Article

The Effect of UV Irradiation on the Z-Tetraol Boundary Lubricant

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The UV irradiation of Z-Tetraol films on amorphous nitrogenated carbon surfaces was investigated. COF₂ evolution, captured in the gas phase, decreased with increasing number of OH end groups in the order: Z > Zdol > Z-Tetraol after UV irradiation. Both UV irradiation and annealing on 11 Å Z-Tetraol films produced virtually identical interfacial properties – surface energy as a function of bonded fraction. The UV-irradiated 11 Å Z-Tetraol films also demonstrated equilibrium behavior exhibiting bonding or debonding to the asymptotic 80% bonded level under ambient conditions. UV-irradiated thick films of Z-Tetraol (~ 20-40 Å) exhibited film properties that differed from the non-irradiated films. The oscillations in the polar component of the surface energy, normally observed in Z-Tetraol films and attributed to amphiphilic structuring, disappeared. Terraced flow exhibited a rapidly moving front below ~ 10 Å compared to the remainder of the irradiated film. Both observations were tentatively attributed to loss of OH functionality. The latter was verified by chemical extraction and subsequent analyses by NMR and TGA.

Keywords: perfluoropolyether, disk lubricant, UV irradiation, surface energy, bonding kinetics

1. Introduction

A major challenge facing boundary lubrication in today's hard-disk drives (HDDs) originates from the nanoscale mechanical clearance between the slider and the disk surfaces. While the slider body flies approximately 8-9 nm above the disk surface, the clearance between the read-write element of the slider and the disk surface is actually as little as several nm due to pole tip protrusion during read/write operations. At these small spacings, the combined effects of the air shear stress, the air bearing pressure, and the van der Waals attractive forces operating between the slider and the disk surfaces can cause lubricant disturbance on the disk surface [1-3]. Isolated and/or periodic lubricant moguls and ripples that form on the disk surface can increase the probability of lubricant transfer to the slider leading to flying instability. Unwanted fly height modulations can hinder read-write functions and increase the probability of intermittent head-disk contacts resulting in a degradation of drive performance. Consequently perfluoropolyether (PFPE) films with increased adhesion to the underlying carbon surface are increasingly being utilized. This is presently achieved in several ways. In the chemical approach, the lubricant

itself can be modified to provide a stiffer main chain and/or increase the molecular polarity to provide a boundary lubricant film that is more resistant to the low-flying slider [4-6]. Alternatively, the annealing or the UV irradiation of the boundary lubricant films can increase their adhesion to the underlying carbon surface [7]. UV curing is now widely used in the HDD industry; however, the detailed understanding of the effects of UV irradiation on the boundary lubrication properties of PFPEs is only now becoming better understood [8-11]. The UV irradiation (185, 172 nm, N₂) of the piperonyl-functionalized (AM3001) perfluoropolyether (PFPE) and the non-functionalized Fomblin Z showed improved corrosion protection which was attributed to increased lubricant bonding and decreased surface energy [12]. The UV irradiation (185 nm, air) of AM3001 decreased both the dispersive and polar surface energies suggesting improved surface coverage [13]. Loss of structure (oscillation) in the polar surface energy as a function of film thickness was attributed to the increased polar interactions between the PFPE and the underlying carbon film. UV irradiation of Z-Tetraol (185 nm, N₂) caused increased bonding and photodissociation [14]. Short-term UV irradiation caused a decrease in the polar component of the surface energy, but little or no

changes in the dispersive surface energy.

In this report, we investigate the effects of UV irradiation (185 nm, 172 nm, N₂) on the thin film properties of the perfluoropolyether Z-Tetraol. We systematically compare as-deposited, annealed and UV-cured Z-Tetraol to quantify possible similarities and differences in the resultant interfacial properties of the boundary lubricant film. Thus lubricant bonding, surface energy, dewetting, and film mobility are directly compared. Thicker films (50 Å) are employed to extract information on chemical changes induced by the annealing and UV processes. COF₂ yields as a function of the number of OH end groups provide a systematic approach to obtain further insight into the photochemical quenching of UV-irradiated PFPEs by the hydroxyl end groups. The decreasing COF₂ yield with increasing number of OH end groups indicates a strong preference for UV chemistry to initiate on the hydroxyl end groups. Based on these data we conclude that the UV chemistry of PFPEs may not be ubiquitous but is instead dependent considerably on the end groups accompanying the PFPE main chain.

