Tribochemistry of Monodispersed ZDOL with Hydrogenated Carbon Overcoats

Chao-Yuan Chen, Walton Fong, and David B. Bogy

Computer Mechanics Laboratory
Department of Mechanical Engineering
University of California at Berkeley, CA 94720

Abstract

Tribo-chemical studies of the lubricant molecular effect on the tribology of the head/disk interface (HDI) were conducted using hydrogenated (CH_x) carbon disks coated with ZDOL lubricant. The studies involved drag tests with uncoated and carbon-coated Al_2O_3-TiC sliders and thermal desorption experiments in an ultra-high vacuum (UHV) tribochamber. The studies showed that the lubricant interaction with carbon overcoat varies as a function of lubricant molecular weight. The friction coefficient increases as the molecular weight increases. The higher friction is owing to the higher viscosity of ZDOL lubricants. The friction and catalytic decomposition mechanisms of ZDOL are described. In general, the PFPE polymers are decomposed by chain scission involving the breakage of the backbone bonds to yield free-radical segments. Chain scission can occur by three mechanisms: (1) random degradation, (2) depolymerization, and (3) weak-link degradation. Our studies further support that catalytic reactions occurred at the endgroup functionals. The lower number of endgroup functionals for ZDOL with higher molecular weight reduces the possibility of the occurrence of the catalytic reactions. Moreover, the ZDOL desorbed peak temperatures shifted to lower temperatures with increasing molecular weight. The spreading diffusion coefficient of ZDOL decreases with increasing molecular weight. As the mobility of the chains decreases, the desorption energy need to break the lubricants increases resulting in higher desorption peak temperatures. The longer chain length of the higher molecular weight ZDOL will cause higher degrees of crosslinking. The crosslinking restricts chain mobility and causes an increase in the desorption peak temperatures.

Keywords: Tribochemistry; Hydrogenated carbon overcoat; ZDOL decomposition; Friction and wear; Thermal desorption; Molecular weight; Spreading; Viscosity, Crosslinking.

I. I. INTRODUCTION

Perfluoropolyethers (PFPE) are employed as lubricants in magnetic recording disk drives to reduce friction and wear. The PFPE lubricant and the hard carbon overcoat on the disks provide the necessary protection of the underlying magnetic film against wear due to sliding at the head-disk interface. Their decomposition mechanisms associated with contact sliding have been extensively studied. Many experiments demonstrate that PFPEs, subjected to electron irradiation, are easily decomposed into smaller fragments [1]. Vurens et al. [2] used low energy electrons to bombard PFPEs and observed that their electron decomposition occurs at an energy below their ionization potential (about 14 eV). Strom et al. [3] suggested that the lubricant degradation reaction was activated by low energy electrons produced at the tribological interface. It is reported that the decomposition rates of PFPEs are higher in the presence of Lewis acid forming materials, such as Fe_2O_3 [4], Al_2O_3 and $AlCl_3$ [5]. Our earlier studies of the decomposition of ZDOL lubricant on nitrogenated carbon overcoats (CNx) [6] indicate that the decomposition rate is significantly affected by the slider materials. The use of uncoated Al_2O_3-TiC sliders leads to the rapid decomposition of ZDOL due to catalytic reactions, while carbon coated sliders produce less intense decomposition due primarily to frictional actions [7]. The thermal stability of PFPE has also been studied extensively. Lin et al. [8] used temperature-programmed reaction/desorption (TRP/D) and electron simulated desorption (ESD) to study the roles of temperature and turboelectric charge in the decomposition of the Fomblin-ZDOL lubricant. They showed that the threshold temperature for its dissociation of the Fomblin-ZDOL molecule is 500-550K in accordance with the known thermal stability of free ZDOL. Vurens [9] also showed that molecules having a CF_2-CF_3 endgroup (Demnum S65) display enhanced thermal stability compared to molecules with the CF_2-CF_2-CH_2-CH_2O-phenyl endgroup (Demnum SP). Gellman [10] showed that the heat of adsorption of hydrocarbon ether was greater than that of the corresponding fluorocarbon ether, suggesting that the ethers are bonded to the films through the donation of electron pairs on the oxygen atom. Gellman also proposed a model in which the electropositive nature of the hydrogen in the a-CH films weakens the extent of electron donation from the ether lone pairs and, hence, weakens the bonding of the ethers to the a-CH films. Furthermore, Perry [11] used temperature-programmed desorption and scanning force microscopy to probe the interaction of ZDOL with both hydrogenated carbon overcoats and nitrogenated carbon overcoats. The data showed that the nitride surfaces are more reactive toward the ZDOL lubricant and, as a result, the thin lubricant film is more tightly bound to the overcoats. In our previous report [12], the friction and catalytic decomposition mechanisms as well as the thermal behavior of ZDOL are described, and data demonstrating the chemical reactions of the lubricant and carbon overcoat are also presented.

The best lubricant should exhibit slow removal and loss, fast recovery, and minimum tribochemistry [13]. Lubricant is also lost by centrifugal flow, or spin-off, and evaporation [14]. Lower molecular weight increases the rate of recovery, and also the rate of loss through spin-off and evaporation. Hence, there is a tradeoff between lubricant loss and recovery by spreading. Waltman et al. [15] showed that the activation energy for lubricant evaporation from the carbon surface increases with increasing molecular weight. They also found that the low activation energies determined for the evaporation and bonding of ZDOL 2000 are attributed to the polydispersity in the ZDOL molecular weight [16]. O'Conner et al. [17] and Ma et al.[18, 19, 20], in their studies of the spreading behavior of PFPE on silica surfaces, suggest that the functional end-groups of ZDOL significantly retard the diffusion process, owing probably to their stronger interactions with the carbon surface. They also showed that the lubricant diffusion coefficient decreases with increasing molecular weight. Min et al. [21] measured the spreading characteristics of PFPE films on silica surfaces by scanning microellipsometer as function of molecular weight, chain-end functionality, and humidity. They found that the effects of molecular weight are much smaller than those of chain-end functionality. Wang et al. [22] have recently reported that the wear durability of the head-disk interface lubricated with a hydroxyl-terminated PFPE (ZDOL) decreases as the mobility of the ZDOL lubricant on the disk overcoat decreases. In our previous work [23], that the lubricant interaction with the carbon overcoat varies as a function of lubricant thickness. Wear durability improves considerably for thicknesses than a monolayer. As the lubricant thickness increases, the end-group effect on the diffusion process decreases, and the diffusion coefficient increases. As a result, faster replenishment of the lubricant occurs on disks with thicker ZDOL on the protective carbon surface, enhancing the wear durability at the interface. These results reflect the importance of the mobile ZDOL layer in providing good wear durability. We believe the role of the mobile layer is to replenish the lube displaced during dragging.

In this report, we study the ZDOL molecular weight effect on hydrogenated carbon films (CHx) using an ultra-high vacuum (UHV) tribochamber equipped with a mass spectrometer. The studies consist of drag tests and thermal desorption experiments in the UHV tribochamber. Two decomposition processes of ZDOL under sliding friction conditions are studied, one is with a carbon film coated slider/CHx coated disk system, and another is with an uncoated Al_2O_3-TiC slider/CHx coated disk system. We illustrate the lubricant molecular weight effect on the tribological performance as well as the strength of the bonding between the lubricant and the carbon surface.

II. EXPERIMENTAL PROCEDURE AND SET-UP

The UHV tribochamber consists of a disk spindle, a slider actuator, a substrate heater, and a high-resolution quadrupole mass spectrometer (QMS) in a vacuum chamber with base pressure $< 2 \times 10^{-8}$ Torr, which was described in details in a previous paper [24]. The QMS provides in-situ detection of the gaseous products generated during drag tests and thermal desorption studies. The QMS can monitor simultaneously 15 different atomic mass units (AMUs) ranging from 1 to 500 along with friction or temperature data from strain gauge transducers or a thermocouple, respectively. It is noted that all AMUs from 1 to 192 of ZDOL decomposition products generated at the Al_2O_3/TiC slider/CHx disk interface were previously investigated under the same test conditions and only the most pertinent AMUs were monitored in this study.

Drag tests in the tribochamber were conducted as follows. Initially, the tribochamber was baked out at 150°F at high vacuum for 24 hours. The chamber was then backfilled with Argon gas as the disk and slider samples were mounted inside. Next, the chamber was pumped down to a base pressure of 2×10^{-8} Torr and the channels of the QMS were assigned to selected AMUs. Background intensities were recorded before the drag tests were initiated with the following parameters: 0.2 m/s drag speed, a load of 30 mN, and a sliding time of 20 minutes. The sliders were 30% (1.2mm by 1mm) negative-pressure Al_2O_3/TiC sliders with and without amorphous carbon films on the air bearing surfaces. The disks were commercial 95mm smooth thin film disks with a 125Å amorphous hydrogenated carbon overcoat (CHx). The hydrogen content in the CHx film was 5 atomic percent. The disks were lubricated with ZDOL by a dipping process. The resulting thickness of ZDOL on the disks in this study was 24Å. The ZDOL lubricants of different molecular weight were obtained by fractionating the commercially available ZDOL. The lubricants were fractionated by the addition of a nonsolvent to a polymer solution, by cooling a solution of polymer, solvent evaporation, zone melting, extraction, diffusion, or centrifugation [25]. Table below lists the narrowly dispersed fractions of ZDOL used in this work.

Lubricant	Number-average molecular weight M_n (g/mole)	Polydispersity (M_w/M_n)
ZDOL-1	4200	1.15
ZDOL-2	7600	1.02
ZDOL-3	8500	1.07

The number-average molecular weight M_n is defined as $M_n = W/N$. Where

W = total sample weight = $\Sigma w_x = \Sigma n_x M_x$,

N = total number of moles in the sample (of all sizes) = Σn_x,

w_x = total weight of x-mer,

M_x = molecular weight of x-mer,

n_x = number of moles of x-mer.

