EFFECT OF PARTIALLY FLUORINATED ALKYL CHAIN ON FRICTION FOR MAGNETIC MEDIA

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SUMMARY
Partially fluorinated carboxylic acid derivatives are synthesized and macroscopic friction and wetting properties are examined. The carboxylic acid adsorbs at the magnetic tape surface with high orientation but the ester has a weak interaction and its film is isotropic, which are suggested by surface energy and FTIR measurements of the film. Friction coefficient does not depend on fluorine content in the lubricant molecules, not only for highly orientated layer but also for the isotropic film. This seems to be caused by the anchoring effect. Macroscopic friction is largely dependent on the polar group not on the outermost surface property.

Keywords: magnetic recording media, fluorocarbon, friction, surface energy, FTIR

1 INTRODUCTION
Organofluorine compounds possess a variety of unique chemical and physical properties. Many of these properties result from the low cohesive interactions between neighboring fluorocarbon chains, which are believed to lead to low surface energy and low friction. These and other properties, e.g. low dielectric constants, thermal and oxidative stability, and effective heat dissipation have led us to use fluorocarbons as the most popular lubricant for magnetic thin film media. Thickness of such film is several nanometer, hence, molecular level descriptions of the interactions that control the friction and chemical properties of these films are fundamentally important. One approach for examining the molecular level details of organic thin films is the use of spontaneously adsorbed monolayer of perfluoro carboxylic acid salt which exhibit a high degree of structural order on the magnetic surface [1]. To date, many studies of the frictional properties of organofluorine compounds have been performed with respect to the magnetic thin film media. Comparatively little is known concerning the wettability and structure of lubricant films of monolayer thickness containing fluorocarbon moieties [2].

This study examines the relation of structure and wetting properties of spontaneously adsorbed monolayer of terminal perfluoroalkyl derivatives (CF₆(CF₂)₉(CH₂)₆COOR; where R=H or C₄H₉) to friction coefficient at the magnetic tape surface. The structure and spatial arrangement of these monolayer were examined by infrared reflection spectroscopy (RAS); the wetting properties were probed by contact angle measurements.

2 EXPERIMENTAL

2.1 Lubricant synthesis
Long chain alkanoic acids with perfluoroalkyl(Rₖ) terminal segment and their derivatives were synthesized with perfluoroalkanes and terminal unsaturated acids.[3] The addition products were reduced to alkanoic acid and have a terminal Rₖ. Two series of terminal segmented acids were prepared. First, the number of carbon atoms in perfluoroalkyl segment is 4 to 12 with the same alkylene segment of 10. Second, the partially fluorinated stearic acid whose total carbon number is 18, however the ratio of hydrocarbon and perfluorocarbon is different. The lubricant were deposited on the magnetic tape by dip coating in n-hexane/ethanol(9/1) solution at the concentration of 0.25 mmol/l, where thickness of the lubricant was approximately monolayer [1].

2.2 Friction measurements
The apparatus is the same as we used in the previous paper [1]. We used magnetic tapes with a magnetic layer of Co-15wt.%Ni thin films of thickness 0.2 mm. The magnetic layer was vapor deposited by the oblique incident method. Coefficients of kinetic friction were measured for 8mm wide tapes sliding around a quadrant of a 4mm diameter polished stainless steel (SUS 304) cylinder. The friction coefficients were calculated from the change in the tension exerted by a 20 g weight hanging from the tape sliding on the cylinder at a speed of 5 mm/s. The tests were performed at 25 % and 60 % relative humidity. The coefficient of friction between the tape and the cylinder was obtained from: \( \mu = \frac{2}{\pi \ln(T_1/T_2)} \)

2.3 FTIR
The structure of the lubricant layers was investigated using FTIR reflection absorption spectra (FTIR-RAS). During measurement, the IR beam of p-polarization was incident at 80 degrees with respect to the substrate normal. The resolution was 2 cm⁻¹ and the number of scans was 250. It is difficult to obtain high quality FTIR-RAS spectra of the lubricant layers on the actual thin film magnetic tapes, because the reflectance of the Co-Ni magnetic layer is too low in the infrared region. Therefore substrates use a prime-evaporated Aluminum layer of about 0.1 μm thickness under the Co-Ni magnetic layer, evaporated under the same condition as the actual thin film tapes [1]. This substrate ensures procurement of high quality spectra even for monolayer, since the IR beam is strongly reflected at the magnetic layer and aluminum layer interface.
2.4 Contact angle

Contact angles were determined at room temperature and nearly 100% relative humidity for water and ambient for methylene iodide. The contact angle was obtained by forming a 1 µL drop of water, lowering the needle until the drop touched the surface, and raising the needle. As the drop detached itself from the needle tip, it advanced over the surface.