2. Experimental

The substrates used in these studies were 95 mm diameter AlMg disks of nominally ≤ 2 Å RMS roughness as measured by a Dimension 5000 AFM with a standard AFM tip used in the tapping mode. The typical scan size for these measurements was $5 \mu\text{m} \times 5 \mu\text{m}$ with a scan rate of 0.5 Hz and 256 lines of resolution. Atop the substrates were sputter-deposited a cobalt-based magnetic recording layer (CoPtCr) and 40 Å of a dual-layered amorphous carbon film comprised of a CVD bottom layer and a sputter-deposited CN_x top layer. The carbon film is comprised nominally of 15 at% N. For simplicity, this dual-layered carbon film is referred to as "CN_x" throughout this work.

Fomblin Z02, Zdol-2000 and Z-Tetraol-GT 2000 were obtained from Solvay-Solexis. Both Z02 and Zdol-2000 were fractionated by supercritical fluid extraction while Z-Tetraol-GT was used directly as received. The number average molecular weights (M_n) as determined by NMR (nuclear magnetic resonance) were 1650, 1600 and 2120 for Z, Zdol, and Z-Tetraol, respectively. The Z-Tetraol films were applied to carbon surfaces from solvent (HFE-7100) using a standard dip-coating methodology, with a typical concentration of 0.1 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 perfluoropolyether films. A standard specular reflection adapter (Harrick, New York) was used to measure the PFPE film on the disk. The FTIR absorption band maximum ($\sim 1280 \text{ cm}^{-1}$) for each unique PFPE was correlated to film thickness by XPS (Phi Quantum 2000 ESCA System) using a takeoff angle of 45° and an electron mean free path of 25 Å [15].

The UV irradiation on all Z-Tetraol thin films was accomplished using a Sen Lights (Japan) low pressure Hg vapor lamp (185, 254 nm) under nitrogen (≤ 50 ppm O₂) at nominally 20°C. The incident power at 185 nm was $4 \pm 2 \text{ mW/cm}^2$, as measured with a Hamamatsu power meter using a model C8026 controller and a H8025-185 detector (Bridgewater, NJ). The UV irradiation of Z, Zdol and Z-Tetraol liquid films for the gas phase infrared experiments (Figs. 3, 4 only) was accomplished using the Xeradex xenon excimer lamp system (172 nm under nitrogen, ≤ 50 ppm O₂) from Osram Sylvania Inc., (Danvers, MA). The incident UV power at 172 nm after transmission through the gas cell quartz window was 2.7 mW/cm^2 , as measured with a Hamamatsu Photonics UV power meter using a model C8026 controller and the H8025-172 detector (Bridgewater, NJ).

Throughout the following, we refer to the PFPE films on the disk surface as either being "bonded" or "mobile". To clarify our definition of these terms, we briefly describe the methodology by which these quantities are determined. Following film deposition, the initial film thickness is measured via specular reflectance FTIR. The disks are then washed in 2,3-dihydro-perfluoropentane (Vertrel-XF, DuPont) to remove any soluble PFPE, and the film thickness is remeasured. The quantity retained by the disk is defined to be the amount "bonded", while the portion removed by the solvent wash process is defined as the "mobile" film. For bonded perfluoropolyether, our experiments do not distinguish between physi- and chemi-sorption.

Information on the stability and dewetting of Z-Tetraol films was obtained by directly imaging the disk surface ellipsometrically for lubricant droplets, by ellipsometric imaging of terraced flow, and by contact angle goniometry. For ellipsometric imaging, an optical surface analyzer (OSA) using both s- and p-polarized light was employed [16]. The Q polarized wave (phase contrast signal between the p- and s-polarized light) provided the highest sensitivity to changes in the lubricant film. Lubricant dewetting was induced by flying a slider over the disk surface as a function of the lubricant film thickness. When the lubricant film thickness exceeded a critical value, i.e., the critical dewetting thickness, lubricant droplets could be observed by OSA.

