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The spreading behaviour of perfluoropolyether droplets on solid surfaces*

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The spread of perfluoropolyether (PFPE) droplets on solid surfaces has been measured from the top-down view through a microscope system. Effects of substrates, molecular weight and end-group functionality on spreading of the PFPE droplets have been studied experimentally and the results were compared with those by molecular dynamics (MD) simulations. Silicon wafer and diamond-like carbon (DLC) substrates were used to study the effect of substrates on spreading. Two types of PFPE, Z-dol and Z-tetraol, with the same chain structure and various molecular weights (2000 and 4000 g/mol) were employed in experiments. Effect of molecular weight has been investigated through comparing the spreading of Z-dol 2000 and Z-dol 4000, and it is found that the increase of molecular weight will decrease the mobility of PFPE. Comparison between spreading of Z-dol and Z-tetraol of the same molecular weight proved that functional end group plays a significant role on the spreading of PFPE, which confirmed the MD simulation results.

Keywords: perfluoropolyether, spreading, thin lubricant films, hard disk driver
PACC: 6810G, 6800

1. Introduction

The spontaneous spreading of perfluoropolyether (PFPE) lubricants on solid substrates has gained intensive attention, because of its great significance to the successful application of PFPE in hard disk drive system. A PFPE lubricant film with the thickness of 1–2 nm is applied to the disk surface. The film has to be stable and compliable enough in lifetime of the disk to guarantee normal reading and writing operations of the system. The study on the spreading behaviour of PFPE is critical for understanding the performance of PFPE films.

Spreading characteristics of PFPE films have been studied experimentally by many investigators. The PFPE films are most often deposited by dip-coating from solution.[1] The film thickness and uniformity are achieved by controlling the concentration of solution and the drawing rate from the solution. In many experimental studies of PFPE spreading, a sharp boundary of the PFPE film was created by partially immersing the disk into the solution. The evolution of the film boundary was recorded as a function of time for observing the film spreading. Many methods, such as the well-known SME (scanning microellipsometry) measurement[2−4] and other sophisticated techniques,[5−8] were applied to measure the time-dependent thickness profiles of PFPF films during the process of spreading. O'Connor *et al*[2,3] and Min *et al*[4] investigated the spreading behaviour of PFPE films on silica surfaces and examined the effects of various factors, such as the initial film thickness, end group functionality, molecular weight, temperature, humidity, etc. Ma *et al*[9,10] studied the spreading of PFPE on amorphous carbon surfaces as a function of the end group and molecular weight. They found a shoulder-like profile and complex molecular layered structure formed in the process of spreading for functional PFPE known as Z-dol, but not in the case of Z-type non-functional PFPE (denoted as Z in the following text). They also reported that the hydrogen and nitrogen contents in the carbon substrate, and the temperature as well, would affect the spreading of Z-dol on amorphous carbon surfaces.[11,12] Tynadll *et al* compared the spreading profiles of Z-dol and Z of different molecular weights on different substrates.[13] For functional and nonfunc-

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tional PFPE spreading on carbon-overcoated disk surfaces, Chen *et al* investigated the effects of surface energy, interfacial adhesion,[14] and humidity.[15] Despite the intensive efforts being made so far, the mechanism of PFPE spreading has not been fully understood. In addition to the above-mentioned experimental studies, another important approach is to observe a small PFPE droplet falling down on to solid surfaces. Li *et al* performed molecular dynamics (MD) simulations of PFPE droplets spreading on solid surfaces and lubricant-patterned substrates, in which the spreading droplets were carefully monitored through front and top views.[16−20] By experiments and Monte Carlo simulations, Zhang *et al* observed the spreading of PFPE droplets on solid surfaces with groove-shaped textures, and studied the effects of molecular weight and end-group functionality.[21,22] However, few experimental researches have been devoted to the top–down observation of PFPE droplets spreading on solid surfaces. The top–down observation can efficiently monitor the shape change of the PFPE droplet, and thus provide important information for understanding the spreading mechanism. In this paper, experiments are conducted for studying the spreading of PFPE droplets on three different solid substrates, and experimental results are compared with the simulations. Based on the experiment and comparison, the effects of substrates, and molecular weight and end-group functionality of the lubricant are discussed.

