

Solvent Effects on Friction Properties of Monolayer Perfluoropolyether Films Coated on Magnetic Disk Surfaces

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Monolayer perfluoropolyether (PFPE) films used for lubrication of magnetic disks are generally dip-coated from the PFPE solutions diluted by fluorinated solvents. In this paper, under lightly loaded (0–1 mN) and slowly rotated (2.1 mm/s) conditions that suppress disturbance of PFPE films during sliding, we investigate the effect of solvents on the friction properties of monolayer PFPE films coated on magnetic disk surfaces. The solvents include HFE-7200 and Vertrel-XF. For polar Zdol2000 and Zdol4000 films, friction fluctuated during one revolution of the disk immediately after film deposition, but became stable with elapsed time. Such transient friction behavior was not observed for nonpolar Z03 films, suggesting that the friction fluctuations exhibited by Zdol2000 and Zdol4000 films result from PFPE microstructure (such as film uniformity and molecular conformation) induced by the polar end groups. Despite of the higher solvent power of Vertrel-XF, the friction fluctuations in the transient state were noticeable for the films applied with Vertrel-XF as compared with those applied with HFE-7200. However, because the friction fluctuations were characterized by intermittent decrease of friction in narrow and sparsely distributed regions, the average value of the friction measured during one revolution of the disk was almost not affected by the friction fluctuations and showed weak dependence on the solvent.

Index Terms—Friction, lubrication, magnetic disk recording, solvent, thin films.

I. INTRODUCTION

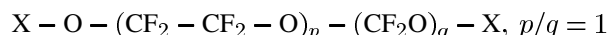
IN HARD disk drives, the head-disk spacing, which is currently less than 10 nm, must be further reduced to achieve higher recording density. However, this will increase the probability of head-disk contact. Monolayer (1–2 nm) liquid lubricant films coated on the disk surfaces exert adhesion and friction forces on the head during contact, directly affecting the flying stability of the head. Therefore, fundamental understanding of the adhesion and friction properties of such thin lubricant films is essential to creating stable flying of the head through a several-nanometer spacing.

As lubricants for disk surfaces, perfluoropolyethers (PFPEs) with polar groups at the chain ends are widely used. The PFPE films are generally dip-coated on disk surfaces by immersing the disks in a solution of PFPE diluted by a fluorinated solvent and then withdrawing them from the solution [1]. On the disk surfaces, the solvent quickly evaporates because of its high vapor pressure (about 0.02 MPa at 25 °C), leaving behind only thin PFPE films. Since different solvents have different ability to disrupt the intermolecular interactions between PFPE end groups, the conformation of PFPE molecules in a solvent varies with the type of solvent [2]. Such a solvent effect may exert influence on the microstructure (such as uniformity and conformation) and even the tribological properties of the PFPE films coated on the disk surfaces. So far, the effect of solvents has mainly been investigated from the standpoint of durability of lubricant films with contact-start-stop tests conducted under the conditions of heavy load and fast rotation. Except at high humidity [3], however, solvent dependence was not observed [4], [5]. This

is possibly due to the disturbance of the PFPE microstructure by the heavy load and fast rotation. In this research, under lightly loaded and slowly rotated conditions that suppress disturbance of the lubricant microstructure, we investigated the effect of solvents on the friction properties of monolayer PFPE films coated on magnetic disk surfaces.

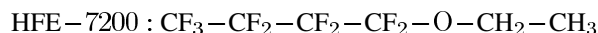
II. EXPERIMENTAL

Magnetic disks with 2.5-in diameter were used. The top surfaces of these disks were amorphous-nitrogenated carbon overcoats with a thickness of 3 nm and an average surface roughness of $R_a = 0.45$ nm. The lubricants used were three types of commercially available Fomblin PFPEs (Solvay Solexis): polar Zdol2000 and Zdol4000, and nonpolar Z03. These lubricants are linear chain copolymers with the following chemical structure:



where X representing the end group is $CF_2 - CH_2OH$ in Zdol2000 and Zdol4000, and CF_3 in Z03. The nominal number average molecular weight and polydispersity were 2000 g/mol and 1.5 for Zdol2000, 4000 g/mol and 1.15 for Zdol4000, and 4000 g/mol and 1.15 for Z03, respectively. Compared to Zdol2000, Zdol4000 has a larger molecular weight, and thereby a lower number density of polar end groups. In this sense, the polarity of Zdol4000 is weaker than that of Zdol2000 [4].

