and new material must diffuse to the surface from the bulk of the fiber. The requirements of this approach on the properties of the surface modifying molecule are quite severe, and, hence, only a few materials have found widespread use. Certainly, chemically bonding the material to the surface can reduce these problems. However, these modifications have usually been performed using small molecules that are unable to cover the entire surface of the fiber unless there is an extremely large number of graft sites on the fiber surface. Some of these problems could be eliminated if polymeric surface modifying agents could be grafted to the fiber surface. This article describes the modification of fiber-fiber friction via chemically grafting macromolecules to the surface of nylon 6.6.

Before proceeding, we need to understand how lubricants function and what determines friction

Journal of Applied Polymer Science, Vol. 73, 129–136 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/010129-08

in polymers. In engineering studies of friction and wear, two major types of lubrication have been found.<sup>1</sup> They are boundary lubrication, which predominates at high pressures and low speeds, and hydrodynamic lubrication, which predominates at low pressures and high speeds. There are, of course, the various intermediate cases.

Hydrodynamic friction is the friction that occurs due to the shearing of a fluid between two surfaces. It is due to the viscous losses in the fluid that is being sheared. The friction coefficient is proportional to the viscosity of the fluid. Hydrodynamic lubrication is the type of lubrication most people think of in everyday experience. However, since the remainder of this article deals with grafted chains, which should not be able to move freely, hydrodynamic friction will not be discussed further.

The adhesion model of friction has often been used to describe boundary friction in polymers.<sup>2</sup> In this model, friction is determined by the interfacial shear strength  $\tau$  in the contact region between the two surfaces. Experimentally, it has been found that

$$\tau = \frac{F}{A} = \tau_0 + \alpha P \tag{1}$$

where F is the shearing force, A is the real contact area,  $\tau_0$  is the adhesive strength,  $\alpha$  is the pressure coefficient for the shear strength, and P is the applied pressure (P = W/A where W is the applied normal load).

The true area of contact at high loads for a sphere on a disk or, equivalently, for two crossed cylinders (fibers) is given by

$$A = \frac{W}{P_y} \tag{2}$$

where  $P_y$  is the yield pressure for the polymer. The frictional force is obtained by combining equations (1) and (2), as follows:

$$F = W \left( \frac{\tau_0}{P_y} + \alpha \right) \tag{3}$$

where the contact pressure  $P = P_y$  since the polymer will continue to yield until the pressure is just equal to the yield pressure. Finally, the friction coefficient  $\mu$  is

$$\mu = \frac{F}{W} = \frac{\tau_0}{P_y} + \alpha \approx \alpha \tag{4}$$

since  $\alpha$  is generally much greater than  $\tau_0/P_y$ . Thus, to obtain low boundary friction, a material with a low interfacial shear strength is required. Typical boundary lubricants are waxy solids, such as sodium stearate, since waxy solids tend to be weak in shear and generally have low interfacial surface tensions, resulting in lower interfacial adhesion.

Recent work in boundary friction<sup>3</sup> has found that self-assembled monolayers of octadecytriethoxysilane tested at very low speeds exhibited many of the characteristics of boundary lubricants, including a stick-slip transition and a low friction coefficient. These idealized tethered chains are not suitable for industrial use on fibers. However, they suggest that grafted chains can act as boundary lubricants. Additional support for this idea is provided by the theories of polymers at interfaces. In the absence of a good solvent and at low surface coverage, end-grafted surface chains will lie down on the surface as dense pancakes with some loops and tails sticking out from the surface if there is a favorable interaction between the tethered chain and the substrate. On the other hand, if the tethered chains are repelled by the substrate, they will stick out from the surface like mushrooms, as described by de Gennes.<sup>4</sup> In addition, these tethered chains will repel each other, even across an interface and do not entangle. These materials would be expected to have low interfacial adhesion and low shear strength, good characteristics for grafted boundary lubricants.