2. Experimental

2.1. Lubricant

The PFPE used in this work are monodisperse Z-dol (Z-dol 2000 and Z-dol 4000) and Z-tetraol (Z-tetraol 2000). These two kinds of lubricants have the same Z type backbone chain of

$$\mathrm{X}-\ [(\mathrm{CF_2}-\mathrm{CF_2}-\mathrm{O})_m-(\mathrm{CF_2}-\mathrm{O})_n]-\mathrm{O}-\mathrm{X}$$
$$(m/n\approx 2/3),$$

where X stands for the end group of the PFPE. The difference between them is that Z-dol has the end group of $-\mathrm{CF_2CH_2OH}$ while the end group for Z-tetraol is $-\mathrm{CF_2CH_2OCH_2CH(OH)CH_2OH}$. Kinematic viscosity values of PFPE are listed in Table 1.

Table 1. Kinematic viscosity of PFPE.

PFPE	Kinematic viscosity(cSt)
Z-dol 2000	85
Z-dol 4000	100
Z-tetraol 2000	2000

2.2. Experimental setup and measurement

To investigate the spreading of PFPE droplets on solid surfaces, measurements are made based on the phenomenon that the edge of the lubricant-covered area on solid surface can be identified and measured by the intensity of the light reflected from the surface of the droplet. In this way, we can record the spreading region of the PFPE droplet, from which further analyses can be made. The experimental setup is illustrated in Fig.1. The substrate was placed horizontally on a two-dimensionally controlled stage such that the acceleration effect caused by the gravity of the lubricant film could be minimized. Horizontal adjustments of the substrate were also allowed by the two-dimensionally controlled devices of the stage. To make the light beam better illuminating the lubricant area and avoid image noise caused by unwanted interference, an incoherent directional light source was used, projecting the light beam vertically through the ocular lens of the microscope. The reflected light beam from the object (solid surface) went through a microscope and received by a colour CCD camera, which transferred the image further to a personal computer, so that the images were identified through a series of image processing software, which would give a clear shape of the spreading droplet and a quantitative estimation of the spreading area.

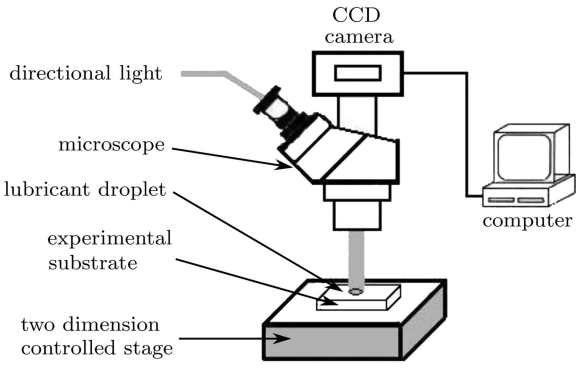


Fig.1. Experimental setup.

The experiments were conducted in the following procedure: First, PFPE of 1 μL was dripped on the solid substrate designated for test. This droplet started spreading on the surface immediately, and then the spreading process was monitored by measuring the shape of the droplet at different times. From the images given in Figs.2 and 4, one will see that the border of the spreading region is dark and clearly distinguished. A conventional microscope was used to receive the reflected light beam and observe the image of the spreading droplet. The images of the spreading droplet were then recorded by a CCD camera, showing the change of spreading area and the dynamic process of spreading. Finally, the images taken over a period of time were processed independently through image processing procedures, as listed in the following, for a quantitative estimation of the spreading.

Step 1 Convert the colour images into grey-scaled images.

Step 2 Identify the edge of the spreading region according to the gradual change of the grey level along the region edge.