The solvents used to dilute the PFPEs were HFE-7200 (3M) and Vertrel-XF (DuPont). Their chemical structures are



The most significant difference between the physical properties of HFE-7200 and Vertrel-XF is solubility of water: 92 and 490 ppm (at 25 °C) for HFE-7200 and Vertrel-XF, respectively. Thus, we infer that Vertrel-XF is a more polar solvent than HFE-7200. PFPE films were dip-coated onto the disk surfaces. By setting the PFPE concentration and the withdrawal speed

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TABLE I
CONDITIONS FOR DIP-COATING OF PFPE FILMS

| Lubricant | Zdol2000 | | Zdol4000 | | Z03 | |
|--------------------------|----------|-------------|----------|-------------|----------|-------------|
| | HFE-7200 | Vertre I-XF | HFE-7200 | Vertre I-XF | HFE-7200 | Vertre I-XF |
| PEPF concentration (wt%) | 0.22 | 0.20 | 0.13 | 0.15 | 0.20 | 0.20 |
| Withdrawal speed (mm/s) | 0.80 | 0.94 | 1.60 | 1.41 | 0.90 | 0.88 |

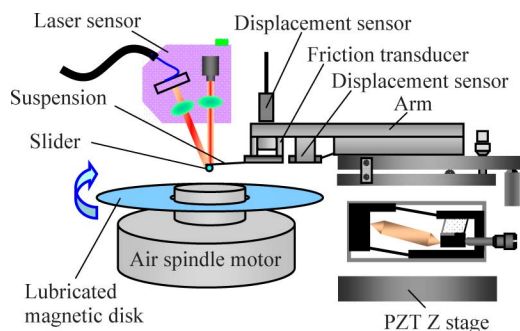


Fig. 1. Schematic diagram of pin-on-disk type tribometer.

as listed in Table I, the applied film thickness was fixed to be 2.1 nm for the three types of PFPEs. Note that such film thickness is thinner than the critical dewetting thickness [6]. Using an optical surface analyzer (Candela Instruments: OSA5130) that measures film thickness at a spatial resolution of 5 μm and a thickness resolution of 0.1 nm, we also confirmed that all the PFPE films used in this study did not dewet.

The self-developed pin-on-disk type tribometer [6]–[8] illustrated in Fig. 1 was used for friction measurements. The tribometer features highly sensitive measurements of adhesion and friction at resolutions of 2.5 and 4 μN under lightly loaded conditions. The slider used was a borosilicated glass (BK7) ball with a diameter of 1.5 mm and an average surface roughness (R_a) of 0.6 nm. In the friction measurements, the slider was loaded at a radius of 20 mm, and the disk was rotated at a speed of 1 rpm. This yielded a sliding speed of 2.1 mm/s. The external load was incrementally applied from 0 to 1 mN. At each external load, friction forces were measured at 60 000 points (sampling interval in terms of distance: 2.1 μm) during one revolution of the disk. Until equilibrium properties were obtained, the measurements were performed at time intervals of 24 h and were repeated for three times at each time step.

To investigate the conformation of PFPE molecules on the disk surfaces, bonded thickness and surface energy of PFPE films were also measured. By using a scanning ellipsometer (FiveLab: MARY-102), the bonded thickness was quantified as the thickness of the PFPE film that remained on the disk surface after 5-min ultrasonic rinsing in HFE-7200 [7]. The surface energy was ascertained with a contact angle meter (Kyowa Interface Science: DM 500). Two types of reference liquid (*n*-hexadecane and water in this case) were dropped onto the lubricated disk surface, and the corresponding contact angles were measured 5 s later. The dispersive and polar surface energy components of the lubricated disk surface were calculated from the contact angles made with the surface by *n*-hexadecane and water respectively [7], [9].

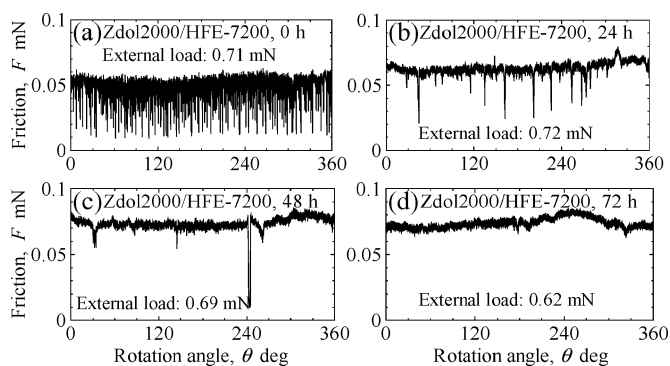


Fig. 2. Friction measured during one revolution of disk at (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h after film deposition for Zdol2000/HFE-7200.