### **EXPERIMENT**

Drawn, finish-free nylon 6,6 yarns of 78 dtex (70 denier) and 34 filaments were used throughout this study. Poly(dimethyl siloxane) (PDMS) and polyethylene (PE) polymers, each containing reactive species, were grafted to the surface of the varns through the amine end-groups of the nylon. These materials are described in Table I. Approximately 2 m of the yarn was wound on a glass ladder, L in Figure 1, and placed in a condenser, W or E, which had been modified by attaching a stopcock to the bottom of the condenser. These condensers were heated by hot water, W, or electrically, E. Test lubricants were dissolved in appropriate solvents, cyclohexane for the PDMS oils and refluxing toluene for the PE samples, at concentrations of 1-3% by weight. These solutions were added to the condenser and heated. A water cooled condenser, C, was attached to the top to

Sample	Source	$M_N$	Graft Site	Sites per Molecule	$\eta @ 23^{\circ}C (cP)$
1,2-Epoxy hexane	Aldrich	100	Epoxy	1	
1,2-Epoxy dodecane	Aldrich	184	Epoxy	1	
BY 16-845 (PDMS)	Dow-Corning	1353	Epoxy	1	191
X2 8558 (PDMS)	Dow-Corning	1600	Carboxyl	20	109
Q2 7119 (PDMS)	Dow-Corning	7745	Carboxyl	3	268
SF 8421 (PDMS)	Dow-Corning	26,132	Epoxy	4	3565
BY 16-839 (PDMS)	Dow-Corning	42,325	Epoxy	11	5550
SF 8413 (PDMS)	Dow-Corning	70,421	Epoxy	20	18760
Fusabond E MB-100D (PE)	DuPont Canada	15,032	Maleic anhydride	1	
Fusabond E MB-110D (PE)	DuPont Canada	10,674	Maleic anhydride	1	
Fusabond E MB-330D (PE)	DuPont Canada	9,512	Maleic anhydride	1	

 Table I
 Description of Test Materials

maintain reflux. The solution was allowed to reflux for at least one half hour and up to 1 h. The solution was drained, and fresh solvent added to



**Figure 1** Yarn minireactor. Yarn is wrapped on glass ladder (L) and placed in a water-heated condenser (W) or in electrically heated condenser (E). Condensers (C) are cooled with tap water to maintain reflux.

extract any unbound lubricant. The solution was drained, and fresh solvent added to extract any unbound lubricant. The solvent was again allowed to reflux for an additional half hour, replaced by fresh solvent, and again refluxed for a half hour. Finally, the solvent was drained; the glass ladder and the sample were removed from the reactor and rinsed with room temperature solvent. This treatment was found adequate to remove nongrafted PDMS and PE. The fibers were air dried before further testing. Single filaments were removed from these yarns and were tested on a single filament friction tester as described below.

Single filament frictions were measured on a single filament frictometer made by Rame-Hart, Inc. and is similar in design to that used by Briscoe and Kremnitzer.<sup>5</sup> This crossed cylinder (fiber) geometry is equivalent to the classical Hertzian contact for a pin-on-disk geometry. Data collection and speed changes were automated in our laboratory. A schematic is shown in Figure 2. A 0.6 g test weight, W, is attached to one end of a single fiber extracted from the treated yarn bundle. The other end of the fiber is hung on a Mettler<sup>®</sup> AE 163 analytical balance with the RS232 Serial Communications option installed. A second fiber from the same yarn bundle is mounted horizontally in a metal bow, and the bow is mounted on a stage. The bow assembly is then moved vertically at various rates via a Compumotor<sup>®</sup> drive. Speeds of 1.27, 10.16, and 81.28  $\mu$ m/s were used in all tests. The fibers were conditioned to 65% relative humidity and 21°C overnight and tested under these conditions. The angle,  $\theta$ , was adjusted to 2, 4, 6, and 8°, and the horizontal fiber was moved at each of the above speeds in both directions. The friction coefficient was determined according to



Figure 2 Single filament friction tester.

$$\mu = \frac{|W - W_a|}{W \tan \theta} \tag{5}$$

where  $W_a$  is the apparent weight measured by the balance as the horizontal fiber X is moving. At least three fibers for each sample were tested, and the results of all specimens of each sample, both directions, all angles, and all speeds were averaged. Thus, the results are averaged over more than 72 tests per sample.

Static friction coefficients  $\mu_s$  were measured on all samples using eq. (5). The static friction coefficient was determined from the maximum load when the cross fiber is moving down and from the minimum load when the cross fiber is moving up whenever stick/slip transitions were observed. This assumes that the fibers are not moving relative to each other up to this load and that they finally break loose from each other and start sliding, hence, static friction. In some cases, no stick/slip transitions were observed. In these cases, the average load over 10 min was used to determine  $\mu_s$ .