The energetics of the lubricant/CN_x interface was determined as a function of lubricant thickness using contact angle goniometry. Thus, the surface energy for

the various PFPE films deposited on the CNx surfaces was determined as a function of lubricant film thickness from contact angle measurements. Hexadecane ($\gamma_l^d \sim \gamma_l = 27.5 \text{ mJ/m}^2$) and water ($\gamma_l^d = 21.8 \text{ mJ/m}^2$, $\gamma_l^p = 51.0 \text{ mJ/m}^2$) were used as the reference liquids for these measurements. In brief, the contact angle, θ , made between a liquid and a solid surface is related to the free energy of the surface, γ_s , via Young's equation:

$$\gamma_l \cos \theta = \gamma_s - \gamma_{sl} \quad (1)$$

where γ_l is the surface energy (tension) of the reference liquid, and γ_{sl} is the solid-liquid interfacial energy. The dispersive component of the surface energy is determined from contact angle measurements using reference liquids capable of interacting with the surface via dispersive forces only (i.e., hexadecane). In this case, the solid-liquid interfacial energy, γ_{sl} , is given by [17]:

$$\gamma_{sl}^d = \gamma_s^d + \gamma_l^d - 2\sqrt{\gamma_s^d \gamma_l^d} \quad (2)$$

The dispersive component of the surface energy is then obtained by the substitution of eq. (2) into eq. (1),

$$\gamma_s^d = \frac{\gamma_l^d (1 + \cos \theta)^2}{4} \quad (3)$$

When the reference liquid is capable of interacting with the surface via both dispersive and polar forces, the interfacial energy can be approximated by [18]:

$$\gamma_{sl} = \gamma_s + \gamma_l - 2\sqrt{\gamma_s^d \gamma_l^d} - 2\sqrt{\gamma_s^p \gamma_l^p} \quad (4)$$

Substitution into Young's equation readily provides an expression for the polar component of the surface energy. The total surface energy is then the sum of the dispersive and polar components.

The vacuum UV spectra on neat 100 μm thick PFPE films (Fig. 3) were taken on a Model U-7000 Vacuum UV (140-300 nm) Spectrophotometer (Hitachi High Technologies Corp.). The PFPE was placed in a liquid cell of MgF_2 windows separated by a 100 μm thick spacer.

The NMR spectra were obtained on a Bruker Avance 500 MHz spectrometer equipped with a 1H/19F cryoprobe. Disk extracts were obtained via one minute, immersion extraction with Vertrel-XF solvent. The extracts from multiple disks were consolidated into a single sample, concentrated into 40 μL of a 5:1 mixture of perfluorobenzene and d4-methanol and introduced into an NMR capillary tube.

The TGA data was obtained on a TA Instruments Q5000 thermogravimetric analyzer. The NMR samples were introduced into platinum TGA pans, the NMR solvent allowed to evaporate under nitrogen gas flow (40 mL/min) leaving the mobile lube extract. The TGA data was obtained under N_2 gas flow (40 mL/min) in "HiRes" mode.

3. Results and discussion

3.1. UV irradiation of thin Z-Tetraol films

The effect of UV irradiation and of annealing on the

bonding of 11 $\text{\AA}$ Z-Tetraol films to the underlying carbon film is first compared. For annealing, we chose 90°C to provide relatively efficient bonding kinetics and simultaneously minimize any film thickness loss due to evaporation. As shown in Fig. 1, both processes increase the bonding of Z-Tetraol to the underlying carbon film, resulting in an asymptotic bonded fraction of $\geq \sim 0.9$, considerably greater than can be attained on the basis of diffusive self-stirring under ambient conditions [19]. As expected, the bonding rate is significantly larger for the UV process compared to annealing. Fig. 1 indicates increasing film thickness loss with increasing UV exposure time. This may originate from loss of molecular polarity and/or disk heating with longer UV exposures. The loss of molecular polarity is discussed in Section 3.5. A few tenths of an Angstrom loss in film thickness on the annealed Z-Tetraol (Fig. 1) is also indicated. This may be consistent with very limited evaporative loss expected at this temperature (see Fig. 14) or possibly within the expected $\pm 2\%$ measurement error in FTIR.

Surface energy measurements on PFPE films can provide direct information on the interaction forces that are operative at an interface. The dispersive surface energy per unit area, γ_s^d , represents the van der Waals

Fig. 1 The (top) UV irradiation and (bottom) annealing of 11 $\text{\AA}$ Z-Tetraol films on CNx as a function of time. The UV irradiation used a 185 nm lamp with an incident power of 4 mW/cm^2 . The annealing was conducted at 90°C and 1% relative humidity.

dispersion forces acting between the perfluorinated ether backbone and the carbon surface while the polar surface energy, γ_s^p , represents the polar interactions acting between the PFPE end groups (i.e., hydroxyl) and the polar functional moieties on the carbon surface. The changes in γ_s^d and γ_s^p as a function of bonded fraction for annealed and UV-irradiated Z-Tetraol (11 Å) are compared in Fig. 2. The surface energy dependence of both γ_s^d and γ_s^p on the bonded fraction is identical for both UV irradiation and annealing, suggesting both processes act on the PFPE films in a surprisingly similar manner. In both cases, a modest increase in γ_s^d is observed as a function of bonded fraction. Based on the data already provided in Fig. 1, we conclude that the increase in γ_s^d as a function of bonded fraction originates from the film thickness loss induced by the UV and annealing processes (see also Fig. 7). This observation cautions against making conclusions on any film thickness-dependent interfacial properties that are measured after UV irradiation based upon as-deposited PFPE film thicknesses.