Step 3 Fill the edge-surrounded region with pixels, and calculate the amount of the pixels contained in the spreading region.

Step 4 Convert the amount of the pixels into the actual area of the spreading region.

3. Results and discussions

3.1. Effect of substrate

Silicon (100) wafer and two kinds of diamond-like carbon (DLC) films were used in our experiment as the substrate for investigating their effects on the spreading of PFPE. One type of the DLC films was prepared by unbalanced magnetron sputtering (UMS) method[23] (denoted as DLC-U in the following), while the other by filtered cathodic vacuum arc (FCVA) method (denoted as DLC-F in the following). Both DLC-U and DLC-F are amorphous carbon films, with fractions of 60% and 70% sp3, respectively. The surface energies of the substrates were obtained with standard contact angle measurement. The Girifalco–Good–Fowkes–Young equation

$$\cos\theta = -1 + \frac{2}{\gamma_{\mathrm{L}}}\left[\left(\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}\right)^{1/2} + \left(\gamma_{\mathrm{S}}^{\mathrm{p}}\gamma_{\mathrm{L}}^{\mathrm{p}}\right)^{1/2}\right] \qquad (1)$$

was used to determine the surface energies from the measured contact angle data. Superscripts d and p refer to the dispersive and polar components of the surface energy, respectively. The dispersive component of the substrate's surface free energy, $\gamma_{\mathrm{S}}^{\mathrm{d}}$, has to be determined first, in terms of the contact angle (θ_{d}) obtained from the dispersive test using liquid n-dodecane with a known $\gamma_{\mathrm{L}}^{\mathrm{d}}$ value ($\gamma_{\mathrm{L}}^{\mathrm{d}} = 25.3\,\mathrm{mN/m}$):

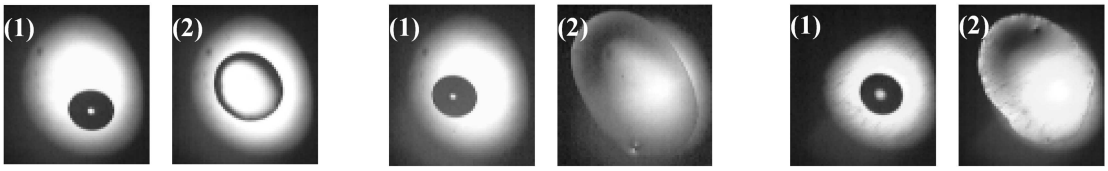
$$\gamma_{\mathrm{S}}^{\mathrm{d}} = \frac{\gamma_{\mathrm{L}}^{\mathrm{d}}\left(1+\cos\theta_{\mathrm{d}}\right)^2}{4}. \qquad (2)$$

Subsequently, the substrate's polar component, $\gamma_{\mathrm{S}}^{\mathrm{p}}$, is determined in terms of the contact angle (θ_{w}), which is measured from the polar test by using liquid deionized water, whose surface energy components are known as $\gamma_{\mathrm{L}}^{\mathrm{d}} = 21.8\,\mathrm{mN/m}$ and $\gamma_{\mathrm{L}}^{\mathrm{p}} = 51.0\,\mathrm{mN/m}$:

$$\gamma_{\mathrm{S}}^{\mathrm{p}} = \frac{1}{4\gamma_{\mathrm{L}}^{\mathrm{p}}}\left[\gamma_{\mathrm{L}}\left(1+\cos\theta_{\mathrm{w}}\right) - 2\sqrt{\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}}\right]^2. \qquad (3)$$

The final surface energy of the substrate $\gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{S}}^{\mathrm{p}}$ is listed in Table 2.

Notably, the surface energy value of silicon wafer is far smaller than those of the DLC films, and between the two DLC films, DLC-U has a surface energy lower than DLC-F. The same amount of Z-dol 2000 (1μL) was dripped on the three substrates，and the images of spreading region were recorded at the beginning and later stages of the test, as shown in Fig.2. It is obvious that the spreading of Z-dol 2000 on DLC films is much faster than that on silicon wafer. The droplet on silicon wafer can still hold its shape 24 h after the dripping, while that on DLC films already spreads over the measuring scope in this time.