Viscosities of the silicone oils, as measured with a Brookfield viscometer at 23°C and at 4–5 speeds, are also given in Table I. Since the measured viscosities were essentially identical at all speeds, they were averaged.

The molecular weights of both the Fusabond<sup>®</sup> samples and for nylon were determined by size exclusion chromatography (SEC) and are shown in Table II. Dow-Corning provided the molecular weights of the silicone fluids (Table I).

Finally, the coverage of the substrate by the grafted PDMS was determined from electron spectroscopy for chemical analysis (ESCA) measurements on nylon 6,6 films performed at three different take-off angles. (ESCA on fibers was found to give poor results due to their highly curved surfaces.) These films were produced by immersing strips of nylon 6,6 films in the appropriate PDMS oil and heating the oil to 120°C for 1.5 h. The film was chosen to have similar molecular weight to that of the fibers. Excess oil was wiped off, and the film samples were individually extracted using Soxhelet extraction with cyclohexane. They were extracted for more than 6 h using a cycle time of about 20 min. The solvent was changed after the first three samples; the remaining four used a second batch of solvent. Both sets of samples were recleaned by sequential 5-min ultrasonic washes in water, ethanol, and Freon<sup>®</sup> F113 immediately before being placed in a PhI LS5600 ESCA system. The atomic fractions of all surface species were measured at 15, 30, and 90° take-off angles.

## **RESULTS AND DISCUSSION**

As shown in Figure 3, the friction coefficient does not increase as the viscosity of the PDMS oil increases, as would be the case for hydrodynamic friction. As mentioned earlier, grafting of a hydrodynamic lubricant to the polymer surface should prevent it from acting as a hydrodynamic lubri-

 Table II
 Molecular Weights of Nylon 6,6 and Fusabond

Sample	$M_N$	$M_W$	$M_V$	$M_Z$	$M_{Z+1}$
Nylon 6,6		33,800		51,600	
Fusabond E MB-100D	15,000	108,000	87,200	422,000	975,000
Fusabond E MB-110D	10,700	54,200	45,200	190,000	498,000
Fusabond E MB-330D	9,510	44,700	37,100	177,000	515,000



**Figure 3** Static friction coefficient for PDMS grafted nylon 6,6 fibers versus viscosity of PDMS oil viscosity.

cant since it is no longer able to flow freely, in agreement with the current results.

The static friction coefficients are shown in Figure 4 for PDMS and Figure 5 for PE versus their respective  $M_N$  values. Both curves show a similar trend, namely,  $\mu$  decreases with increasing  $M_N$ , then jumps to a higher value at high  $M_N$ .

Boundary friction is believed to be due to adhesion between asperities on the surfaces of two bodies. Boundary lubricants are believed to function by providing a low shear strength layer that keeps these asperities apart. As the thickness of the lubricant increases, fewer and fewer of the asperities come into contact, and, hence, the friction is reduced. To test this mechanism, ESCA, also known as X-ray photoelectron spectroscopy (XPS), was used to determine the thickness of the grafted PDMS oil layer. The results are shown in Figure 6.

The intensity of the ESCA spectral peaks is proportional to the amount of the atomic type



**Figure 5** Static friction coefficient for PE grafted nylon 6,6 fibers versus  $M_N$  of PE.

being analyzed and the take-off angle for collecting the electrons according to

$$I \propto A e^{-t/\delta \sin \theta} \tag{6}$$

where A is proportional to the amount of the atomic type, t is the distance from the surface of the film,  $\delta$  is a characteristic escape depth of the electron for the material, and  $\theta$  is the take-off angle measured from the plane of the film. Since PDMS contains Si atoms, but nylon 6,6 does not, the intensity of this peak as a function of  $\theta$  can be used to determine  $t/\delta$ . Thus the friction coefficient and the thickness of the lubricant layer are strongly correlated. However, it would seem that the higher the molecular weight of the lubricant, the thicker the lubricant layer should be. Comparing Figures 4 and 6, it is clear that the highest molecular weight oil does not give the thickest



**Figure 4** Static friction coefficient for PDMS grafted nylon 6,6 fibers versus  $M_N$  of PDMS oils.



**Figure 6** The static friction coefficient versus thickness of grafted PDMS oil on nylon 6,6 film. The abscissa is the thickness *t* divided by the electron escape depth  $\delta$ .

coating and, hence, does not give the lowest friction. A different explanation is needed.