Any analytical technique that determine the number of moles present in a sample of known weight, regardless of their size, will give the number-average molecular weight. Rather than count the number of molecules of each size present in a sample, it is possible to define an average in terms of the weights of molecule present at each size level. The weight-average molecular weight M_w is defined as $M_w = \Sigma w_x M_x / \Sigma w_x$. The number-average molecular weight is the first moment of the molecular weight distribution, analogous to the center of gravity in mechanics. The weight-average molecular weight, the second moment of the molecular weight distribution, corresponds to the radius of gyration in mechanics. It may be shown that $M_w \geq M_n$ (since $w_x \geq n_x$) [25]. These two averages are equal only for a perfect monodisperse (all molecules the same size) polymer. The ratio M_w/M_n is known as the polydisperse index, and is a measure of the breadth of the molecular weight distribution. Polydisperse values range from about 1.02 for carefully fractionated polymers to over 50 for some commercial polymers. In our study, the polydispersity of these monodisperse ZDOL lubricants are between 1.02 and 1.15, which are much lower than those of non-fractionated ZDOL lubricants (polydispersity above 1.4).

In preparation for the thermal desorption tests in the tribochamber the heater was baked at 600^{o}F at high vacuum for 4 hours to bake out the residual lubricants left on the heater after each thermal desorption test. A CHx/ZDOL disk was cut into 2cm squares. The lubricated samples were mounted on the heater and the temperature was measured by a thermocouple in contact with the heater near the heated sample. As with the drag tests, the chamber was pumped down to 10^{-8} Torr and the channels of the QMS were assigned to selected AMUs. A typical experiment consisted of heating a sample at a rate of 0.3^{o}F/sec starting at room temperature and stopping before $500^{o}F$. A mass spectrum was collected on a computer every two seconds during the heating. Afterwards, the spectra were analyzed in order to obtain the thermal desorption profile for each mass as a function of sample temperature.

III. Results

A. Results from the UHV drag tests

In this section, we present the results from the UHV drag tests. Figures 1 through 3 part (a) show the friction coefficient curves for the ZDOL lubricated CHx disks against an uncoated and a DLC coated Al_2O_3/TiC pico sliders. Before starting the friction tests, the background intensities were recorded for 80 seconds by the mass spectrometer. Figures 1 through 3 part (b) show the integrated mass spectra of ZDOL fragments produced from the head-disk interface. The four primary peaks belong to mass fragments CFO (47), CF_2O (66), CF_3 (69), and C_2F_5 (119). In our previous studies [12] of CHx carbon overcoats paired with carbon-coated sliders, the primary mechanism of ZDOL was due to frictional effects, and it was characterized by the generation of CFO (47), and CF_2O (66). The absence of a carbon-coating led to a more complex catalytic decomposition mechanism of ZDOL , and it was characterized by the generation of CF_3 (69) and C_2F_5 (119).

Figure 1(a) shows the friction coefficient curves for the **24Å monodispersed ZDOL MW4200** lubricated disk. For the 70Å DLC coated Al_2O_3/TiC slider, the friction coefficient started at 1.2 and increased steadily to 1.4 within 1990 drag cycles before wear occurred. For the uncoated Al_2O_3/TiC slider, the friction coefficient started at 1.3 and increased steadily to a peak value of 1.9 within 295 cycles, then dropped to 0.3 after reaching its peak value. A wear track was observed on the disk just after the friction coefficient dropped.The friction variation, as shown in figure 1(a), is most likely due to three body contact resulting from small wear particles that were generated at the head-disk interface. These results indicate that 24Å monodispersed ZDOL MW4200 has good lubricating action against the DLC coated slider, but provides little protection against the uncoated slider. Figure 1(b) shows the integrated mass spectra of the major ZDOL decomposed fragments produced from the head-disk interface. This mass spectrum for the 70Å DLC coated Al_2O_3/TiC slider is similar to that of ZDOL vapor as reported by Kasai et al. [5], where the primary decomposition peaks are masses 47 (CFO) and 66 (CF_2O) due to frictional heat [12]. Because no contact with Lewis acid is possible in this case, the ZDOL decomposition is caused by friction/thermal actions only. In general, PFPE polymers are susceptible to thermal degradation, which can occur either by chain scission involving the breakage of the backbone bonds to yield free-radical segments or by nonchain scission involving the elimination of a small molecule from a substitute group and double-bonded formation [26]. Karis et al. [27] presented that the mechanical scission must occur at points along the chain where the shear stress is sufficiently concentrated to overcome the bond energy in a short enough time, so that bonds are broken before the stress relaxation by segmental motions can take place. Chain scission can occur by three mechanisms: (1) random degradation, where the chain is broken at random sites; (2) depolymerization, where monomer units are released at an active chain end; and (3) weak-link degradation, where the chain breaks at the lowest-energy bonds. The weak-link degradation should be directly related to the molecular bond energies. The relevant bond dissociation energy [28] is used to judge the bond strength and possible decomposition trends. Because the weakest bonds in ZDOL are C-O-C and C-C, the ZDOL molecule is expected to cleave preferentially at these locations. A radical mechanism proposed by Sianesi et al. [29] postulates that PFPEs dissociate by breaking the weaker C-C bonds followed by β scission to form perfluorinated aldehyde and alkene. Therefore, masses 47 (CFO) and 66 (CF_2O) are the primary fragments due to mechanical shear/frictional heat action. For the uncoated Al_2O_3/TiC slider, the mass intensities of the four major ZDOL fragments are higher than those in the DLC coated slider case. The decomposition mechanisms of ZDOL in the case of the uncoated Al_2O_3/TiC slider are much more complicated than those with the DLC coated slider. For the uncoated slider, catalytic reactions control the ZDOL decomposition and the catalytic reactions lead to the generation of masses 69 (CF_3) and 119 (C_2F_5). Therefore, masses 47 (CFO) and 69 (CF_3) are the highest peaks in the uncoated slider case as shown in figure 1(b).

Figure 2(a) shows the friction coefficient curves for the **24Å monodispersed ZDOL MW7600** lubricated disk. For the 70Å DLC coated Al_2O_3/TiC slider, the friction coefficient started at 1.5 and increase steadily to 2 within 2420 drag cycles before wear occurred. For the uncoated Al_2O_3/TiC slider, the friction coefficient started at 1.4 and increased to a peak value of 1.6 within 150 cycles, then dropped to 0.3 after reaching its peak value. A wear track was observed on the disk just after the friction coefficient dropped. These results are very similar to those of the monodispersed ZDOL MW4200 disk. The above results indicate that a disk with 24Å mono-dispersed ZDOL MW7600 has good lubricating action against the DLC coated sliders, but provides little protection against the uncoated slider. Moreover, there is added benefit in using ZDOL MW7600 versus ZDOL MW4200 in the DLC coated slider case, while worse performance in the uncoated slider case. More discussion will be presented later. Figure 2(b) shows the integrated mass spectra of the major ZDOL decomposition fragments produced from the head-disk interface. When the ZDOL molecular weight increases from 4200 to 7600, the degradation intensities of the major ZDOL decomposition fragments decrease. The primary decomposition peaks are masses 47 (CFO) and 66 (CF_2O) for both the DLC coated slider and the uncoated slider cases, which are different from those of the monodispersed ZDOL MW4200. When the ZDOL molecular weight increases from 4200 to 7600, the catalytic reactions have been reduced significantly. Therefore, fragment CF_3 (69) is not the highest decomposition peak in the uncoated slider case.

Figure 3(a) shows the friction coefficient curves for the **24Å monodispersed ZDOL MW8500** lubricated disk. For the 70Å DLC coated Al_2O_3/TiC slider, the friction coefficient started at 2 and increased steadily to 2.2 within 2775 drag cycles before tests stopped and no wear track was observed. For the uncoated Al_2O_3/TiC slider, the friction coefficient started at 1.5 and increased to a peak value of 1.6 within 175 drag cycles, then dropped to 0.5 after reaching its peak. A wear track was observed on the disk just after the friction coefficient dropped. These results are similar to those for the ZDOL MW4200 or ZDOL MW7600 disks. These results indicate that 24Å monodispersed ZDOL MW8500 has very good lubricating action against the DLC coated slider, but provides little protection against the uncoated slider. Furthermore, enhanced wear durability is achieved by using ZDOL with higher molecular weight (MW8500) against DLC coated sliders, while no such benefit in the uncoated slider case. Figure 3(b) shows the integrated mass spectra of the major ZDOL decomposition fragments produced from the head-disk interface. When the molecular weight increases from 7600 to 8500, the degradation intensities of the major ZDOL decomposition fragments further decrease. The primary decomposition peaks are masses 47 (CFO) and 66 (CF_2O) for both the DLC coated slider and the uncoated slider cases, which are similar to those of the mono-dispersed ZDOL MW7600 disk. Again, when the molecular weight increases from 4200 to 7600 or 8500, the catalytic reactions have been reduced significantly and fragment CF_3 (69) is not the highest decomposition peak in the uncoated slider case. These results indicate that strong catalytic reactions occur with the uncoated slider when the ZDOL molecular weight is lower.

Figure 4 shows the degradation intensities of (a) mass 47 (CFO), and (b) mass 69 (CF_3) during UHV drag tests on CHx disks with different lubricant molecular weight. The degradation intensities of the frictional fragments 47 (CFO) and 66 (CF_2O) decrease with both the uncoated sliders and DLC coated sliders as the molecular weight increases. Figure 4(b) shows the similar result for the catalytic fragments 69 (CF_3) and 119 (C_2F_5). However, the degradation intensities of the catalytic fragments decrease more rapidly than those of the frictional fragments as the molecular weight increases. These results indicate that less decomposition of ZDOL lubricants occurred with higher molecular weight.