(a) (b) (c)

Fig.2. Comparison of Z-dol 2000 spreading on different substrates: (a) on silicon wafer for (1) 30 s and (2) 24 h after dripping; (b) on DLC-U for (1) 30 s and (2) 24 h after dripping; (c) on DLC-F for (1) 30 s (2) 24 h after dripping.

Since the spreading area A of the droplet changes with time t, the time evolution of the spreading area can be regarded as a good measurement of a spreading process. Spreading area of Z-dol 2000 on the three substrates is plotted in Fig.3, against elapsed time t in a logarithmic scale, where A is the area increment defined as the difference between the current spreading area and its initial value. As is shown, two stages of spreading are clearly visible that the spreading curves in stage I exhibits a larger slope than that in stage II, which agrees with the observations from other investigators.[3,21,22] A possible explanation for the phenomenon is that spreading in the first stage is a combination of downward flow and the horizontal molecule movement along the substrate; and after most of the molecules landed on the substrate, spreading is dominated by molecule diffusion.[17] It is this different nature in molecule motion results in the difference between spreading speeds as is shown in Fig.3.

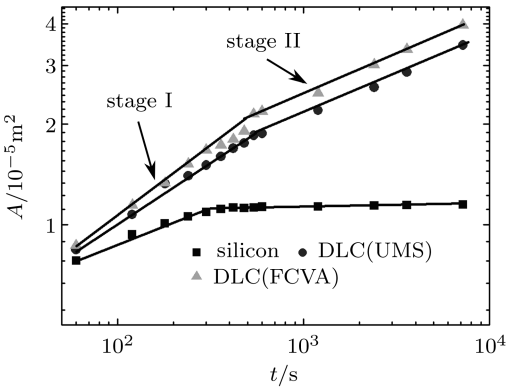


Fig.3. A–t plot for Z-dol 2000 on different substrates.

Comparing the spreading on DLC films with that on silicon wafer in Fig.3, it is obvious that the spreading rate on DLC is much faster. There are two possible reasons for the result: First, the surface energy of DLC is higher (Table 2), and the higher surface energy will enhance the surface-molecular interaction that can overcome the cohesion of spreading substance, caused by the attractive intermolecular interaction, and thus prompt the spreading. Second, the DLC films used in our experiment consist mostly of amorphous carbon, which is chemically inactive with PFPE molecules[11] while the Si atoms on the surface of silicon wafer can easily interact with Z-dol hydroxyl end groups and decrease the mobility of Z-dol 2000 on the substrate.[24] Accordingly, it is much easier for Z-dol to spread on DLC-U and DLC-F than on silicon wafer. However, there is an unexpected result to be noticed in Fig.3 that although the surface free energy of DLC-F is much higher than DLC-U as listed in Table 2, the spreading rates of Z-dol 2000 on both DLC films seem very close to each other. There is no detailed explanation for this phenomenon at present. This implies the complication of the way that a substrate would affect spreading behaviour, hence further investigations are required.

Table 2. Surface energies of experimental solid substrates.