As regards the polar surface energy, Fig. 2, the decrease in γ_s^p as a function of bonded fraction is

Fig. 2 The changes in the (top) dispersive, γ_s^d , and (bottom) polar, γ_s^p , surface energies as a function of bonded fraction for 11 Å Z-Tetraol films on CNx. The Z-Tetraol films were separately exposed to UV irradiation (185 nm, 4 mW/cm²) and to annealing (90°C). The Z-Tetraol film thicknesses were quantified after the UV and annealing treatments.

Fig. 3 The vacuum UV spectra for 100 μm PFPE films of Z, Zdol and Z-Tetraol.

attributed to the bonding of Z-Tetraol to the underlying carbon film [3]. The hydroxyl end groups of Z-Tetraol interact with the polar sites on the carbon surface resulting in a decrease in γ_s^p . Since both sets of data fall on an identical curve, UV irradiation and annealing both act directly on the tetraol adduct. This is corroborated by the observations that UV-irradiated Fomblin Z bonds to the underlying carbon film [9] while annealed Fomblin Z does not [20]. Therefore no measurable changes in γ_s^p should be expected in the absence of hydroxyl end groups.

The preferential absorption of UV light by the tetraol adduct is further illustrated in Fig. 3 comparing the vacuum UV spectra of Fomblin Z, Zdol and Z-Tetraol. These data show increasing UV light absorption near 185 nm with increasing number of hydroxyl end groups. Therefore it is reasonable to assume that the UV chemistry could become increasingly isolated on the tetraol adduct and as a consequence both UV and annealing produce similar thin films while leaving the main chain intact.

Several additional experiments were conducted to directly probe the preferential absorption of UV light by the tetraol adduct. Since the UV irradiation of non-functionalized Fomblin Z produces COF₂ [9], its yield should decrease with increasing molecular polarity (OH groups): Z > Zdol > Z-Tetraol. Second, the UV irradiation of chemical mixtures of Z-Tetraol and Z should produce less COF₂ with increasing Z-Tetraol concentration. In both sets of experiments, the PFPEs were irradiated in a gas cell that allowed both UV and IR transmission for irradiation and detection, respectively [9]. A schematic of the gas cell is shown in the inset of Figure 4. Thus a small quantity of neat PFPE, typically 50 - 100 μm thick (0.2 g), was coated on a quartz window at the bottom of the UV/IR gas cell. Thicker films were used here to minimize possible surface-induced catalytic effects during the UV irradiation. The cell was purged with nitrogen (approx. 50 ppm O₂) and isolated by gas valves. Transmission IR spectra were taken through the NaCl windows while the UV irradiation was done through the quartz windows.

Referring first to Fig. 4, COF_2 was readily detected in the gas phase after the UV irradiation of non-functionalized Z. The COF_2 originates from main chain scission [9]. The yield of COF_2 clearly decreases with increasing molecular polarity (compare identical 7 min UV irradiation) in the order: $\text{Z} > \text{Zdol} > \text{Z-Tetraol}$. Even when Z-Tetraol is UV-irradiated for a significantly longer 30 min, no COF_2 is detected in the gas phase. Fig. 5 shows the analogous effect of decreased COF_2 evolution by the addition of Z-Tetraol into Z followed by UV-irradiation. These data therefore highlight the complicated nature of the UV photochemistry of PFPEs which can preferentially occur either on the main chain or the end group or both, depending upon the UV or VUV absorption characteristics of the pendant functionality.

Fig. 4 The gas-phase infrared spectra of Z, Zdol and Z-Tetraol after UV irradiation using a 172 nm UV lamp at an incident power of 2.7 mW/cm². The exposure times are specified in the figure.

Fig. 5 The gas-phase infrared spectra of Z and a mixture of Z and Z-Tetraol after UV irradiation using a 172 nm UV lamp at an incident power of 2.7 mW/cm² for 7 minutes.