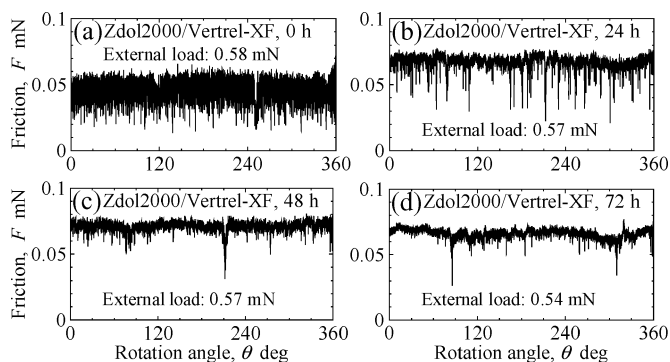


Fig. 3. Friction measured during one revolution of disk at (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h after film deposition for Zdol2000/Vertrel-XF.

All measurements were conducted in a clean room of class 10 000, in which the temperature was 22–25 $^{\circ}\text{C}$ and relative humidity was 20–48%.

III. RESULTS AND DISCUSSION

Figs. 2 and 3 show the friction forces measured during one revolution of the disk at (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h after film deposition for Zdol2000/HFE-7200 and Zdol2000/Vertrel-XF, respectively. For both solvents, the frictions fluctuated considerably immediately after film deposition, but became stable with elapsed time. We confirmed the reproducibility of this phenomenon and thus conclude that a transient friction behavior was observed with our experimental method. Such transient behavior possibly affects the properties of the PFPE films after being treated by such as ultraviolet irradiation which is industrially employed. Comparing Figs. 2 and 3, however, we know that the friction fluctuations were more noticeable for Vertrel-XF than for HFE-7200, especially at 24, 48, and 72 h after film deposition. This indicates that the process of friction stabilization is slower for Vertrel-XF than for HFE-7200.

To allow for detailed examination of the friction fluctuations, the friction within the rotation angle range of 0–15 $^{\circ}$ in Fig. 2(a) is expanded in Fig. 4. It is evident that the friction fluctuations consisted of no stick region, but mainly intermittent decrease of friction. We also calculated the autocorrelation of the friction distributions presented in Fig. 2(a). Fig. 5 shows the result. Periodicity was not observed, indicating that the friction fluctuations observed in Figs. 2(a) and 4 were random in location and

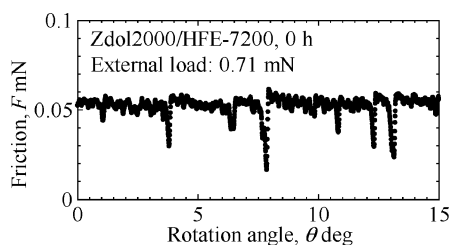


Fig. 4. Expansion of the friction within the rotation angle range of 0-15° shown in Fig. 2(a).

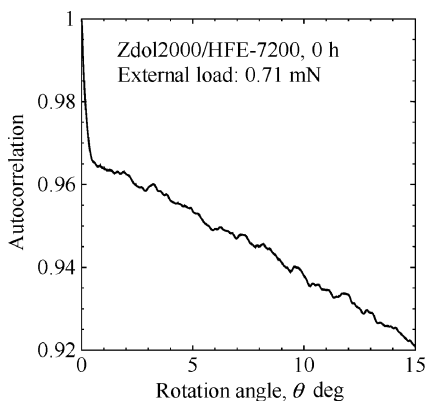


Fig. 5. Autocorrelation of the friction distributions shown in Fig. 2(a).