Figure 5(a) shows the wear durability of these CHx disks as a function of ZDOL molecular weight. With DLC coated sliders, the wear durability was improved as lubricant molecular weight increased. However, the wear durability, with uncoated sliders, was not monotonically improved with increasing molecular weight. More discussion will be presented later. Figure 5(b) shows the friction coefficient of these CHx disks as a function of ZDOL molecular weight. The friction coefficient increased as the molecular weight increased. It has long been known that larger molecules will impede flow more than smaller ones and give a higher viscosity. Studies of the intrinsic viscosity of essentially monodisperse polymer fractions indicate a rather simple relation as known as Mark-Houwink-Sakurada (MHS) relation [30]:

$$[\eta]_x = K(M_x)^a \ , \qquad (0.5 < a < 1)$$

where $[\eta]_x$ = viscosity of x-mer, “K” and “a” are MHS constants.

The measured intrinsic viscosity of a mixture of monodisperse fractions is a weight average:

$$[\eta] = \Sigma[\eta]_x w_x/\Sigma w_x.$$

The viscous component is dominant in liquids, hence their flow properties may be described by Newtonian dashpot relation [31]:

$$\tau = \eta\, d\gamma/dt$$

where τ is the applied shear stress, and $d\gamma/dt$ is the rate of strain

With higher molecular weight, the higher viscosity (η) will cost higher friction (τ) during the head-disk sliding.

Table 1 listed the normalized mass spectra of the major ZDOL decomposition fragments to the highest peak mass 47 (CFO) against DLC coated sliders and uncoated sliders with respect to different molecular weight. The normalized percentage of some fragments increased as molecular weight increased, but reversed for the other fragments. The number of the endgroup functionals (-CF_2-CH_2-OH) dominates these phenomena. As the molecular weight increases, the number of the endgroup functionals decreases if the lubricant thickness is controlled. Therefore, the normalized degradation intensity of fragments 31 (CF), 50 (CF_2), and 51 (CF_2H) originating from the endgroup functionals decreases. These result indicates that these three decomposition fragments are mostly due to the lubricant depolymerization at the active endgroup functional, which is the second type of the chain scission. However, the normalized degradation intensity of mass 66 (CF_2O) increases as the molecular weight increases. This result indicates that mass 66 (CF_2O) fragment is mostly from the lubricant decomposition within the main body consists of two backbone groups 66 (CF_2O) and 116 (CF_2CF_2O). In addition, this decomposition is due to the weak-link degradation at the lowest-energy bonds, which is the third type of the chain scission. The normalized degradation intensity of the catalytic reaction fragments 69 (CF_3) and 119 (C_2F_5) decreases as molecular weight increases. These results further support that the catalytic reactions occurred at the endgroup functionals, where the fluorine atom transfer is from the endgroup to the internal sector with the presence of Al_2O_3 surface. The lower number of endgroup functionals with higher lubricant molecular weight reduces the possibility of the occurrence of the catalytic reactions.

B. Results from UHV thermal desorption tests

In this section, we present and discuss the results from UHV thermal desorption experiments. Figure 6 shows the thermal desorption history profiles for masses 47 (CFO) and 66 (CF_2O) of CHx disks with different molecular weight ranging from 4200 to 8500 at a heating rate of 0.3^oF/sec. These two fragments are characteristic of friction/mechanical shear actions and electron bombardment [12] in drag tests. Figure 7 shows the thermal desorption history profiles for masses 69 (CF_3) and 119 (C_2F_5) of CHx disks with different molecular weight ranging from 4200 to 8500. These two fragments are used to monitor the catalytic decomposition. In our previous work [12], it is found that the thermal desorption mass spectrum of mobile ZDOL is very similar to the decomposition mass spectrum of the sliding at the carbon slider/CHx disk interface. Karis et al. [27] also observed that the thermally degraded polymer fragments are almost the same as the mechanically degraded polymer fragments. These results indicated that frctional heat is the primary decomposition mechanisms of ZDOL in the carbon-coated slider/CHx disk case. In general, two thermal desorption peaks were found during these experiments: one is between 100^oF and 250^oF, and the other is between 250^oF and 450^oF.

In our previous work [23], we conclude that most of the mobile lubricant is desorbed during the first thermal desorption period, and the bonded lubricant increased a little due to the annealing effect at temperatures above 150^oF. These results are similar to those found by Waltman et al. [15]. In their paper, they found that the initially applied mobile ZDOL is depleted via evaporative loss as well as bonding of the lubricant to active sites on the carbon surface at the elevated temperatures between 140^oF to 250^oF, which is the operating temperature of the disk drives. The relative branching into the evaporation and bonding channels is molecular weight dependent, with increasing molecular weight favoring bonding. The activation energy for ZDOL evaporation is highly dependent on molecular weight, decreasing rapidly with decreasing molecular weight. Therefore, the lower molecular weight components present in ZDOL will preferentially evaporate from the disk surface. In our current case of ZDOL MW4200 (low molecular weight), evaporation is the dominant channel responsible for the depletion of mobile ZDOL MW4200 and the first desorption peak between 100^oF to 250^oF was observed in figure

6(a). For ZDOL with higher molecular weight (MW7600, and MW8500), bonding is the dominant channel responsible for the depletion of mobile ZDOL and the first desorption peak disappeared. In our previous work [23], we also conclude that only the mobile ZDOL layer is desorbed during the first thermal desorption period and the residual bonded ZDOL layer is desorbed during the second thermal desorption period. This indicates that the desorption energy of bonded ZDOL lubricant is higher than that of mobile ZDOL lubricant. Waltman et al. [32] also showed similar results that the surface energy of the bonded lubricant is substantially lower than the mobile lubricant, reflecting the increased interaction strength that occurs as a result of bonding.

Figures 6 and 7 illustrate that CFO (47) and CF_2O (66) are the primary thermal desorption fragments from the first peak, which corresponds to desorption of the mobile ZDOL layer. These results are consistent with Lin and Kasai's results [8, 33]. During the second thermal desorption peak (between 250^oF and 450^oF), the bonded ZDOL layer was desorbed and all four primary fragments were observed. The generation of fragments CF_3 (69) and C_2F_5 (119) may be a consequence of the desorption of bonded lubricant from the CHx surface [12].

Moreover, the ZDOL desorbed peak temperatures shifted to lower temperatures with increasing molecular weight as shown in figures 6 and 7. This result indicates that the desorption energy of bonded lubricant increases with increasing molecular weight. It has been known that the desorption peak temperatures of polymers depend on five factors: (1) the free volume of the polymer; (2) the attractive forces between the molecules; (3) the internal mobility of the chains; (4) the stiffness of the chains; and (5) the chain length. Ma et al. [18] showed that the spreading diffusion coefficient of ZDOL lubricant decreases with increasing molecular weight. As the mobility (freedom to rotate about bonds) of the chains decreases, the desorption energy need to break the lubricants increases resulting in higher desorption peak temperatures. In addition, the glass transition temperatures varies according to the empirical relation:

$T_g = T_g^{\infty} – C/X$,

where T_g^{∞} is the asymptotic value of the glass transition temperature at infinite chain length,

C is a constant, X is the chain length

The glass transition temperature T_g is a property of the polymer, and whether the polymer has glassy (hard, rigid) or rubbery (soft, flexible) properties depends on whether its application temperatures is above or below its T_g [34]. The decrease in T_g with decreasing the chain length X reflects the increased ease of motion for shorter chains. Similarly, the desorption peak temperatures of ZDOL increase with increasing molecular weight due to increasing the chain length. The longer chain will cause higher degrees of crosslinking. Crosslinking is the chemical (covalent bond) attachment of one chain to another chain in the 3-dimensional structures. The crosslinking restricts the chain mobility and causes an increase in the desorption peak temperatures.

In figure 6(a) with ZDOL MW4200, two desorbed peak temperatures (364^{o}F and 427^{o}F) of fragment 66 (CF_2O) were observed. However, only one peak was found in figures 6(b) & 6(c). The polydispersity of ZDOL MW4200 is 1.15, which is higher than those of ZDOL MW7600 (polydispersity = 1.02) and ZDOL MW8500 (polydispersity = 1.07). These results indicate that the ZDOL MW4200 with higher polydispersity was desorbed in the broader range of temperatures.

IV. Discussions and Conclusions

The experiments presented here illustrate the complex chemical relationships that occur at the head/disk interface during drag tests. The UHV tribochamber was used to monitor in situ the gaseous wear products generated at the HDI during dragging. The ZDOL lubricants of different molecular weight were obtained by fractionating the commercially available ZDOL. The molecular weight of the monodispersed ZDOL lubricant used in our study are 4200, 7600, and 8500. The corresponding polydispersities of these ZDOL are 1.15, 1.02, and 1.07. The UHV drag tests show that less lubricant decomposition occurs when the molecular weight is higher. With higher molecular weight, the thermal desorption energy of bonded lubricant increases, so the decomposition of ZDOL becomes more difficult. The corresponding wear durability of ZDOL against the DLC coated sliders improves as increasing the molecular weight. This enhanced performance with heavier ZDOL may be due to the slower lubricant decomposition rate. However, there was no such benefit in using higher molecular weight for the uncoated slider cases. Strong catalytic reactions occurred with the uncoated and these strong catalytic reactions speeded up the depletion of the lubricant layer. Hence, the reflow rate of mobile ZDOL in the wear track dominates the wear durability against uncoated sliders. The wear durability of the ZDOL MW4200 lubricated disk is better than those of the ZDOL MW7600 or MW8500 lubricated disks. The enhanced wear durability with lower molecular weight is due to their better mobility. The mobile ZDOL lubricants reflow in the wear track and improve their wear durability against uncoated sliders. For the DLC coated sliders, the depletion rate of lubricant layer is much lower than that of the uncoated slider cases. The lubricant mobility is not as crucial as the lubricant-consuming rate. Hence, the lubricant decomposition rate dominates its wear durability against DLC coated sliders.