The equilibrium nature of the bonding and surface properties of UV-irradiated Z-Tetraol is next established. Both the changes in the bonded fraction and polar surface energy as a function of time after UV irradiation are shown in Fig. 6 (left) and (right), respectively. Z-Tetraol exhibits the characteristic fractal bonding kinetics reaching an asymptotic bonded fraction of approximately 0.8 under ambient conditions (20°C, 50% RH) [19]. When the bonding kinetics of UV-irradiated Z-Tetraol is monitored under identical conditions, the bonded fraction converges to the same asymptotic value of ~ 0.8 regardless of the initial UV bonded fraction. The polar surface energy, being kinetically correlated to the PFPE bonding, exhibits a similar result, Fig. 6 (right). Thus, depending upon storage conditions, the bonded fraction of UV-irradiated PFPEs can change with time. Thus the characterization of any interfacial property that depends on the bonded fraction must be carried out at time-of-test for meaningful conclusions to be made. The “debonding” or displacement of some fraction of the bonded lubricant film on carbon surfaces has been attributed to environmental water. In the absence of water, no debonding is observed [21].

Fig. 6 The ambient (left) bonding kinetics and (right) changes in the polar surface energy of 11 Å Z-Tetraol films on CN_x as a function of time after UV irradiation (185 nm lamp, incident power of 4 mW/cm²).

3.2. Surface energy versus film thickness

For PFPE lubricants terminated with functional end-groups, the lubricant film forms a layered structure due to intermolecular interactions between the polar sites on the carbon surface and the PFPE end groups. This surface-induced ordering produces oscillations in the polar component of the surface energy (γ_s^p) as a function of film thickness. In order to allow for the oscillations in γ_s^p to develop, sufficient lubricant bonding to the underlying carbon film is necessary. Therefore, these measurements were made approximately six weeks after lubricant film application. During this storage time, the disks were sealed in a cassette and stored in partial vacuum (400 mbar) to minimize contamination adsorption from the ambient.

Fig. 7 shows the dispersive surface energy (γ_s^d) as a function of film thickness for Z-Tetraol (top) and UV-irradiated Z-Tetraol (bottom) 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. Quantitatively, the dependence of γ_s^d on the applied lubricant film thickness h , i.e., $\gamma_s^d(h)$, can be described using $\gamma_s^d(h) = \gamma_l^d + \Delta\gamma^d(h)$ where:

$$2\Delta\gamma^d(h) = \frac{1}{12\pi} \frac{A^*}{(d_o + h)^2} \quad (5)$$

d_o is a constant and A^* is the “effective” Hamaker constant [22]. The d_o values used to fit the dispersive surface energy curve via Eq. (5), $d_o = 2.5 \text{ \AA}$, 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 fits to the experimental dispersive surface energy data using these d_o values provide an A^* equal to $1.9 \times 10^{-19} \text{ J}$ for

Fig. 7 The changes in the dispersive (γ_s^d) surface energy as a function of Z-Tetraol film thickness on CNx without UV irradiation (top) and with UV irradiation (bottom). The UV irradiation was for 20 sec at all film thicknesses using a 185 nm UV lamp with an incident power of 4 mW/cm^2 . The Z-Tetraol film thicknesses were quantified after the UV irradiation. No dewetting was observed by OSA for the films interrogated here.

Z-Tetraol, and $2.0 \times 10^{-19} \text{ J}$ for UV-cured Z-Tetraol, respectively. They are essentially identical; at least, a strong UV effect on the dispersive surface energy is not indicated.

The corresponding polar surface energy as a function of film thickness is shown in Fig. 8. Here significant differences are observed. First, a distinct oscillation in γ_s^p is observed only for Z-Tetraol without the UV irradiation. As shown in the figure, the structure is propagated through several or more monolayers. For UV-irradiated Z-Tetraol, the anticipated oscillation in γ_s^p has virtually vanished. Second, the magnitude of γ_s^p is significantly smaller for the UV-irradiated samples of film thickness greater than approximately $7 \text{ \AA}$, although this would be expected on the basis of the increased Z-Tetraol bonding (Fig. 6). Below approximately $7 \text{ \AA}$, the γ_s^p is observed to rapidly increase in both cases due to a lack of lubricant film coverage of the underlying carbon film. For Z-Tetraol, the first minimum in γ_s^p