In searching for an alternative explanation, it is instructive to consider the grafting chemistry. The PDMS oils and the PE polymers can react only to the amine ends of nylon 6,6. Approximately one-third of the end groups are amine ends, and there are only 2 mol of ends for every 20,000 g of polymer. The density of nylon 6,6 is  $1.14 \text{ g/cm}^3$ . Using these numbers and assuming that an amine end must be within 1 nm of the surface to react, there are only 0.011 amine ends/ nm<sup>2</sup>; i.e., the surface area per graft site is approximately 90 nm<sup>2</sup>. Clearly, the smaller molecules cannot completely cover the surface.

The adhesion model for boundary lubrication has not previously been used to describe such a surface. However, it is easily extended to two or more different surface materials. Comparing the load ranges used by Briscoe and Kremnitzer,<sup>5</sup> 0-50 mN, to those used in the current study, 200-800 mN, the current tests should be well within the plastically deformed region, eq. (4) should apply for a clean nylon 6,6 surface, and  $\mu$ should be independent of the apparent contact area. However, if two materials with different shear strengths are present on the surface, then the frictional force and the friction coefficient would be expected to take the following forms.

$$F = \tau_1 A_1 + \tau_2 A_2 \tag{7}$$

$$\mu = \frac{1}{P_{y}}(\tau_{1}\phi_{1} + \tau_{2}\phi_{2}) = \mu_{1}\phi_{1} + \mu_{2}\phi_{2}$$
$$= \mu_{1} - (\mu_{1} - \mu_{2})\phi_{2} \quad (8)$$

where  $\mu_1$  and  $\mu_2$  are the friction coefficients for materials 1 and 2, respectively, and  $\phi_1$  and  $\phi_2$  are the surface area fractions. If the surface is covered by two materials with  $\mu_1 \neq \mu_2$ , then  $\mu$  should depend only on the relative amounts of the two materials on the surface and their respective friction coefficients.

In the present case, the surface of the fiber should consist of either nylon 6,6 or the grafted PDMS or PE macromolecules. The surface area covered by a single macromolecule should be proportional to  $\pi R_G^2$ , where  $R_G$  is the radius of gyration of the macromolecule and can be estimated according to Flory.<sup>6</sup> The relative area is just this area divided by the average area per graft site, that is, 90 nm<sup>2</sup>/graft site. Thus, the relative area of a lubricant macromolecule is just  $\pi R_G^2/90$  nm<sup>2</sup>. Figure 7 shows  $\mu$  as a function of the ratio



**Figure 7** Friction coefficient versus area per lubricant molecule divided by the area per graft site for PDMS oils: ( $\bullet$ )  $\pi R_G^2/90 \text{ nm}^2$ , that is, the nearest neighbor distance; ( $\bullet$ )  $\pi R_G^2/270 \text{ nm}^2$ , that is, next nearest neighbor distance, for highest molecular weight oil. Line is a linear regression for all oils, except the highest molecular weight one.

 $\pi R_G/90 \text{ nm}^2$ . A linear regression is shown for the PDMS oils excluding the highest molecular weight oil. This corresponds to eq. (8), provided that the volume fraction  $\phi$  is proportional to  $\pi R_G^2/90 \text{ nm}^2$ .

Note that only the highest  $M_N$  sample does not fit this simple model. This can be explained as follows. If the surface molecule is larger than the spacing between graft sites, then a single molecule will graft to more than one site or cover the nearest neighbor sites so that no other lubricant molecule can graft to it. The next available graft site will then be the next nearest neighbor site, which, for a hexagonal close packed array, is just  $\sqrt{3}$  further away, resulting in an effective area  $3 \times$  larger than for the nearest neighbor sites, or 3  $\times$  90 = 270 nm<sup>2</sup>. The rescaled relative area for the highest  $M_N$  is shown in Figure 7. It is seen that this rescaling accounts for the friction coefficient observed when this high  $M_N$  oil is used. A similar trend is seen with the grafted PE polymers, as shown in Figure 8. Although there are not enough different molecular weights of PE to establish a linear relationship between  $\mu$  and the relative surface areas, the existing data can be fit via this simple treatment. Thus, it seems that eq. (8) adequately describes the boundary friction for a polymeric substrate with a surface-grafted polymeric lubricant where  $\phi$  is fractional coverage.