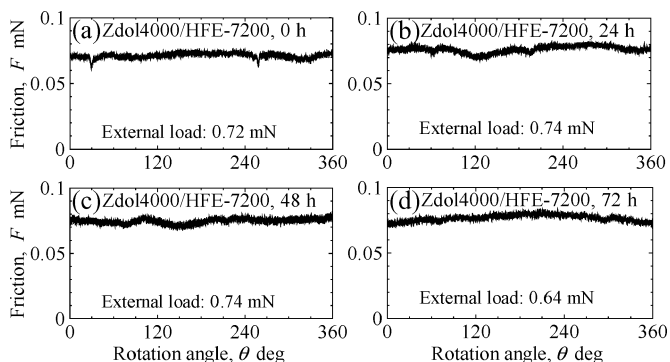


Fig. 6. Friction measured during one revolution of disk at (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h after film deposition for Zdol4000/HFE-7200.

contained no distinct frequency component. These results confirm that the friction fluctuations were not self-excited stick-slip oscillations. We speculate that the friction fluctuations are attributed to microstructure such as uniformity and conformation of the PFPE films. Because the fluorocarbon backbone of PFPE exhibits only weak van der Waals interaction, we conclude that the microstructure of PFPE films is mainly affected by the PFPE polar end groups, which show strong hydrogen-bonding interaction. Thus, we suppose that, with decreasing polarity of PFPE, the friction fluctuations will be suppressed, and the influence of solvents will also decrease.

For confirmation, we measured the friction of Zdol4000, which is less polar than Zdol2000, and the friction of nonpolar Z03. The results are presented in Figs. 6–9. Compared with the results for Zdol2000 (Figs. 2 and 3), friction fluctuations were small for Zdol4000 (Figs. 6 and 7), and specifically not observed for Zdol4000/HFE-7200. In contrast to polar

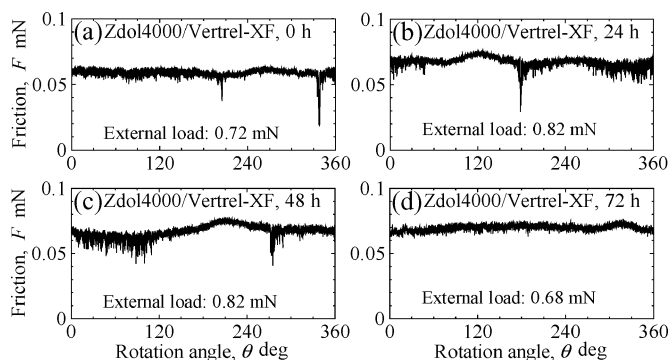


Fig. 7. Friction measured during one revolution of disk at (a) 0 h, (b) 24 h, (c) 48 h, and (d) 72 h after film deposition for Zdol4000/Vertrel-XF.

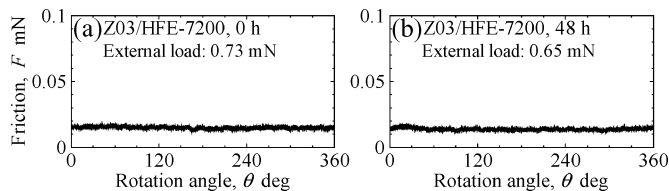


Fig. 8. Friction measured during one revolution of disk at (a) 0 h and (b) 48 h after film deposition for Z03/HFE-7200.

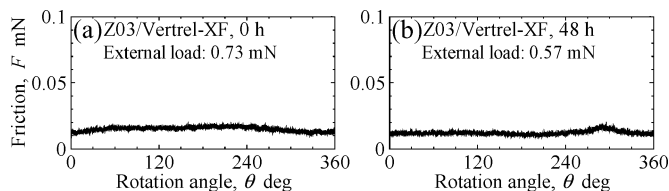


Fig. 9. Friction measured during one revolution of disk at (a) 0 h and (b) 48 h after film deposition for Z03/Vertrel-XF.

Zdol2000 and Zdol4000 films, the friction of nonpolar Z03 films presented in Figs. 8 and 9 remained stable during one revolution of the disk and during the 48 h measurement, showing no dependence on the solvent used in the dip-coating process. These results demonstrate that the friction fluctuations observed for Zdol2000 and Zdol4000 are attributed to their end group polarity. On the other hand, similar to the results of Zdol2000 presented in Figs. 2 and 3, the results of Zdol4000 presented in Figs. 6 and 7 also show that the friction fluctuations were larger for Vertrel-XF than for HFE-7200. Compared with HFE-7200, Vertrel-XF has a higher solvent power, effectively disrupting the hydrogen bonding between PFPE polar end groups via strong solvent-solute interaction and thus dispersing PFPE molecules uniformly [2], [4]. In particular, the lower molecular weight components contained in the polydisperse Zdol2000 will be more soluble in Vertrel-XF than in HFE-7200 [4]. It was expected that friction fluctuations would be smaller for Vertrel-XF. The contradictory results obtained in this work suggest that friction stability is not exclusively determined by the uniform distribution of PFPE molecules in the solvent.

