Boundary Lubricant Film Properties versus Molecular Polarity of Perfluoropolyethers Containing a Pendant Chain

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The thin film properties of some novel branched perfluoropolyether (PFPE) boundary lubricants are investigated as a function of molecular polarity and end-group bonding to the underlying carbon film. The PFPE main chain, comprised of *n*-perfluoroethylene oxide monomer units, is stiffer than the Fomblin Z main chain that is a copolymer of perfluoro-methylene oxide and -ethylene oxide monomer units. Terraced flow and bonding kinetics show decreased lubricant mobility compared to PFPEs based on a Fomblin Z main chain. Lubricant pick-up is reduced for the tetraol adduct due to the larger Hamaker constant and increased intermolecular cohesion.

Keywords: tribology, perfluoropolyether, disk lubricant, surface energy, bonding kinetics

1. Introduction

Recently there is increased interest in utilizing multifunctional or multidentate perfluoropolyether (PFPE) boundary lubricant films on hard-disk drives (HDDs) with a low-flying head, $< \sim 2$ nm [1-3]. Ab initio quantum chemical computations indicate that the pendant chain acts to increase confinement of the PFPE in the direction perpendicular to the disk surface thereby allowing increased mechanical clearance [4]. Tailoring the molecular polarity and the molecular weight of these additionally tethered PFPEs could provide boundary lubricant films that simultaneously satisfy many of the current HDD requirements for a robust head-disk interface. We therefore investigate the thin film properties of some novel boundary lubricants having a pendant chain. The focal point of this study is to identify relevant interfacial properties as a function of the end group chemical structure that could provide both good flyability (lubricant pick-up) and durability (head wear), i.e., a structure-property correlation. This study will show that the end-group polarity of the pendant chain is a significant determinant for balancing flyability and durability.

2. Experimental

The experiments were conducted on glass disks that were sputter-deposited with a cobalt-based magnetic recording layer (CoPtCr) and nominally 30 Å of an amorphous carbon film comprised of 15 at% N. For simplicity, the carbon film is referred to as “CN_x” throughout this work.

The perfluoropolyethers (PFPEs) TA-30, TG-30 and TX-30 are investigated here. Their chemical structures

Fig. 1 Chemical structures of the lubricants

are shown in Fig. 1. Each was fractionated by supercritical fluid extraction (CO₂) to provide a narrow molecular weight distribution. The number average molecular weights were 3000-3300 by NMR (nuclear magnetic resonance). All PFPE films were applied to the carbon surfaces from solvent using a standard dip-coating methodology with PFPE concentrations of ~0.03 g/liter and a typical disk withdrawal rate of several mm/sec.

Specular reflection FTIR (Nicolet Magna Model 560) was used to quantify the thickness of the applied PFPE films. A standard specular reflection adapter (Harrick, New York) was used. The FTIR absorption band maximum for each PFPE was correlated to film thickness by XPS (Phi Quantum 2000 ESCA System) as described previously [5].

Lubricant bonding to the carbon surface was quantified as follows. First, the initial lubricant thickness was measured via specular reflectance FTIR. The disks were then rinsed with 2,3-dihydroperfluoropentane (Vertrel-XF, DuPont) for 1 min to remove any soluble lubricant, and the lubricant thickness was re-measured. The lubricant retained by the disk is defined as the amount "bonded". The bonded fraction is obtained by normalizing to the initial lubricant thickness. This method does not distinguish chemisorbed from physisorbed lubricant.

Terraced flow profiles and lubricant dewetting were obtained by directly imaging the disk surface ellipsometrically (Candela 6120) [6]. The energetics of the lubricant/CNx interface was determined as a function of lubricant film thickness using contact angle goniometry [7]. Hexadecane ($\gamma_1^d \sim \gamma_1 = 27.5$ mJ/m²) and water ($\gamma_1^d = 21.8$ mJ/m², $\gamma_1^p = 51.0$ mJ/m²) were used as the reference liquids for these measurements.

