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The stability of ultra-thin perfluoropolyether mixture films on the amorphous nitrogenated carbon surface

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Abstract

The thermodynamic stability of boundary lubricant films based upon mixtures of liquid perfluoropolyethers (PFPEs) is reported. Mixtures of A20H-2000 with Zdols 2000, 2500, and 4000 and Zdol-TX 2200 on amorphous carbon nitride films are investigated. An optical surface analyzer is used to image the autophobic dewetting of the mixture PFPE films. The critical dewetting thickness coincides with the monolayer thickness of the adsorbed mixture PFPE films as determined by the changes in the surface energy as a function of lubricant film thickness. The critical dewetting thickness varies linearly with mixture concentration.

Keywords: Perfluoropolyether; Perfluoropolyether mixtures; Autophobic dewetting; Surface energy

1. Introduction

Micro- and nano-technological devices such as MEMS (micro-electromechanical systems) and hard-disk drives (HDDs) have contacting surfaces that require a boundary lubricant film to reduce wear. In MEMS, lubricant films derived from self-assembling monolayers of methylated or fluorocarbon compounds have been employed [1] while the rigid magnetic media in HDDs have relied almost strictly on topically applied liquid, low molecular weight perfluoropolyether (PFPE) films. Recently, PFPE lubricants have also been applied to MEMS actuator devices [2]. The use of boundary lubricants under repetitive contact conditions requires both a bound and a mobile phase for durability and reflow ("healing"). One methodology by which the ratio of the bound to mobile lubricant phases can be adjusted is by the use of mixtures having different chemical end groups. Lubricant mixtures could be advantageous over neat lubricants because the bound ratio can be altered and furthermore the interfacial friction and adhesive forces between the two contacting surfaces can be manipulated.

An important criterion for the employment of liquid, low molecular weight monomolecular polymer films on surfaces is their thermodynamic stability [3,4]. This is dependent on the intermolecular interactions that occur between the lubricant molecules and between the lubricant molecule and the underlying surface [5–7]. When the non-polar PFPE main chain is functionalized with polar end groups, acid–base interactions with the polar sites on the underlying surface occur. This could allow the preferential orientation of the non-polar polymer backbone at the air/film interface, resulting in the ordering of the first monolayer perpendicular to the surface thereby leading to a minimum in the surface free energy as a function of surface coverage [8,9]. When the monolayer film thickness is exceeded, the inability of the next liquid layer to spread on its own monolayer leads to autophobic dewetting [1–4]. The dewetting of boundary liquid films on surfaces can be undesirable in technological applications. It could lead to increased stiction of contacting surfaces leading to device failure. Since autophobic dewetting is strongly dependent on the physico-chemical properties of the lubricant itself such as the chemical structure of the end groups, predicting the dewetting of lubricant mixtures can become complicated and thus represents the motivation for this work.

In this report, we investigate the thin film stability of some mixtures of perfluoropolyethers with substituted end groups using contact angle goniometry and ellipsometric imaging. A lin-

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ear dependence of the critical thickness for dewetting as a function of mixture concentration is observed.

2. Materials and methods

The chemical structures for the Zdol, Zdol-TX, and A20H lubricants are represented in Fig. 1, and the materials data are summarized in Table 1. The substrates used in these experiments were 65 mm diameter glass disks with a nominal RMS roughness of 5 Å as determined by AFM measurements. The roughness was measured using an AFM Dimension 5000 with a standard AFM tip used in the tapping mode. The typical scan size was 5 µm × 5 µm with a scan rate of 0.5 Hz, and 256 lines of resolution. The following layers were then sequentially sputter-deposited onto the glass disks: an underlayer of Cr, a cobalt-based magnetic layer, and 45 Å of an amorphous carbon nitride (CNx) film. The elemental composition of the CNx surface has been previously quantified using XPS, Auger electron spectroscopy (AES), and Rutherford backscattering (RBS) [10]. The CNx surface contained both oxygen and nitrogen. The nitrogen content in CNx was $10.0 < x < 13.8$ at%. The oxygen content was determined to be 7 at%, and no hydrogen was detected in these films (RBS).

The lubricants were applied to the disks from solutions of $CF_3CF_2CF_2CF_2OCH_3$ (HFE-7100, 3M) using the dip-coat method. The lubricant film thicknesses were quantified using FTIR (Nicolet Model 560), calibrated to film thickness by XPS as previously described [11].