surface	surface energy(mN/m)
silicon wafer	0.258
DLC-U	1.179
DLC-F	11.022

3.2. Effect of molecular weight

To investigate the effect of molecular weight, the spreading of Z-dol 2000 and Z-dol 4000 on silicon wafer was measured, and their corresponding images of spreading regions are shown in Figs.4(b) and 4(c), respectively. From the images recorded during the spreading process, the A–t plot in a logarithmic scale (spreading area versus time) is obtained as illustrated in Fig.5. The two-stage spreading appears again, which is explained by the same reason mentioned above in discussing the effect of solid substrate. Compared with Z-dol 2000, the spreading of Z-dol 4000 is much slower with a longer stage I. As the molecular weight increases, both intermolecular and substrate-molecular interactions will be strengthened, of which the result is somewhat complicated. The increased intermolecular interactions will lead to a stronger cohesion of the spreading lubricant, which means an increase in resistance to the molecule motion, but on the other hand, the enhanced substrate-molecule interaction is expected to provide a larger driving force for the spreading. Figure 5 demonstrates that as a whole the spreading of Z-dol 4000 on silicon wafer is slower, and in particular with a longer stage I, in comparison with that of Z-dol 2000, which means that it will take more time for Z-dol 4000 molecules in the upper layers to reach the surface of substrate. We also find that the spreading behaviour of PFPE in stage I may also be affected by the lubricant's viscosity. As is shown

in Table 1, the kinematic viscosity of Z-dol 4000 is higher than that of Z-dol 2000, indicating that it will be easier for Z-dol 2000 to spread out than for Z-dol 4000 at the first stage. However, viscosity will show little effect on the second stage when the spreading is dominated by molecule diffusion.

3.3. Effect of end group functionality

To study the effect of end group functionality, the spreading of Z-dol 2000 and Z-dol 4000 on silicon substrate will be compared with that of Z-tetraol 2000 on the same substrate. The images of spreading region for the lubricants concerned are shown in Fig.4 with their A–t plots compared in Fig.5. The first comparison is made between two types of lubricants, Z-tetraol 2000 and Z-dol 2000, which have the same molecular weight but have the end group of different functionalities. Figure 5 shows that the spreading rate of Z-tetraol 2000 is remarkably slower, indicating that the functionality does have a significant effect on spreading. Z-tetraol 2000 has two hydroxyl groups on its each end, which are able to form chemical bond with Si atoms on the silicon wafer and slowing the spreading, while Z-dol 2000 has such a functional group only at one end. So the adhesion of Z-tetraol 2000 to the substrate will be enhanced and the spreading rate will be reduced. The significant role of the end group functionality can be further revealed by comparing the

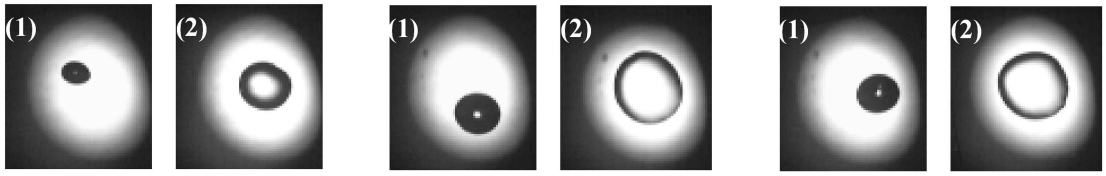


Fig.4. Comparison between different PFPE spreading on silicon wafer: (a) Z-tetraol2000 for (1) 30 s and (2) 24 h after dripping;(b) Z-dol 2000 for (1) 30 s and (2) 24 h after dripping;(c) Z-dol 4000 for (1) 30 s and (2) 24 h after dripping.

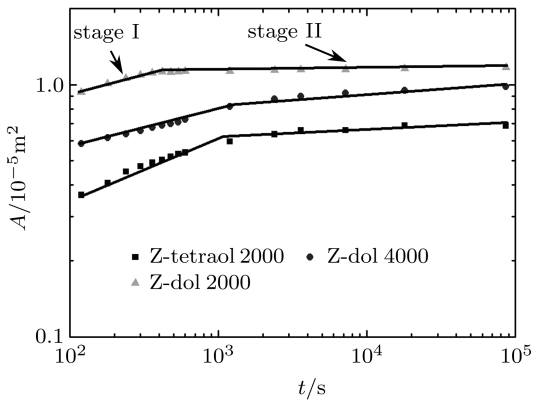


Fig.5. A–t plots for Z-dol 2000, Z-dol 4000 and Z-tetraol 2000 spreading on silicon wafer.

spreading of Z-tetraol 2000 with that of Z-dol 4000. As is also illustrated in Fig.5, the mobility of Z-tetraol 2000 molecules appears lower than that of Z-dol 4000, even though its molecular weight is half that of Z-dol 4000, suggesting that the functionality effect in this case is stronger than the effect of molecular weight. In view of the effect of viscosity, we find that the kinematic viscosity value of Z-tetraol 2000 is much higher than that of Z-dol, as compared in Table 1. Hence the spreading ability of Z-tetraol 2000 at the first stage will be weakened dramatically. The difference in end groups has led to a huge difference in kinematic viscosity values, which indicates the importance of end group effect on spreading behaviour of PFPE lubricants.