The friction coefficient increased as the molecular weight increased. According to Mark-Houwink-Sakurada equation, the intrinsic viscosity of essentially monodisperse polymer increases as the polymer molecular weight increases. The larger molecules will impede flow more than smaller ones and give a higher viscosity. Hence, with higher molecular weight, the higher viscosity will cost higher friction during the drag tests.

In general, the PFPE polymers are decomposed by chain scission involving the breakage of the backbone bonds to yield free-radical segments. Chain scission can occur by three mechanisms. The first mechanism is random degradation: initial chain scission occurs at random followed by depropagation from the newly formed chain ends. The second one is depolymerization: monomer units are released at an active chain end. Three ZDOL decomposition fragments 31 (CF), 50 (CF_2), and 51 (CF_2H) are mostly due to the lubricant depolymerization at the active endgroup functionals ($-CF_2-CH_2-OH$). The third one is weak-link degradation: the chain breaks at the lowest-energy bonds. Because the weakest bonds in ZDOL are C-O-C and C-C, the ZDOL molecule is expected to cleave preferentially at these locations. Therefore, the masses 47 (CFO) and 66 (CF_2O) are the primary fragments from the lubricant decomposition within the ZDOL main body by breaking these weakest C-O-C and C-C bonds. The normalized degradation intensity of the catalytic reaction fragments 69 (CF_3) and 119 (C_2F_5)

decreases as molecular weight increases. These results further support that the catalytic reactions occurred at the endgroup functionals, where the fluorine atom transfer is from the endgroup to the internal sector. The lower number of endgroup functionals with higher molecular weight reduces the possibility of the occurrence of the catalytic reactions.

Based on the thermal desorption experiments, only mobile ZDOL lubricant was desorbed during the first thermal desorption peak (between 100°F and 250°F), and the residual bounded ZDOL lubricant was desorbed during the second thermal desorption peak (between 250°F and 450°F). The ZDOL desorbed peak temperatures shifted to lower temperatures with increasing lubricant molecular weight. This result indicates that the desorption energy of bonded lubricant increases with increasing lubricant molecular weight. It has been showed that the spreading diffusion coefficient of ZDOL lubricant decreases with increasing molecular weight. As the mobility (freedom to rotate about bonds) of the chains decreases, the desorption energy need to break the lubricants increases resulting in higher desorption peak temperatures. In addition, the desorption peak temperatures of ZDOL increase with increasing lubricant chain length. The longer chain will cause higher degrees of crosslinking. The crosslinking restricts the chain mobility and causes an increase in the desorption peak temperatures.

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REFERENCES

[1] Pacansky J. and Waltman R. J., "Electron Beam Irradiation of Polyperfluoroethers: Experimental Analysis of Main-chain Degradation", Chem. Mater. 5, pp486-494, (1993).

[2] Vurens G., Zehringer R. and Saperstein D., "The Decomposition Mechanisms of Perfluoropolyether Lubricants during Wear", Surface Science Investigations in Tribology, Chung Y.W., Homola A. M. and street B., Eds, Washington, D. C.: American Chemical Society, pp169-180, (1992)

[3] B.D. Strom, and D.B. Bogy, "Gaseous Wear Products from Perfluoropolyether Lubricant Films", Wear, 168, pp31-36, (1993)

[4] M.J. Zehe and O. O. Faut, "Acid Attack of Perfluorinated Alkyl Ether Lubricant Molecules by Metal Oxide Surfaces", Tribology Trans., 33, pp634-640, (1990)

[5] P.H. Kasai, "Degradation of Perfluoropolythers Catalyzed by Lewis Acids", Adv. Info. Storage Syst. 4., pp291-314, (1992)

[6] Jianjun Wei, Walton Fong, D. B. Bogy and C. S. Bhatia, "The Decomposition Mechanisms of a Perfluoropolyether at the Head/Disk Interface of Hard Disk Drives", Tribology Letters, Vol. 5, pp203-209, (1998)

[7] D. B. Bogy, X. H. Yun, and B. J. Knapp, " Enhancement of Head-Disk Interface Durability by Use of DLC Overcoats on the Slider's Rails", IEEE Trans on Magnetics, Vol. 30, No.5, pp369-373, (1994)

[8] Jong-Liang Lin, C. Singh Bhatia, and John T. Yates, Jr., "Thermal and Electron-simulated Chemistry of Fomblin-ZDOL Lubricant on a Magnetic Disk", J. Vac. Sci. Technol. A 13(2), pp163-168, (1995)

[9] G. H. Vurens and C. M. Mate, "The Thermal Stability of Perfluoropolythers on Carbon Surfaces", Applied Surface Science, 59, pp281-287, (1992)

[10] Laura Cornaglia and Andrew J. Gellman, "Fluoroether Bonding to Carbon Overcoats", J. Vac. Sci. Technol. A 15(5), pp2755-2765, (1997)

[11] Scott S. Perry, Philip B. Merrill and Hyun I. Kim, "Comparative Studies of Perfluorinated Lubricants Adsorbed on Hydrogenated Amorphous Carbon and Amorphous Carbon Nitride", Tribology Letters 2, pp393-404, (1996)

[12] C.Y. Chen, W. Fong, D. Bogy, and C. Bhatia, "The decomposition mechanisms and thermal stability of ZDOL lubricant on hydrogenated carbon overcoats", CML Technical Report No. 98-016, submitted to Journal of Tribology

[13] Novotny, V.J., and Baldwinson, M.A., "Lubricant Dynamics in Sliding and Flying", J. Appl. Phys., 70, 10, pp5647-5652, (1991)

[14] Forcada, M.L., and Mate, C.M., "The Flow of Thin Viscous Liquid Films on Rotating Disks", J. Coll. Int. Sci., 160, pp218-225, (1993)

[15] R.J. Waltman, and G.W. Tyndall, "The evaporation and bonding of ZDOL polyperfluorinated Ether lubricants on CHx carbon overcoated rigid magnetic media. 1. Effect of Molecular Weight.", submitted to J. Phys. Chem.

[16] R.J. Waltman, and G.W. Tyndall, "The evaporation and bonding of ZDOL polyperfluorinated Ether lubricants on CHx carbon overcoated rigid magnetic media. 2. Effect of Polydispersity in the Molecular Weight", submitted to J. Phys. Chem.

[17] T.M. O'Connor, M.S. Jhon, C.L. Bauer, B.G. Min, D.Y. Yoon, and T.E. Karis, "Surface diffusion and flow activation energies of perfluoropolyaklether", Tribology Letters 1, pp219-223, (1995)

[18] X. Ma, J. GUI, L.Smoliar, K. Grannen, B. Marchon, M.S. Jhon, and C.L. Bauer, “Spreading of perfluoropolyalkyether films on amorphous carbon surfaces”, J. of Chemical Physics, vol. 110, no. 6, pp3129-3137, (1999)

[19] X. Ma, J. Gui, K. Grannen, L.Smoliar B. Marchon, M.S. Jhon, and C.L. Bauer, “Spreading of PFPE lubricants on carbon surfaces: effect of hydrogen and nitrogen content”, Tribology Letters, 6, pp9-14, (1999)

[20] X. Ma, J. Gui, L.Smoliar, K. Grannen, B. Marchon, M.S. Jhon, and C.L. Bauer, “Complex terraced spreading of perfluoropolyalkyether films on carbon surfaces”, Physical Review E, vol. 59, no. 1, pp722-727, (1999)

[21] B.G. Min, J.W. Choi, H.R. Brown, D.Y. Yoon, T.M. O’Connor, and M.S. Jhon, “Spreading Characteristics of Thin Liquid Films of perfluoropolyaklethers on solid surfaces. Effect of Chain-end Functionality and Humidity.”, Tribology Letters, 1, pp225-232, (1995)

[22] Wang, R-H., White, R.L., Meeks, S.W., Min, B.G., Kellock, A., Homola A., and Yoon, D., IEEE Trans. Mag., 32, pp3777, (1996)

[23] Chao-Yuan Chen, Walton Fong, David B. Bogy, and C. Singh Bhatia, “Lubricant Thickness Effect on Tribological Performance of ZDOL lubricated Disks with Hydrogenated Overcoats”, CML Technical Report No. 99-00?, submitted to Tribology Letters, (1999)

[24] X. H. Yun, D. B. Bogy, and C. S. Bhatia, “Tribochemical Study of Hydrogenated Carbon Coatings with Different Hydrogen Content Levels in Ultra High Vacuum”, J. Tribology, 119, pp437-443, (1997)

[25] Seymour R.B., and Carraher C.E. Jr., “Polymer Chemistry- an Introduction”, 2nd ed., pp93-98, (1987)

[26] Jellinek, H.H.G., “Degradation and Depolymerization Kinetics”, Aspects of Degradation and stabilization of polymers, pp1-24, (1978)

[27] T.E. Karis, V.J. Novotny, and R.D. Johnson, “Mechanical Scission of Perfluoropolyethers”, J. Applied Polymer Science, Vol. 50, pp1357-1368, (1993)

[28] A. Steritwieser, and C. H. Heathcock, “Introduction to Organic Chemistry”, Macmillan Publishing Co., Inc., New York, (1976)

[29] D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binaghi, “Perfluoropolyethers: their physical properties and behavior at high and low temperatures”, Wear, 18, pp85-100, (1971)

[30] Seymour R.B., and Carraher C.E. Jr., “Polymer Chemistry- an Introduction”, 2nd ed., pp73-77, (1987)

[31] Seymour R.B., and Carraher C.E. Jr., “Polymer Chemistry- an Introduction”, 2nd ed., pp59-61, (1987)

[32] R.J. Waltman, D.J. Pocker, and G.W. Tyndall, “Studies on the interactions between ZDOL Perfluoropolyether lubricant and the carbon overcoat of rigid magnetic media”, Tribology Letters 4, pp267-275 (1998)

[33] P.H. Kasai, W.T. Tang and P. Wheeler, “Degradation of Perfluopolyethers Catalyzed by Alumina Oxide”, Appl. Surf. Sci. 51, pp201-211, (1991)

[34] Seymour R.B., and Carraher C.E. Jr., “Polymer Chemistry- an Introduction”, 2nd ed., pp31-33, (1987)

CAPTIONS

Figure 1: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW4200 lubricated disk; (b) mass spectrum of the major ZDOL decomposed fragments.