3. Results and Discussion

Fig. 2 (left) shows the dispersive surface energy, γ_s^d , as a function of film thickness for TA-30, TG-30 and

Fig. 2 (left) Dispersive (γ_s^d) and (right) polar (γ_s^p) surface energy as a function of PFPE film thickness

TX-30 on CNx. The γ_s^d decreases monotonically with increasing film thickness in all cases, approaching what is expected to be the bulk dispersive surface energy in the 13-14 mJ/m² range. Quantitatively, the dependence of γ_s^d on the applied lubricant film thickness h , i.e., $\gamma_s^d(h)$, can be described using $\gamma_s^d(h) = \gamma_1^d + \Delta\gamma^d(h)$ where:

$$2\Delta\gamma^d(h) = -\frac{1}{12\pi} \frac{A^*}{(d_o + h)^2} \quad (1)$$

d_o is a constant [8], and A^* is the "effective" Hamaker constant [8]. The d_o values used to fit the dispersive surface energy curves via Eq. 1, $d_o = 2.4 \pm 0.5$ Å, is indicative that the interaction between the PFPE main chain and the underlying carbon film is relatively weak and hence cannot provide significant adhesion. The corresponding A^* are equal to 1.8×10^{-19} J, 3.0×10^{-19} J and 2.2×10^{-19} J for TA-30, TG-30 and TX-30, respectively. The A^* values decrease in the order: TG-30 > TX-30 > TA-30. Thus, TG-30 is expected to show the least lubricant disturbance on the disk surface under a low-flying slider [9].

The corresponding polar surface energy, γ_s^p , as a function of film thickness is also shown in Fig. 2 (right). The distinct oscillations in γ_s^p for TA-30 and TG-30 as a function of film thickness are indicative of molecular layering in the PFPEs induced by the polar interactions with the underlying surface, much as observed previously for Zdols [10]. As shown in the figure, the structuring is propagated through several or more monolayers. The first minimum corresponds to the film thickness at which the surface becomes saturated with lubricant, i.e., the monolayer film thickness, which is approximately 19 Å for TA-30 and 21 Å for TG-30. Unfortunately, TX-30 did not exhibit the expected oscillation in γ_s^p here and so the monolayer thickness could not be determined under these conditions. The identical TX-30 disks were subsequently imaged by an optical surface analyzer (OSA) and films greater than 28 Å were observed to have spontaneously dewetted, Fig. 3. The observed dewetting suggests that the droplets used in the contact angle measurements were only probing the first monolayer. Spontaneous dewetting in TA-30 and TG-30 were not observed during the surface energy measurements (Fig. 2).

Fig. 2 shows that γ_s^p decreases as a function of film

Fig. 3 Spontaneous dewetting on TX-30 films observed after the surface energy measurements in Fig. 2 were completed. Film thicknesses are in Angstroms

thickness in the order: TA-30 > TG-30 > TX-30. γ_s^p typically decreases with increasing bonded fraction, discussed in detail below. The lubricant film instability predicted by the surface energy data was experimentally verified for TA-30 films on CNx by ellipsometric imaging above and below the monolayer thickness (the minimum in γ_s^p in Fig. 2). Lubricant dewetting on a disk surface is readily induced by flying a head over the disk surface when the lubricant film thickness exceeds a monolayer. As shown in Fig. 4, TA-30 films having thicknesses less than nominally 20 ± 1 Å are contiguous and display no signs of dewetting. However, when the TA-30 film thickness is increased to above its monolayer, the thermodynamic instability causes the formation of lubricant “droplets” which are represented by the darker spots on the imaged surface. Table 1 summarizes the critical thickness for dewetting as determined by the various methods discussed thus far.

Fig. 4 Dewetting on TA-30 films after head-flying. Film thicknesses are in Angstroms

Table 2 Film dewetting thicknesses in Angstroms for TA-30, TX-30 and TG-30 on CNx

PFPE	γ_s^p (Fig. 2)	OSA Image (Fig. 4)	Terraced Flow (Fig. 5)
TA-30	20	$18.2 \leq h_c \leq 20.3$	18
TX-30	~ 22	-	17
TG-30	20	-	20

Terraced flow profiles for TA-30, TX-30, and TG-30 are shown in Fig. 5. The Poiseuille-like flow is driven by the disjoining pressure gradient [10]. Since this disjoining pressure component favors complete wetting at all film thicknesses, Fig. 2 (left), it accounts for the rapidly spreading front observed in the flow profiles. However, the terracing is a direct manifestation of the polar component of the surface energy gradient, Fig. 2 (right). At film thicknesses that correspond to positive surface energy gradients, the film will be completely wetting and flow will be observed. The first stable flow region is labeled as the “shoulder” in Fig. 5. The film thickness at the top of the shoulder is correlated directly with the film thickness at which the surface energy gradient becomes negative, or equivalently, just beyond the first minimum in the surface energy. The absence of flow into this unstable film thickness regime appears in the spreading profile as the “vertical step”.