Fig. 8 The changes in the polar (γ_s^p) surface energy as a function of Z-Tetraol film thickness on CNx without UV irradiation (top) and with UV irradiation (bottom). The UV irradiation was for 20 sec at all film thicknesses using a 185 nm UV lamp with an incident power of 4 mW/cm^2 . The Z-Tetraol film thicknesses were quantified after the UV irradiation. The solid lines are polynomial fits of the experimental data. No dewetting was observed by OSA for the films interrogated here.

corresponds to the film thickness at which the surface becomes saturated with lubricant, i.e., the monolayer film thickness, which is approximately 22 Å. For the UV-irradiated Z-Tetraol, the minimum in γ_s^p is no longer observed. The removal of the oscillation in γ_s^p may possibly be due to the reduced number of free hydroxyl groups as a result of UV-induced bonding and/or changes in molecular polarity. Fig. 9 compares the bonded thickness of Z-Tetraol as a function of film thickness with and without UV irradiation, taken immediately after the surface energy measurements (Figs. 7, 8) were made. Higher bonding is assumed to be equivalent to a reduced number of Z-Tetraol free hydroxyls. Within the first monolayer (~ 22 Å), the data in Fig. 9 indicates that the bonded fraction for the UV-irradiated Z-Tetraol is approximately 0.68 compared to 0.36 for the non-irradiated Z-Tetraol. Consequently amphiphilic layering may be more probable for the non-irradiated Z-Tetraol. For the Zdol system, the magnitude of the oscillations was observed to decrease with increasing molecular weight or equivalently, with decreasing number of hydroxyl groups [20]. Similar observations of loss in film structure in the polar surface energy after UV irradiation have been reported by other workers [13,14].

Fig. 9 The bonded thickness for Z-Tetraol as a function of total film thickness on CNx with and without UV irradiation. The UV irradiation was for 20 sec at all film thicknesses using a 185 nm UV lamp with an incident power of 4 mW/cm².

3.3. Film stability

Ellipsometric imaging of UV-irradiated and non-irradiated Z-Tetraol films as a function of CNx film thickness was used to corroborate the surface energy data for critical dewetting. As shown in Fig. 10, Z-Tetraol films having thicknesses $\leq \sim 22$ Å are contiguous and display no signs of dewetting. However, when the Z-Tetraol film thickness is increased to above its monolayer, 23 ± 1 Å, the thermodynamic instability causes the formation of lubricant “droplets” which are readily observed as the darker spots on the imaged

surface. UV-irradiated Z-Tetraol films appear to dewet at a slightly thicker 24 to 30 Å. Table 1 summarizes the critical thickness for dewetting determined by the various methods discussed thus far.

Fig. 10 OSA images identifying the critical thickness for dewetting, h_c , for Z-Tetraol on CNx without UV irradiation (left) and with UV irradiation (right). The UV irradiation was for 20 sec at all film thicknesses using a 185 nm UV lamp with an incident power of 4 mW/cm². The PFPE droplets are identified by the dark spots on the disk surface. The dewetting was induced by flying a head over the disk surfaces as a function of Z-Tetraol film thickness. The films showed no evidence of dewetting prior to the head-flying.

Table 1 Summary of critical dewetting thicknesses (h_c)

Z-Tetraol	γ_s^p	OSA
No UV	21 Å	$22 \leq h_c \leq 24$ Å
UV Irradiated	N/A	$24 \leq h_c \leq 30$ Å

3.4. Terraced flow

Terraced flow profiles for Z-Tetraol films on CNx are shown in Fig. 11. The first stable flow region is labeled as the “shoulder” in Fig. 11 (top). The absence of flow into the unstable film thickness regime appears in the spreading profile as the “vertical step” [23]. The shoulder height for both Z-Tetraol and UV-irradiated Z-Tetraol is the identical 22 Å, suggesting the monolayer and hence the critical dewetting thicknesses are the same. This result apparently contradicts the slightly higher dewetting thickness observed ellipsometrically for UV-irradiated Z-Tetraol in Fig. 10. Since the films used to develop the terraced flow are substantially thicker than those used for the ellipsometric imaging, it is possible that the Z-Tetraol films used in the terraced flow experiments are not significantly different between the UV-irradiated and non-irradiated films. If we use bonded fraction as a

criterion for the extent of the UV irradiation effect imparted to the two sets of samples, the bonded fraction is approximately 0.40 and 0.25 for the irradiated and non-irradiated samples, respectively. The bonded fractions do not appear to be significantly different. Conversely, close scrutiny of the spreading front clearly shows the UV-irradiated Z-Tetraol has developed additional “structure” that flows at a higher rate near 8-9 Å film thickness. A similar thinner, rapidly spreading front was also observed in UV-irradiated AM3001 but was not explained [13]. A higher mobility could be associated with chains having lower molecular weight and/or lower polarity as a result of the UV irradiation. We attribute the enhanced flow primarily to the latter which will be discussed below in more detail.