The stability and dewetting of molecularly-thin PFPE lubricant films were studied using two techniques. In the first method, an optical surface analyzer (OSA) using both s- and p-polarized light was employed to directly image the disk surface for lubricant dewetting [12]. For these purposes, 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.

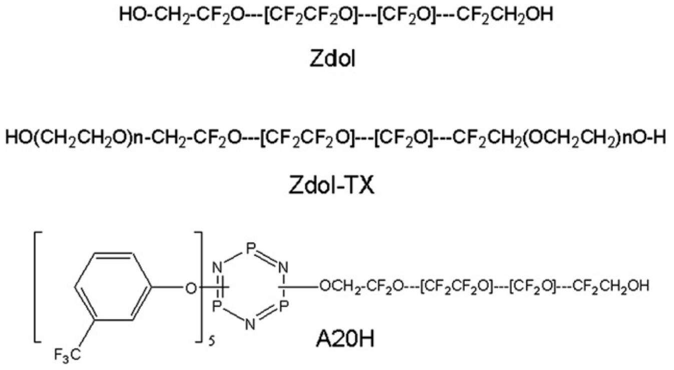

Fig. 1. The chemical structures of the PFPE molecules used in this study.

Table 1
NMR data for the perfluoropolyether liquids (CTP = cyclotriphosphazene)

Lubricant	M_n	% end group
Zdol 2000	1970	⩾99
Zdol 2500	2540	⩾99
Zdol 4000	3560	⩾99
Zdol-TX 2200	2200	⩾99
A20H-2000	3200	54% OH 46% CTP

In the second method, the energetics of the lubricant/CNx interface were determined as a function of lubricant thickness using contact angle goniometry. Thus, the surface energies for PFPE films on CNx were determined as a function of PFPE film thickness from contact angle measurements using hexadecane ($\gamma_l^d \sim \gamma_l = 27.5\ \mathrm{erg/cm^2}$), methylene iodide ($\gamma_l^d \sim \gamma_l = 50.8\ \mathrm{erg/cm^2}$), and water ($\gamma_l^d = 21.8\ \mathrm{mJ/m^2}$, and $\gamma_l^p = 51.0\ \mathrm{mJ/m^2}$) as the reference liquids.

3. Results and discussion

When the monolayer thickness is exceeded for an end-functionalized PFPE, the PFPE film can dewet. The instability of the PFPE films on CNx with thicknesses in excess of a monolayer were verified experimentally by imaging the CNx disks lubricated with a series of film thicknesses both below and above the monolayer film thickness. Representative images for some A20H:Zdol systems are presented in Fig. 2. Referring to Fig. 2 (left), when the 1:1 mixture of A20H-2000:Zdol-2500 is applied to the disk surface at a film thickness of nominally <17.2 Å, the resulting films are contiguous and display no evidence of lubricant droplets (i.e., dewetting). However, when the A20H-2000:Zdol-2500 thickness is increased to approximately 18.4 Å, lubricant droplets corresponding to dewetting is observed. The lubricant droplets are shown as the dark spots in the bottom image. Based upon previous spreading experiments [5,6] the lubricant droplets are a result of the segregation of the lubricant film into regions of stable thicknesses, i.e., one monolayer thickness (light areas in the image) and three monolayers thickness (dark droplets in the image). We note that the droplets can be readily removed by a subsequent immersion of the disk in a perfluorinated solvent such as HFE-7100 ($C_5H_3F_9O$, 3M) or Vertrel-XF ($C_5H_2F_{10}$, DuPont) and serves to verify the perfluorinated nature of the observed droplets. Representative images for the direct observation of critical dewetting for 1:1 mixtures of A20H-2000:Zdol-4000 and A20H-2000:Zdol-TX 2200 are shown in Fig. 2 (middle, right). The critical dewetting thicknesses obtained from the OSA imaging data are summarized in Table 2. The dependence of the critical dewetting thickness for mixtures of A20H-2000 with Zdol-2500, Zdol-4000, and Zdol-TX 2200 as a function of A20H-2000 concentration is shown in Fig. 3. A linear dependence on mixture ratio is observed.

The dispersive and polar components of the surface energy for a 1:1 mixture of A20H-2000:Zdol-2500 as a function of film thickness on CNx are shown in Fig. 4 as an illustrative example. The dispersive surface energy per unit area, γ_s^d, represents the van der Waals dispersion forces acting between the perfluorinated ether backbone and the carbon surface. The polar surface energy per unit area, γ_s^p, reflects the hydrogen bonding interactions between the lubricant end groups and the polar sites