To evaluate the solvent effect quantitatively, the 60 000-point friction forces measured during one revolution of the disk at each external load were averaged. As an example, the results for Zdol2000 films are shown in Fig. 10. Only the initial and equilibrium results measured 0 and 72 h after film application

TABLE II
BONDED THICKNESS AND SURFACE ENERGY

| | Zdol2000/HFE-7200 | | Zdol2000/Vertrel-XF | |
|----------------------------------|---------------------------|----------------------------|---------------------------|----------------------------|
| | 0 h after film deposition | 72 h after film deposition | 0 h after film deposition | 72 h after film deposition |
| Bonded thickness (nm) | 0.1 | 0.3 | 0.1 | 0.3 |
| Dispersive surface energy (mN/m) | 13.78 | 13.65 | 14.06 | 13.95 |
| Polar surface energy (mN/m) | 17.95 | 11.98 | 17.04 | 10.65 |
| Total surface energy (mN/m) | 31.73 | 25.63 | 31.09 | 24.55 |

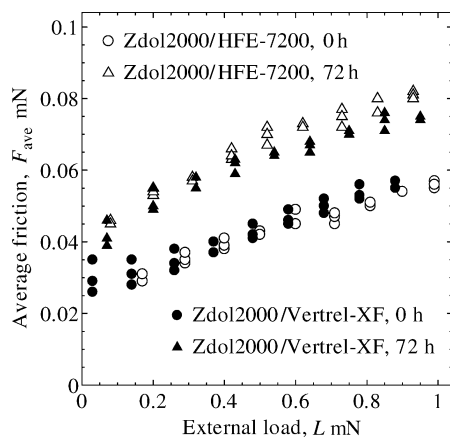


Fig. 10. Comparison of load-friction properties of Zdol2000 films coated with HFE-7200 and Vertrel-XF.

are shown for simplicity. The increase of friction with elapsed time was due to the development of lubricant bonding to disk surfaces, as discussed in [7]. In contrast to Figs. 2 and 3, solvent dependence was absent for the averaged friction forces. As seen from Fig. 4, the friction fluctuations were characterized by intermittent decrease of friction in narrow and sparsely distributed regions on the disk surfaces. Consequently, the average friction force was not affected very much by the friction fluctuations, and hence was roughly equal to the value of friction in the steady state, which is almost independent of the solvent.

The initial and equilibrium results of bonded thickness and of surface energy measured 0 and 72 h after film application for Zdol2000/HFE-7200 and Zdol2000/Vertrel-XF are listed in Table II. For both solvents, the bonded thickness increased, and the surface energy, in particular the polar component, decreased with elapsed time. PFPE molecules are subjected to the interaction from disk surfaces once after being coated. Therefore, PFPE molecules on the disk surfaces possibly maintain their conformation in solvents immediately after deposition, but will eventually transit to their equilibrium state determined mainly by the interaction with the disk surfaces. The transient behavior of friction approaching stabilization is considered to correspond to such changes in PFPE conformation. However, solvent dependence was not observed from the measurement results of bonded thickness. For surface energy, compared with Zdol2000/HFE-7200, Zdol2000/Vertrel-XF showed a slightly larger dispersive component, a slightly smaller polar component, and a slightly smaller value for the summation of the two components. However, at this time we cannot conclude whether this

result is meaningful. As seen from Fig. 4, the length scale of the friction fluctuating regions was less than 0.5° , which corresponds to 100- μm -order considering that the friction measurements were made at the disk radius of 20 mm. The difference in 100- μm -order microstructure of PFPE films induced by the solvents used for film deposition may not be discerned from the bonded thickness and surface energy measurements, which provide only macroscopic evaluations at the length scale of a millimeter. Measurement methods at high spatial resolution are needed for further investigation.

IV. CONCLUSION

Under the conditions of light load and slow rotation, we measured the friction properties of monolayer PFPE films coated on magnetic disk surfaces with the solvents HFE-7200 and Vertrel-XF. A transient friction behavior was observed for polar Zdol2000 and Zdo4000 films but not for nonpolar Z03 films. In the transient state, the films applied with Vertrel-XF exhibited remarkable friction fluctuations during one revolution of the disk as compared with those applied with HFE-7200. However, solvent dependence was absent for the average value of the friction during one revolution of the disk.

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