Fig. 11 Terraced flow for Z-Tetraol on CNx as a function of time without UV irradiation (top) and with UV irradiation (bottom). The UV irradiation was for 20 sec at all film thicknesses using a 185 nm UV lamp with an incident power of 4 mW/cm².

The mobility of UV-irradiated and non-irradiated Z-Tetraol can be described by an “effective” diffusion coefficient that scales with time as [23]:

$$R(t) = (D_{\text{eff}} t)^{1/2} \quad (6)$$

$R(t)$ is the distance travelled by the film in time t and D_{eff} is the effective diffusion constant. D_{eff} fundamentally differs from the conventional diffusion constant used to describe random motion of a polymer

chain in a liquid. Since the flow of molecularly-thin films (typically $\leq \sim 50$ Å) is driven by a pressure gradient, as mentioned above, D_{eff} is usually equated to $D_{\text{eff}} = -mh(d\Pi/dh)$ where m is the mobility and h is the film thickness. D_{eff} is therefore film thickness-dependent [23]. Since all of the films used here are of comparable film thickness, i.e., 39 ± 1 Å, the results show that the flow rate decreases with UV curing. This is vividly summarized in the summary plot of Fig. 12. Table 2 summarizes the D_{eff} values obtained from the flow data. We caution that D_{eff} may be a function of bonded fraction and hence the tabulated values are appropriate for the specified bonded fractions.

Fig. 12 Terraced flow distance versus time for Z-Tetraol on CNx with and without UV irradiation.

Table 2 Terraced flow diffusion coefficients

Lubricant	Z-Tetraol No UV	Z-Tetraol UV
D (m ² /sec)	1.9×10^{-12}	4.2×10^{-13}

3.5. UV irradiation of thicker 50 Å Z-Tetraol films on carbon

The chemical changes induced by the UV irradiation of Z-Tetraol films were probed using thicker 50 Å films to facilitate characterization. Since NMR is used to quantify the changes in the irradiated films, this methodology depends upon solvent extraction of the irradiated film followed by analysis of the extracted material. Table 3 summarizes the UV irradiation conditions and the measurable changes induced on the disk surface. With increasing UV exposure, the bonded fraction increases substantially. This means the solvent-extractable portion for the subsequent NMR analyses also decreases. Since we could not remove the bonded Z-Tetraol from the carbon surface, data interpretation will be limited because we do not know whether or not the analysis on the extractable fraction is representative of the non-extractable fraction. With this cautionary statement, Table 4 summarizes the chemical

changes in the extractable fraction of Z-Tetraol as a function of UV exposure. Surprisingly the NMR data indicates that the Z-Tetraol main chain remains largely unaffected by the UV irradiation. In retrospect, this may be the expected result on the basis of the gas phase IR data that indicated decreased COF₂ evolution (main chain) with increasing OH functionality. On the other hand, NMR reveals that there is significant chemical conversion of the tetraol adduct to the dol adduct indicating loss of molecular polarity. This finding is consistent with the disappearance of the expected oscillation in γ_s^p (Fig. 8) and the more rapidly spreading front in UV-irradiated Z-Tetraol in the ~ 9 Å film thickness range (Fig. 11). The loss in molecular polarity of Z-Tetraol after UV irradiation is shown in the corresponding ¹⁹F NMR spectra of the extracted material, Fig. 13. The end group peaks assigned to the tetraol adduct, -78 and -80 ppm, decrease significantly concomitant with the evolution of the dol adduct, near -81 and -83 ppm, as a function of UV irradiation. For comparison, NMR analysis on annealed Z-Tetraol is

shown in Table 5. Similar to UV-irradiated Z-Tetraol, there is loss of the secondary alcohol and an increase in the dol adduct with both disk aging under ambient storage conditions and annealing. In both cases Z-Tetraol bonding also increases with time. NMR analyses clearly indicate that UV irradiation and annealing affect the tetraol adduct in a similar manner. The loss of the secondary alcohol may simply be a manifestation of the enhanced bonding exhibited by Z-Tetraol compared to Zdol with the primary alcohol.