Figure 2: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW7600 lubricated disk; (b) mass spectrum of the major ZDOL decomposed fragments.

Figure 3: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW8500 lubricated disk; (b) mass spectrum of the major ZDOL decomposed fragments.

Figure 4: integrated degradation intensity of ZDOL during UHV drag tests on CHx disks with different ZDOL molecular weight. (a) mass 47 (CFO) under frictional action, and mass 69 (CF_3) under catalytic reaction.

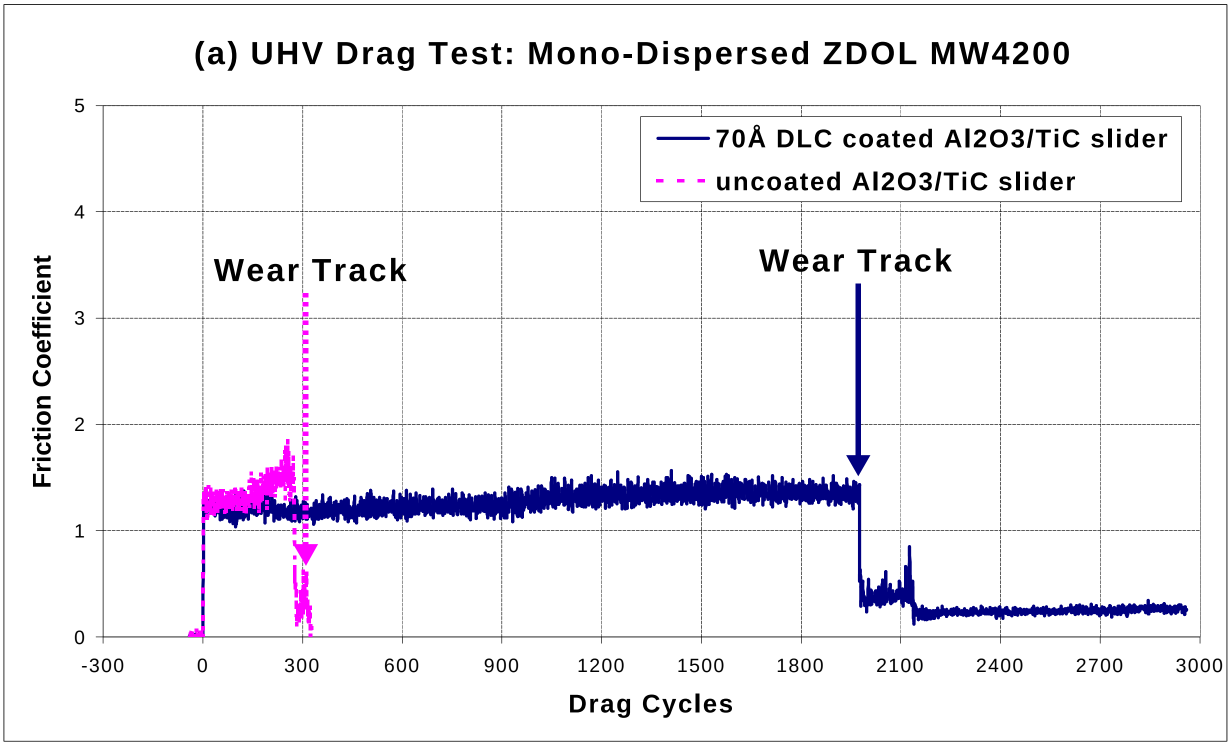
Figure 5: (a) wear durability and (b) friction coefficient of CHx disks with different ZDOL molecular weight during UHV drag tests against coated or uncoated Al_2O_3/TiC sliders.

Figure 6: thermal desorption history profiles of mass 47 (CFO), and mass 66 (CF_2O) during the thermal desorption tests on (a) ZDOL MW4200, (b) ZDOL MW7600, and (c) ZDOL MW8500 lubricated disks.

Figure 7: thermal desorption history profiles of mass 69 (CF_3), and mass 119 (C_2F_5) during the thermal desorption tests on (a) ZDOL MW4200, (b) ZDOL MW7600, and (c) ZDOL MW8500 lubricated disks.

	31-CF	**47-CFO**	**50-CF2**	**51-CF2H**	**66-CF2O**	**69-CF3**	**119-C2F5**
ZDOL 4200/coated slider	24%	100%	9%	17%	38%	5%	12%
ZDOL 4200/uncoated slider	42%	100%	34%	38%	67%	89%	58%
ZDOL 7600/coated slider	23%	100%	4%	10%	43%	4%	14%
ZDOL 7600/uncoated slider	22%	100%	14%	12%	74%	73%	42%
ZDOL 8500/coated slider	13%	100%	4%	11%	53%	5%	14%
ZDOL 8500/uncoated slider	19%	100%	3%	5%	78%	59%	37%

Table 1: Normalized mass spectra of the major ZDOL decomposition fragments during the UHV drag tests with respect to different ZDOL molecular weight.



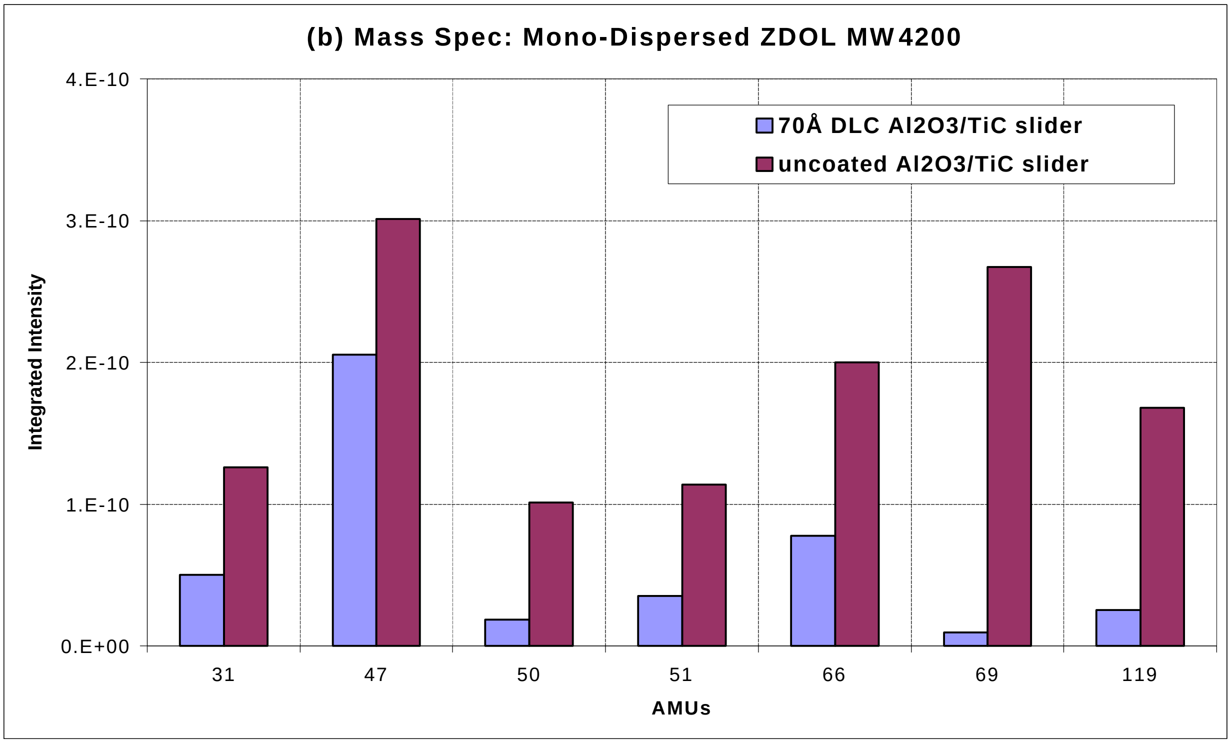


Figure 1: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW4200 lubricated disk; (b) mass spectrum of the major ZDOL decomposition fragments.