Fig. 5 Terraced flow for TA-30, TX-30 and TG-30 as a function of time in days (inset legend) under ambient conditions

Fig. 5 shows that the flow rate decreases in the order: TA-30 > TX-30 > TG-30. The flow can be described by an “effective” diffusion coefficient that scales with time as [10]:

$$R(t) = (D_{\text{eff}} t)^{1/2} \quad (2)$$

$R(t)$ is the distance travelled by the film in time t and D_{eff} is the effective diffusion constant. D_{eff} is film thickness-dependent, i.e., $D_{\text{eff}} = -mh(d\Pi/dh)$, where m is the mobility and h is the film thickness [10]. Since all of the films used here are of comparable film thickness, 37 ± 3 Å, the results show that the flow rate decreases with increasing PFPE molecular polarity (TG-30) and/or increasing bonded fraction (TX-30). Table 2 summarizes the D_{eff} values obtained from the flow data. A comparison of the terraced flow kinetics to Zdol, Z-Tetraol-GT, D-4OH, and ZTMD at similar molecular weights allows the isolation of both end group and main chain effects. The kinetic plots derived from these data, Fig. 6, clearly shows the decreased mobility of the current set of PFPE lubricants with increased molecular polarity (TG-30) and higher bonding rates (TX-30). The higher mobility of both Zdol (vs. TA-30) and Z-Tetraol

Table 1 Terraced flow effective diffusion coefficients

Lubricant	TA-30	TX-30	TG-30
D (m ² /sec)	5.7×10^{-12}	4.5×10^{-13}	1.6×10^{-13}

(vs. TG-30) is attributed to the increased segmental mobility provided by adjacent $-\text{CF}_2\text{O}-$ monomer units that are present in the Fombin Z main chain. These aspects are well-understood in terms of the barriers to internal rotation and chain confinement effects due to the pendant branch and are therefore fully anticipated results [3,4]. We also note that the monolayer thickness derived from the terraced flow for TA-30 reported here, $\sim 18 \text{ \AA}$, is substantially larger than reported by Tagawa et al., $\sim 9 \text{ \AA}$ [11]. A reason for this difference is not yet understood.

Fig. 6 Terraced flow for some PFPEs as a function of time under ambient conditions. Initial film thicknesses are all near $37 \pm 3 \text{ \AA}$

Fig. 7 (Left) Ambient bonding kinetics versus time; (Right) Changes in the bonded fraction as a function of time under ambient conditions for initially UV-bonded TA-30 films: 40% (blue); 70% (green); 90% (red); and no UV (black)

The segmental mobility of the boundary lubricant films is additionally quantified by bonding kinetics. The bonding kinetics for $11 \text{ \AA}$ TA-30, TX-30 and TG-30 on CNx are compared at 20°C and 50 % RH in Fig. 7

(left). Upon application of the lubricant films to the carbon surface, a fraction of the lubricant bonds at room temperature within the time required to allow for solvent evaporation and to conduct the initial thickness measurements. The initial bonded fraction is observed to increase with increasing number of OH groups (TG-30). All of the PFPEs exhibit increasing bonding to the CNx surface with increasing time, reaching an asymptotic bonded fraction of approximately 0.75 for TA-30, 0.80 for TG-30, and 0.90 for TX-30. TX-30 shows the highest bonding due to the increased mobility of the TX end group [12]. Verification of the equilibrium nature of the bonded fraction under ambient conditions for TA-30 is provided in Fig. 7 (right). Initial bonded fractions either below or above the asymptotic bonded fraction is observed to re-converge to the asymptotic value. The displacement of some fraction of the bonded lubricant on carbon surfaces has been attributed to environmental water. In the absence of water, no “debonding” is observed [13].

Some of the basic properties that are quantified here for TA-30, TX-30 and TG-30 can be used to indicate their expected tribological behavior. For example, the larger Hamaker constant for TG-30 compared to TA-30 and TX-30 suggests an increased resistance to lubricant pick-up by a low-flying slider. Fig. 8 indicates a significantly lower lubricant transfer rate to the low-flying slider in an accelerated component test used to quantify lubricant transfer. Intermolecular cohesion appears to be a significant determinant, as discussed previously for polar PFPE lubricants [9].

Fig. 8 Component test lube pick-up versus A^* . The slider flies at 8-9 nm with pole-tip clearance of 0.8 nm at 55°C . The disk is swept for 22 hr from i.d. to o.d. at 0.2 Hz. Inset images are representative showing slider lube pick-up (lighter area, top right corner). The lube pick-up area derives from the averages of 4 measurements per PFPE type

4. Conclusion

TA-30, TX-30 and TG-30 are novel lubricants based on the addition of a perfluoropolyether pendant branch to the perfluoropolyether main chain. Some boundary lubricant film properties relevant to HDDs were quantified on the basis of surface energy and mobility measurements. Lubricant pick-up was an area of definitive improvement using a polar pendant branch.

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