Table 3 Effect of UV processing on Z-Tetraol extract from disk

UV Process Time (min)	Total Thickness (Å) After UV	Bonded Thickness (Å) After UV
0	52	4
1	51	22
2	50	36

Fig. 13 ¹⁹F NMR of Z-Tetraol as a function of UV irradiation on solvent-extracted films. The UV irradiation was conducted on 50 Å Z-Tetraol films on CNx for 0 (green), 1 (blue) and 2 (red) minutes using a 185 nm UV lamp with an incident power of 4 mW/cm².

Table 4 NMR of solvent-extracted Z-Tetraol from disk as a function of UV exposure time

Z-Tetraol Structural Unit	No UV	1 min UV	2 min UV
$-(CF_2CF_2O)_n-$	12.7	12.5	13.4
$-(CF_2O)_n-$	11.1	11.1	11.8
$-CF_2CH_2OCH_2CH(OH)CH_2OH$	1.26	0.93	0.42
$-CF_2CH_2O-R_x$	0.64	0.69	0.83
$-CH_2OH$	0.10	0.39	0.76
Mn	2400	2370	2470

Table 5 NMR of solvent-extracted Z-Tetraol from disk as a function of ambient aging and annealing at 60°C

Z-Tetraol Structural Unit	No anneal 1 day aged	No anneal 25 days aged	Annealed 60°C
$-(CF_2CF_2O)_n-$	9.5	9.7	9.2
$-(CF_2O)_n-$	9.8	10.1	8.6
$-CF_2CH_2OCH_2CH(OH)CH_2OH$	1.07	0.28	0.30
$-CF_2CH_2O-R_x$	0.89	1.61	1.00
$-CH_2OH$	0.05	0.10	0.70
Mn	2020	2040	1820

To provide further insight into the chemical changes of the tetraol adduct, the extracted lubricant from the carbon surface were also thermogravimetrically analyzed (TGA), Fig. 14. Fig. 14 (top) shows the weight loss of material as a function of temperature. With increasing UV irradiation, the weight loss onset occurs at lower temperatures. Since the NMR data discussed above quantifies no significant main chain degradation, this observation is consistent with the loss primarily of intermolecular hydrogen bonding due to the conversion of the tetraol adduct to the dol adduct (as opposed to, say, main chain scission). The derivative spectra (Fig. 14 bottom) reveal a substantial broadening of the Z-Tetraol peak in the $\sim 200^\circ\text{C}$ region as a function of UV irradiation. The evolution of a small peak in the 300–400°C region suggests that perhaps some higher molecular weight component(s) may have been created. Again, the current set of measurements is not able to distinguish possible chemical changes such as end-to-end links or even crosslinks to have taken place. We additionally limit the interpretation of these data to only the solvent-extractable fraction of the UV-irradiated Z-Tetraol films and caution that they do not necessarily represent or reflect the chemical composition of the non-extractable Z-Tetraol film that remained adhered to the disk surface.

4. Conclusions

The UV irradiation of Z-Tetraol films on amorphous

Fig. 14 Thermogravimetric data of Z-Tetraol as a function of UV irradiation on solvent-extracted films. The UV irradiation was conducted on 50 Å Z-Tetraol films on CNx for 0, 1 and 2 minutes using a 185 nm UV lamp with an incident power of 4 mW/cm².

nitrogenated carbon films was investigated. COF₂ evolution in the gas phase decreased with increasing number of OH end groups in the order: Z > Zdol > Z-Tetraol after UV irradiation. Therefore UV photochemistry was preferentially initiated on the OH end groups and not the perfluoropolyether main chain. Both UV irradiation and annealing on 11 Å Z-Tetraol films produced a virtually identical surface. Thus the surface energy as a function of bonded fraction was identical. The UV-irradiated 11 Å Z-Tetraol films also demonstrated equilibrium behavior exhibiting bonding or debonding to the asymptotic 80% bonded level under ambient conditions. UV-irradiated thick films of Z-Tetraol (~ 20 –40 Å) exhibited film properties that differed from the non-irradiated films. The oscillations in the polar component of the surface energy, normally observed in Z-Tetraol films and attributed to amphiphilic structuring, disappeared. Terraced flow exhibited a rapidly moving front below ~ 10 Å compared to the remainder of the irradiated film. Both observations were tentatively attributed to loss of OH functionality. The latter was verified by chemical extraction and subsequent analyses by NMR and TGA. For technologically relevant film thicknesses near 10 Å, this work demonstrates the high efficiency of the UV process for PFPE bonding compared to annealing and establishes the equivalent interfacial film properties between UV irradiation and annealing.

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