3 RESULTS AND DISCUSSIONS

3.1 Frictional results

The frictional characteristic of the partially fluorinated carboxylic acid is shown in Figure 1. The friction coefficient is plotted as a function of the number of reciprocating motion. The friction coefficient was constant and was about 0.30 after several reciprocating motions. In this paper friction coefficient after 100 motions were used.

![Figure 1: Change in friction of metal evaporated tape coated with partially fluorinated carboxylic acid (C8F17C9H18COOH).](image1)

In order to investigate the effect of the number of fluorinated carbon on friction coefficient, the carboxylic acid with different fluorinated carbon chains were synthesized, but the hydrocarbon chain length (number of methylene) was fixed by 10. The results of the surface properties and friction coefficient were plotted in Figure 2.

The surface energy was gradually reduced with the carbon number and remained nearly constant at 10 erg/cm² above the fluorinated carbon number of 6, which agrees with values obtained for the perfluoro octanoic acid monolayer. This indicates that the carboxylic acid group is adsorbed on the magnetic layer and the outermost part is occupied by CF₃ group. The lower contact angles are likely due to greater disorder (or diminished amphiphile density on the surface) resulting from the short chain length of perfluoroalkyl chain. In light of the stabilization energy from Van der Waals interaction, longer fluorocarbon chain has a higher cohesive energy.

The results of friction measurements are also presented in Figure 2. This shows plots of the friction coefficient after 100 reciprocating motions vs. number of fluorocarbons in the molecule. The friction coefficients were about 0.31 and was shown to be independent of the number of fluorocarbons.

![Figure 2: Relation between surface energy and friction of partially fluorinated carboxylic acid CₙF₂₅C₁₀H₂₀COOH.](image2)

However, since the total carbon number of the acid is different in this measurement, we can not conclude in the strict sense of the word that the friction coefficient does not reflect the surface energy.

Next, we synthesized partially fluorinated stearic acids which have 18 carbon atoms but the ratio of hydrocarbon and fluorocarbon is different. Figure 3 shows the results of friction coefficient and surface energy of these acids. For stearic acid without fluorocarbon the surface energy was higher than the partially fluorinated stearic acids, that have nearly the same value of 10 erg/cm², but the friction coefficient was of around 0.3. It can be said that there is no correlation between the surface energy for the friction coefficient of stearic acid and the partially fluorinated stearic acid.

![Figure 3: Relation between the surface energy and friction of partially fluorinated stearic acid](image3)
The friction tests were carried out for the butyl esters of the above acids, because the ester group has a weaker interaction on the surface compared to the carboxylic acid. The results are shown in Figure 4. For these esters, the friction coefficient was higher than the acid and were almost constant in spite of the surface energy decreasing with the fluorinated proportion.

![Figure 4: Relation between surface energy and friction coefficient of partially fluorinated butyl stearate.](image)

3.2 Characterization of FTIR

The structure and molecular orientation of the film of terminal perfluorinated acids and their derivatives were probed with RAS. Table 1 lists the observed wave-numbers assigned to the appropriate mode [3].

The peaks near 2850 and 2920 cm\(^{-1}\) are the symmetric and asymmetric methylene stretches respectively. For the acid, the peak of the bulk acid of 2918 and 2849 cm\(^{-1}\) indicates the solid-phase absorption. However the shift toward the higher frequency was observed in the lubricant film, which was interpreted as the result of a more liquid like environment of the methylene units. The methylene group in the film has been perturbed with the incorporated perflouro species at the molecular scale. That is, the cross-sectional occupied area of hydrocarbon and fluorocarbon is about 20\(\nu\)\(^2\) and 40\(\nu\)\(^2\) respectively, therefore, the hydrocarbon sequence is covalently bonded to a fluorocarbon helix which has an inherently larger cross section preventing any close approach of the other alkyl portion. For the ester, the absorption of both the bulk and the film in the higher frequency region shows a liquid phase.