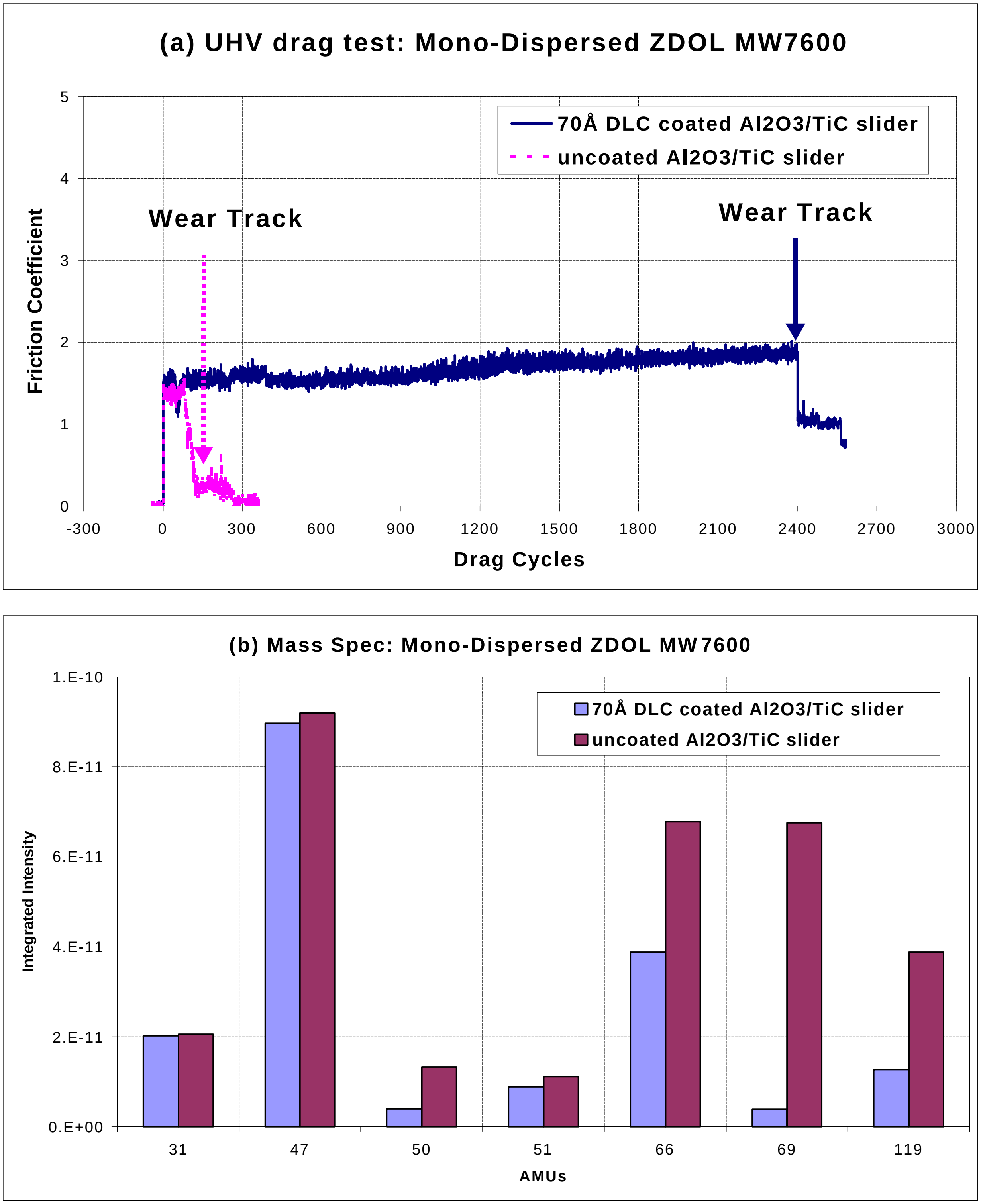
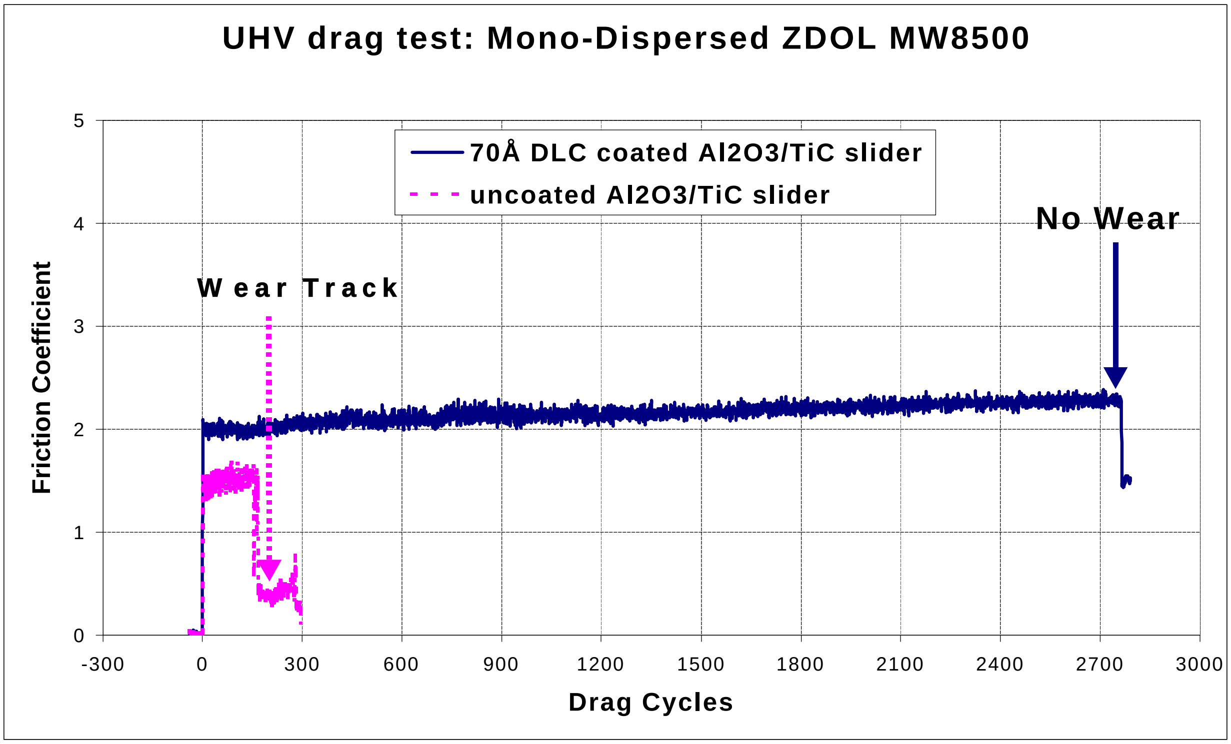


Figure 2: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW7600 lubricated disk; (b) mass spectrum of the major ZDOL decomposition fragments.



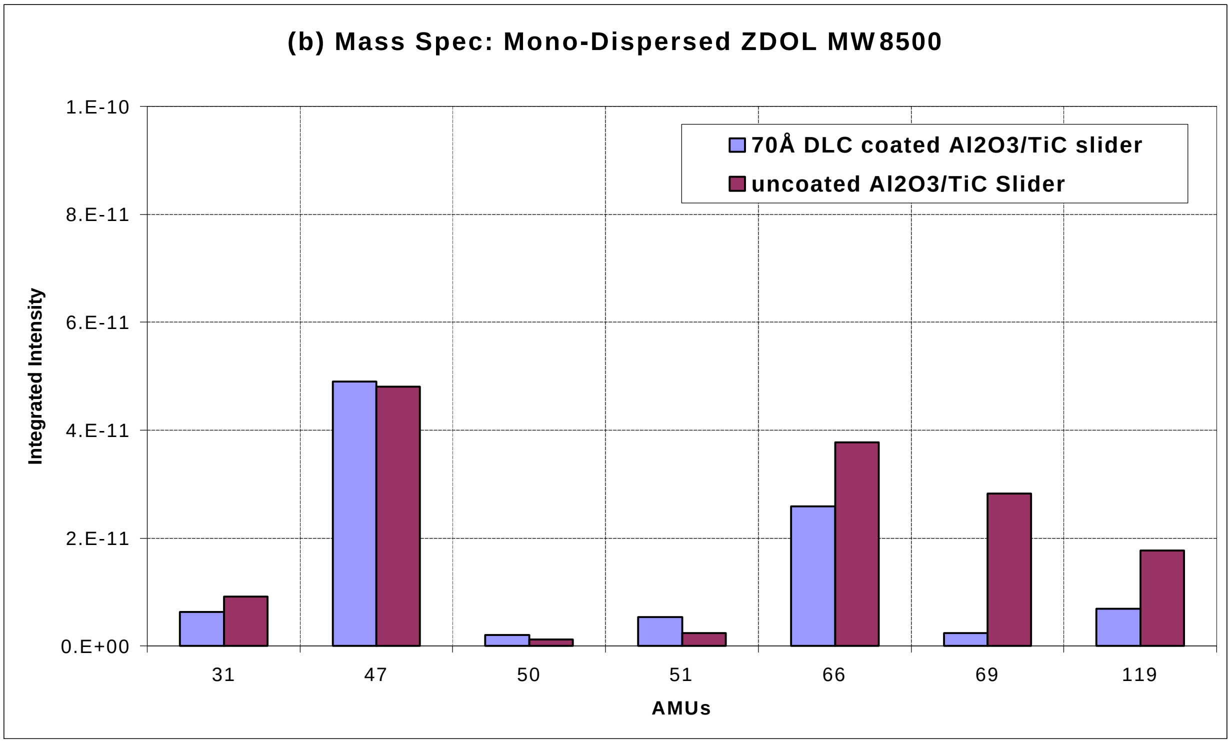
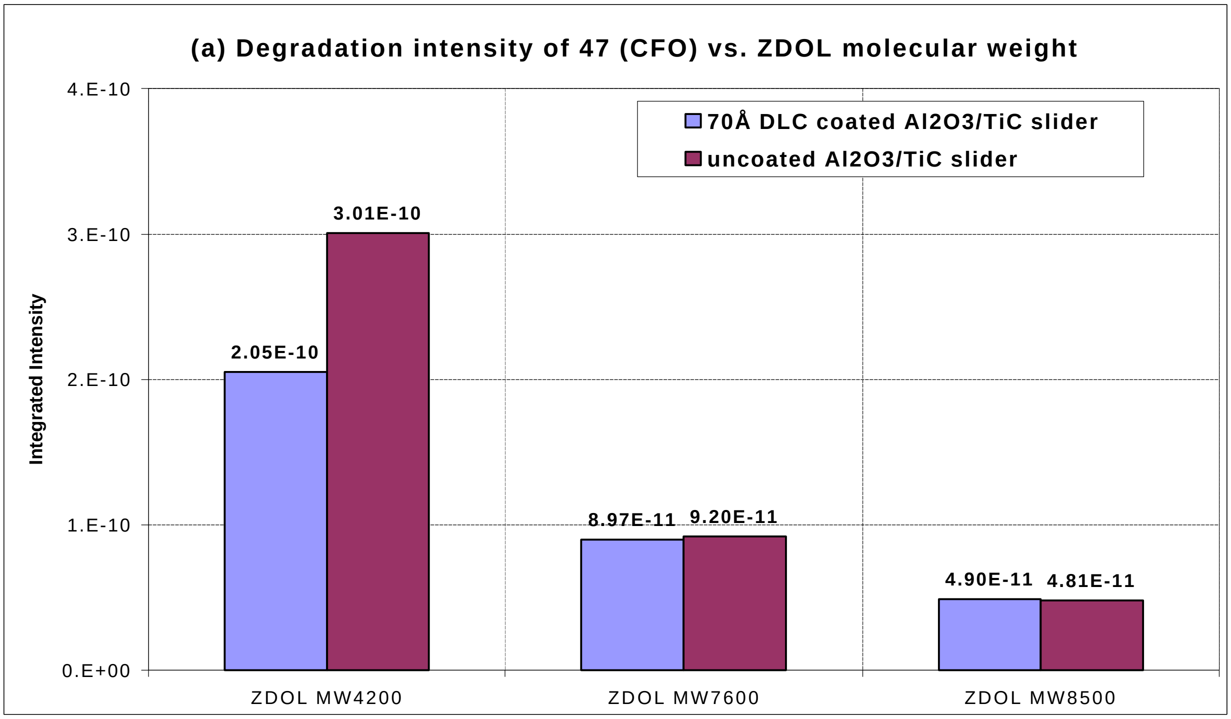