The other term in eq. (8) that is needed is  $(\mu_1 - \mu_2)$  or simply  $\mu_2$ . In the case of a PE lubricant,  $\mu_2$  could be chosen to be equal to that of a PE substrate sliding on a PE substrate. However, it is not at all clear that this is a correct choice since



**Figure 8** Friction coefficient versus area per lubricant molecule divided by the area per graft site for PE lubricants: (•)  $\pi R_G^2/90 \text{ nm}^2$ ; (•)  $\pi R_G^2/270 \text{ nm}^2$ .

the surface morphologies in these two cases may be vastly different. No such choice is available for the PDMS oils since they are liquids at room temperature. In the case of tethered chains, whether pancakes or mushrooms, there should be no chain entanglements across the interface. In fact, the chains on opposite sides of the interface are thought to repel each other. In this case,  $\mu_2$ should be zero since there should be no adhesion across the interface and, hence, no shear strength. This would imply that for a surfacegrafted lubricant with  $\phi = 1$ , the boundary friction coefficient  $\mu = 0!$  Although this seems preposterous, we note that for the PE-coated nylon 6,6,  $\mu \sim 0.1$ , or roughly one-third the value of  $\mu$ for a PE substrate,  $\mu_{\rm PE} = 0.33.^7$  This indicates that  $\mu_2$  for the case of PE must be much less than  $\mu_{\rm PE}$ . Indeed, if  $\mu_2 = 0$ , then all grafted lubricants should lie on the same line given by

$$\mu = \mu_s (1 - \phi) \tag{9}$$

where  $\mu$  is the boundary friction coefficient for the coated substrate,  $\mu_s$  is the boundary friction coefficient of the uncoated substrate, and  $\phi$  is the surface area fraction of the grafted polymeric coating. In Figure 9, the PDMS and PE data are combined, and a single regression is performed on all of the data. This regression fits the data within the experimental error of  $\pm 0.03$  in the friction coefficient.

Although this analysis agrees well with the tethered chain characteristics described above, some caution is needed. Note that the  $R_G$ 's were calculated, not measured; the molecular weights were determined by three different laboratories, one for each polymer type; and the polydispersities are vastly different, about two for nylon 6,6 and PDMS and from 4.7 to 7.2 for PE. It is also not clear whether the analysis using  $M_N$  as in this study or one using  $M_W$  is preferred. Nevertheless, it is intriguing that such a simple analysis can account for the boundary friction data. It appears that eq. (8) must be correct and that the friction is linearly dependent on the fractional surface area. Furthermore, it is plausible that eq. (9) is correct and that it may be possible to obtain  $\mu = 0$  for boundary friction by using tethered chains as lubricants. Future studies are planned to determine the effects of molecular weight distribution and different graft site densities. Other studies will attempt to determine the generality of this analysis.

## **CONCLUSIONS**

It has been shown that it is possible to permanently attach boundary lubricants to fiber surfaces. By carefully matching the molecular size of the lubricants to the density of graft sites available on the surface of the underlying fiber, reductions in the friction of over  $6 \times$  have been achieved. The friction coefficient for boundary friction for tethered chains has been modeled with a two-component surface model in which the friction coefficient is proportional to 1 minus the fractional surface coverage of lubricant. This model is an extension of the adhesion model of friction. It has been proposed that boundary friction can be eliminated in these materials by ensuring complete coverage of the substrate with grafted chains.

The author thanks K. M. Stika for performing the ESCA tests, and S. Threefoot and R. Fuller for determining the



**Figure 9** Combined data for all lubricants tested: ( $\bullet$ )  $\pi R_G^2/90 \text{ nm}^2$  and ( $\blacktriangle$ )  $\pi R_G^2/270 \text{ nm}^2$  for PDMS oils; and ( $\blacksquare$ )  $\pi R_G^2/90 \text{ nm}^2$  and ( $\blacklozenge$ )  $\pi R_G^2/270 \text{ nm}^2$  for PE lubricants. The line is linear regression for all points.

molecular weight distributions of nylon and polyethylene, respectively. In addition, the author thanks T. J. Proffitt, Jr., for sharing his expertise in fiber friction. Furthermore, M. G. Jones deserves considerable credit for many helpful discussions and encouragement.

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