3.4. Comparison to simulations

For further examination of the effect of end-group functionality on the PFPE spreading, we compare the experiments with the prediction from the MD simulations, obtained in Ref.[25]. The simulations were performed for the PFPE droplets with end-groups of different functionalities, spreading on the same kind of substrate. More details for the simulation can be found in Ref.[25]. Spreading profiles of the PFPE droplets at the time steps $t = 500000$ are plotted on the X–Y plane, as shown in Fig.6, which mimics a top view of spreading droplets. Results showing in Figs.6(a) and 6(b) are, respectively, for the PFPE

with moderate end-group functionality corresponding to Z-dol, and the PFPE with strong end-group functionality corresponding to Z-tetraol. Based on the discussions in Section 3.3, it is revealed experimentally that on the same kind of substrate, silicon wafer, spreading speed of Z-dol is obviously faster than that of Z-tetraol. From the simulation point of view, the spreading speed of PFPE with moderate end-group functionality is apparently faster than that of PFPE with strong end-group functionality, as can be seen in Fig.6. Simulations and experiments reach the same conclusion that end-group functionality makes a great contribution to the mobility of PFPE, and that the molecules with stronger functionality move slower on solid surfaces.

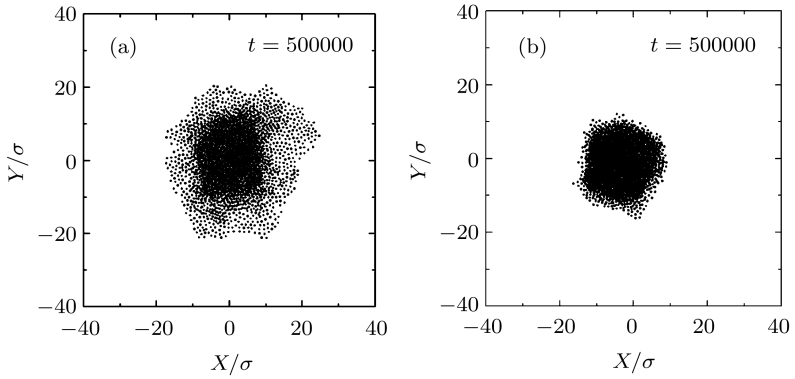


Fig.6. X–Y spreading profiles of simulation for PFPE droplets with different end-group functionalities $t = 500000$ molecular dynamic steps. (a) PFPE with moderate end-group functionality; (b) PFPE with strong end-group functionality.

4. Conclusions

Spreading of PFPE (Z-dol and Z-tetraol) droplets on DLC films and silicon wafer has been studied by measuring the changes in spreading area, with the main concern on the effects of substrate, molecular weight and end group functionality. From the time evolution of the spreading area, it is observed that spreading appears to be a two stages process. The spreading in the early stage, which consists of both downward flow and horizontal movements of molecules, proceeds faster than the spreading in the final stage which is mainly surface diffusion. Spreading rate will increase in general for the lubricants on substrates with higher surface energy. Besides, chemical activity between the substrate and lubricant molecules may also contribute to the spreading behaviour. An increase in molecular weight can lead to a decrease in lubricant mobility mainly because of the increase of intermolecular cohesion. The end-group functionality definitely plays an important role in spreading, and it caused molecules with stronger end-group functionality to exhibit lower mobility and longer spreading time, which agrees with the prediction from MD simulations.

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