Figure 3: (a) friction coefficient of UHV drag test on 24Å mono-dispersed ZDOL MW8500 lubricated disk; (b) mass spectrum of the major ZDOL decomposition fragments.



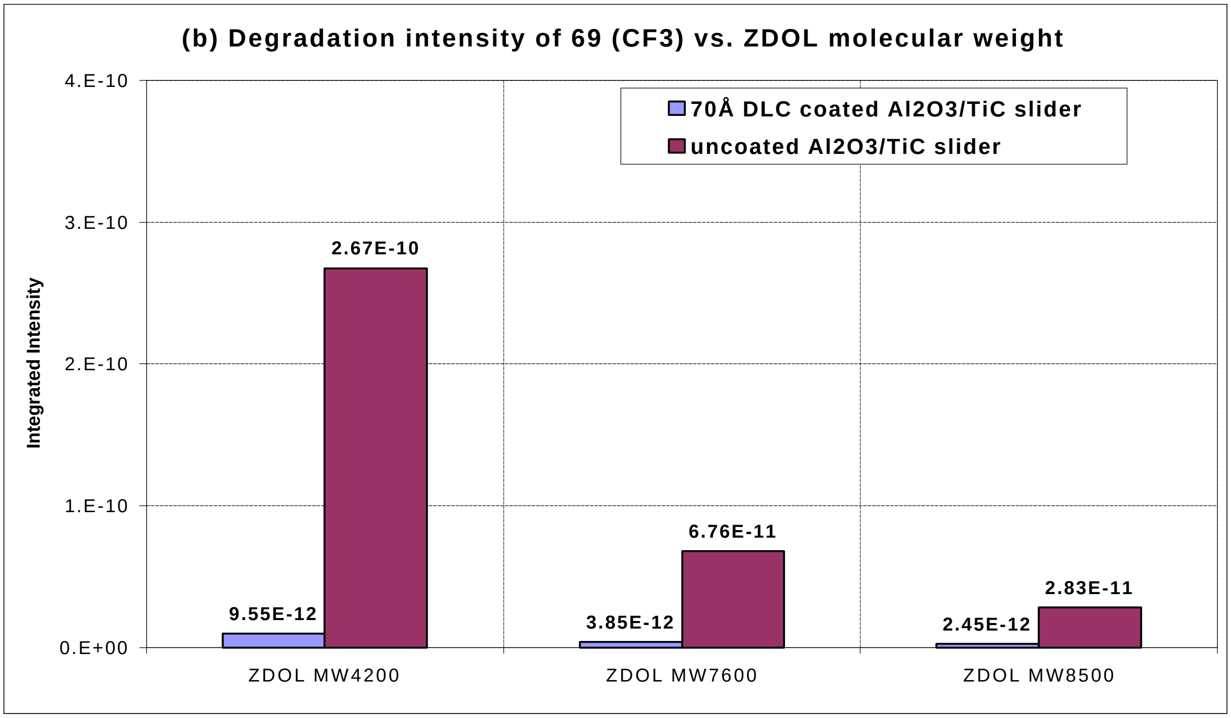
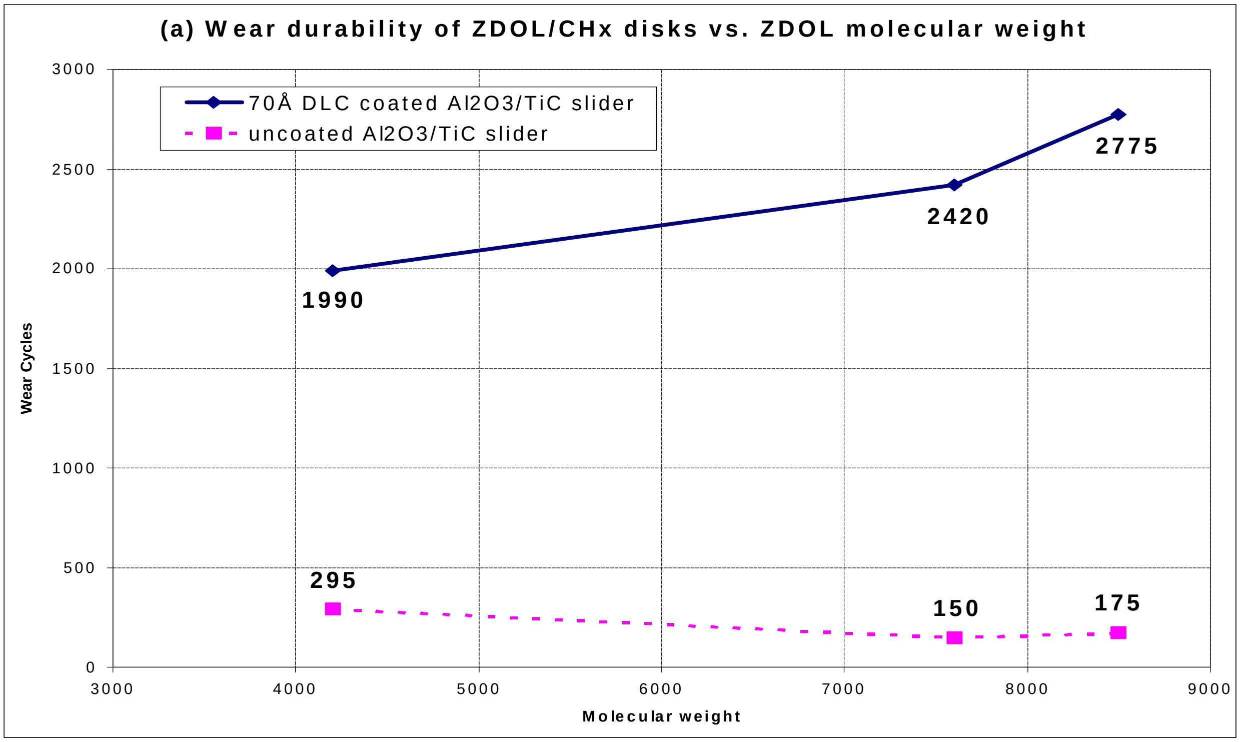


Figure 4: integrated degradation intensity of ZDOL during UHV drag tests on CHx disks with different ZDOL molecular weight. (a) mass 47 (CFO) under frictional action, and (b) mass 69 (CF3) under catalytic reaction.



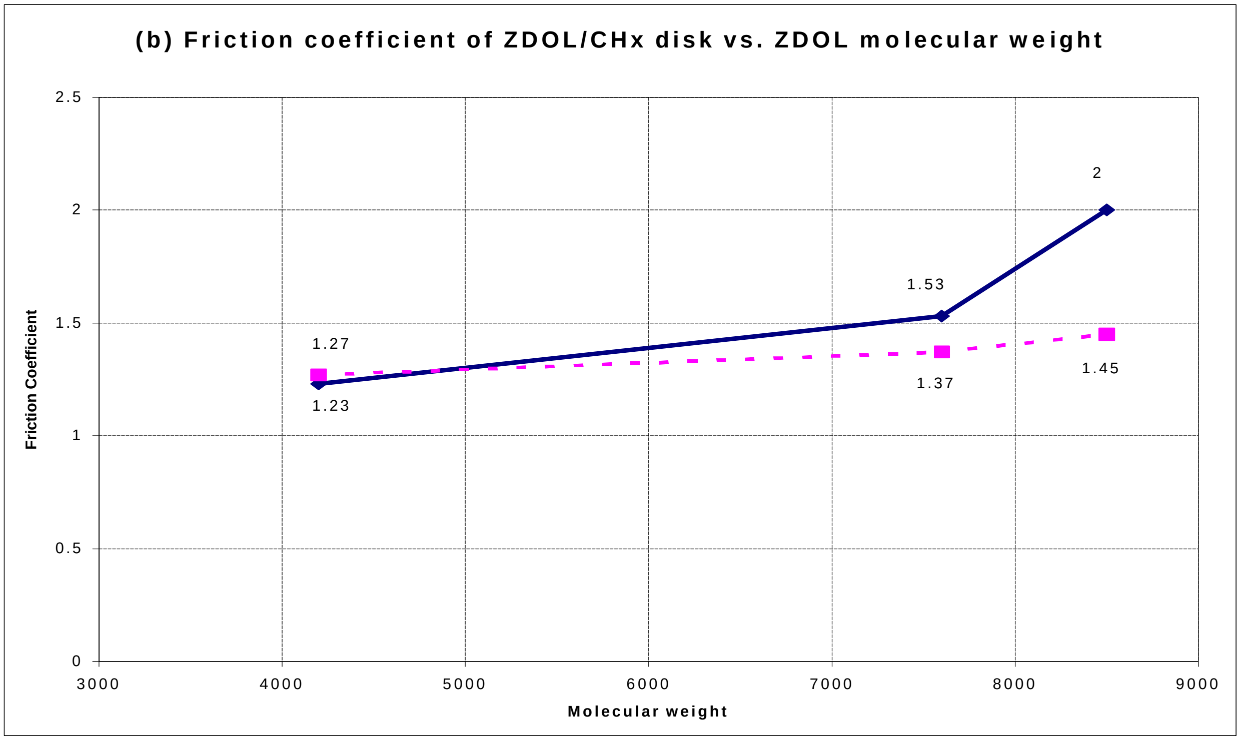


Figure 5: (a) wear durability and (b) friction coefficient of CHx disks with different ZDOL molecular weight during UHV drag tests with DLC coated or uncoated Al$_2$O$_3$/TiC sliders.

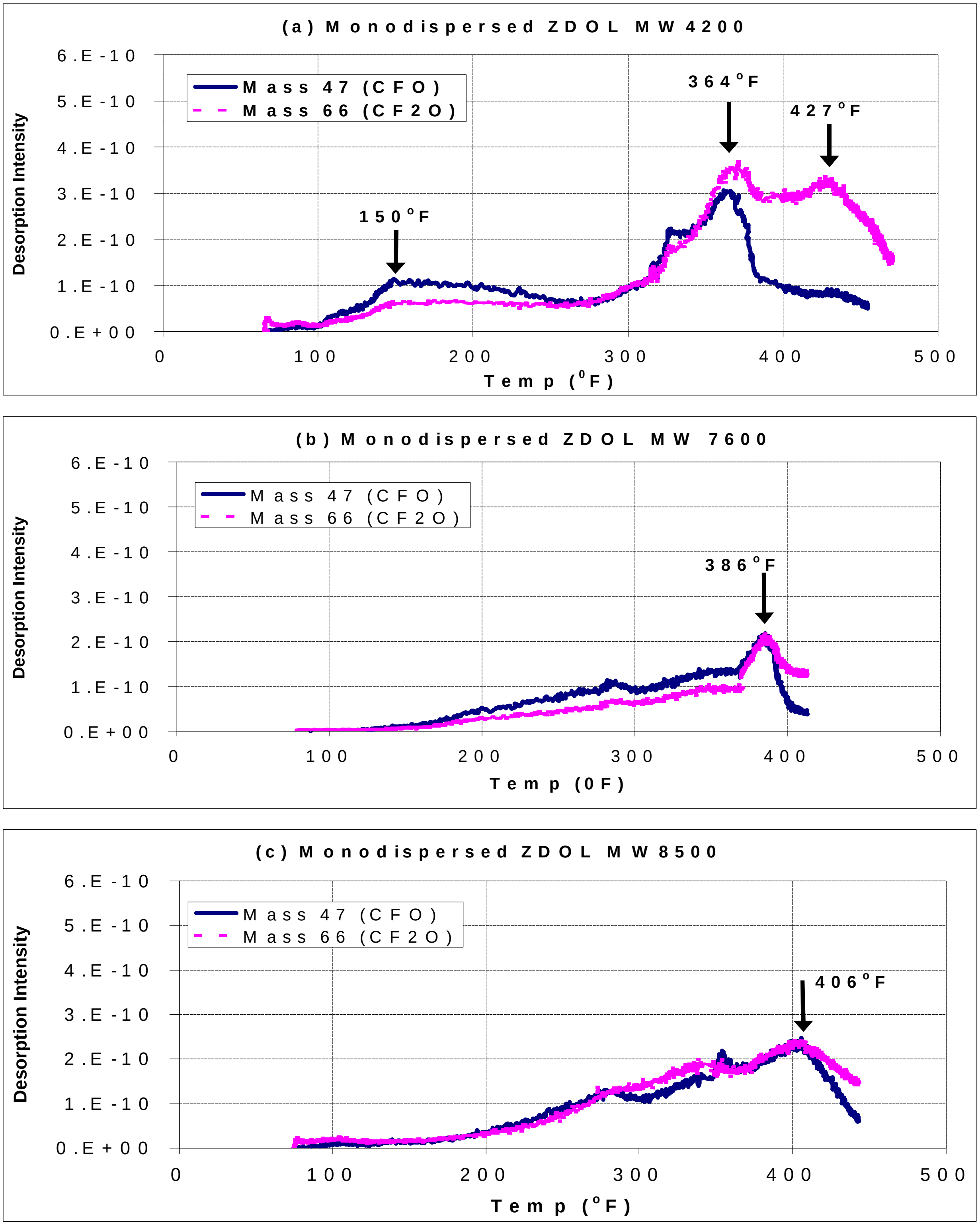


Figure 6: Thermal desorption profiles of mass 47 (CFO) and mass 66 (CF_2O) on (a) ZDOL MW4200, (b) ZDOL MW7600, and (c) ZDOL MW8500 lubricated disks.

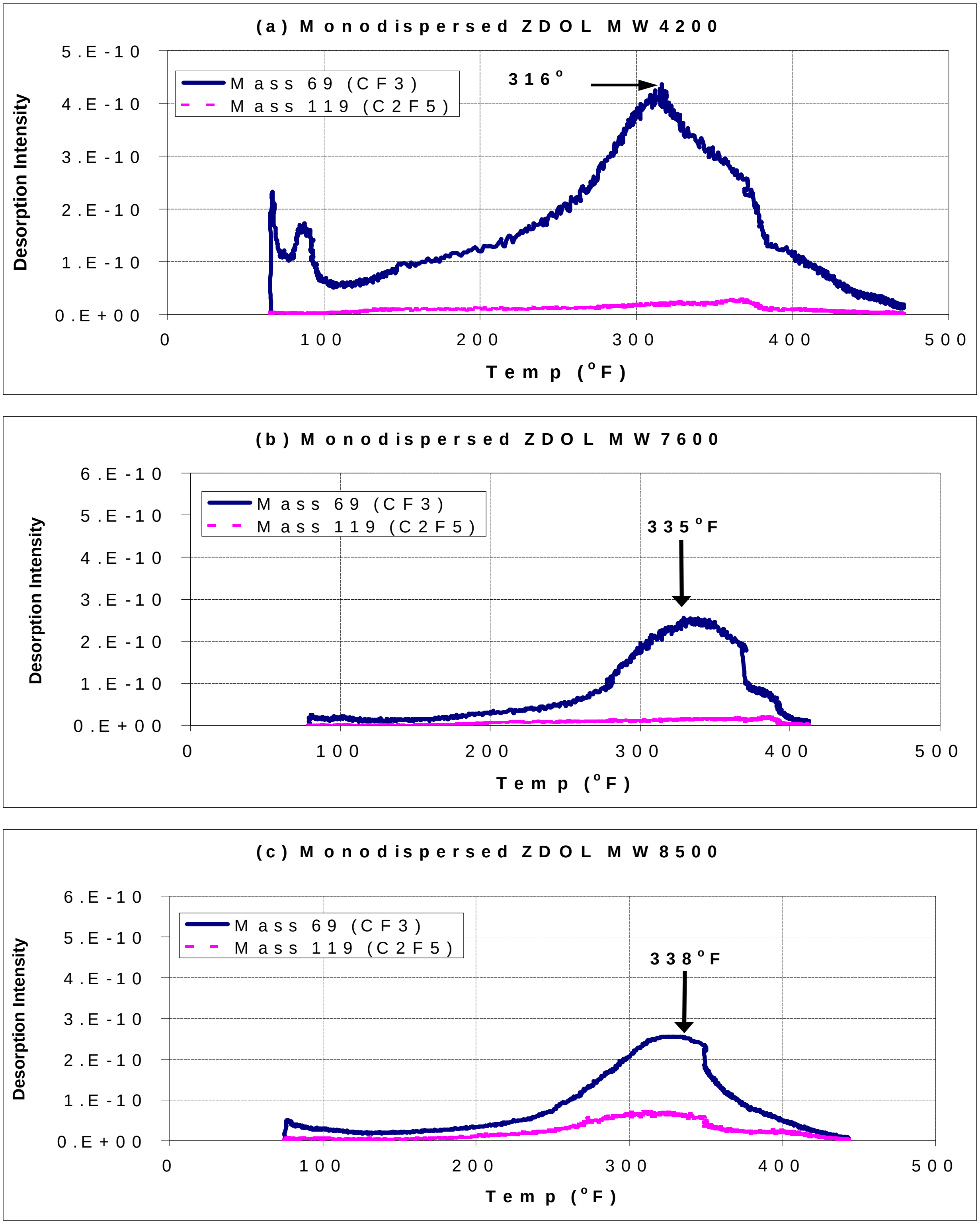


Figure 7: Thermal desorption profiles of masses 69 (CF_3) and 119 (C_2F_5) on (a) ZDOL MW4200, (b) ZDOL MW7600, (c) ZDOL MW8500 lubricated disks.