We focus here on the CF stretching region (Figure 5) which can give us an insight into the packing and orientation of the fluorinated alkane chain. For the acid, (a)Acid note the substantial differences in the relative intensities between the monolayer and the bulk(isotropic). In the isotropic spectrum, 1248 cm\(^{-1}\) band is observed as a medium shoulder on the high frequency side of the more intense 1220 cm\(^{-1}\) band [4]. As seen in Figure 5 an increase of the 1248 cm\(^{-1}\) band relative to that at 1220 cm\(^{-1}\) reveals the orientation of fluorocarbon chains.

| Peak position, cm\(^{-1}\) | Vibration mode  \\
<table>
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<tbody>
<tr>
<td>Bulk</td>
<td>As monolayer</td>
</tr>
<tr>
<td>2918 (s)</td>
<td>(v_d(CH_2))</td>
</tr>
<tr>
<td>2849 (s)</td>
<td>(v(CH_2))</td>
</tr>
<tr>
<td>1369 (m)</td>
<td>(v(CF_2, A_1))</td>
</tr>
<tr>
<td>1300 (m)</td>
<td>(v(CC, E_1))</td>
</tr>
<tr>
<td>1249 (m)</td>
<td>(v(CF_2, E_1))</td>
</tr>
<tr>
<td>1205 (m)</td>
<td>(v(CF_2, A_2)+v(CF_3))</td>
</tr>
</tbody>
</table>

\(v\) – stretch; \(v_s\) – symmetric stretch; \(v_a\) – asymmetric stretch

Table 1: Mode assignment and peak position for partially fluorinated carboxylic acid(a) and ester(b) in bulk and as monolayer adsorbed at CoNi evaporated tape.

These similar effects are observed in the IR spectra of Langmuir-Blodget film of perfluorinated carboxylic acid [5] and the spontaneously adsorbed fluorinated alkane thiol on gold [4]. Of the strong absorption in Figure 5, 1242 and 1158 cm\(^{-1}\) belong to the E1 symmetry and exhibit perpendicular dichroism. The fact that both of these bands show up in this polarization, i.e. perpendicular direction with respect to fluorocarbon helix axis, indicates that the fluorocarbon helices are tilted relative to the surface.

For the ester group, the CF\(_2\) stretching with A\(_2\) and E\(_1\) symmetry is the same as the spectrum of the bulk. Thus, the fluorocarbon chain in the lubricant film tended towards the isotropic orientation.

Several studies have demonstrated that the atomic force microscopy (AFM) can provide an important new view of ultra-thin well-ordered organic films such as Langmuir-Blodget films. Friction force microscopy enriched the AFM scanning technique providing a material specific distinction on the nanometer scale. Generally speaking, fluorocarbon films have a higher friction force than the hydrocarbon films with very small load on the order of 10^{-8} N [7]. However practically, 8mm video system uses the tension of 10^{-1} N, which brings about different consideration between microscopic and macroscopic results.
From our experimental, friction coefficient largely depends on the hydrophobic group but not surface energy, that is the outermost surface, and not slight disorder of the hydrophobic chain in the film. This indicates that the surface contact occurs throughout the film and reaches the polar group, therefore anchoring effect of the lubricant becomes important factor for friction reduction in the real condition. The ester with smaller affinity to the surface gives rise to higher friction than the carboxylic acid with larger affinity.

FTIR study reveals that the partially fluorinated carboxylic acid film forms like a self-assemble layer but the orientation of their ester is isotropic. These seem to be also caused by difference in strength of affinity of the polar group.

4 CONCLUSIONS

Partially fluorinated carboxylic acid derivatives are synthesized and macroscopic friction and wetting properties are examined. From FTIR investigation, the carboxylic acid adsorbs at the tape surface with high orientation but the ester film is isotropic, which are also suggested by surface energy of the film. Frictional coefficient does not depend on fluorine content in the lubricant molecules, not only for highly orientated layer but also for the isotropic film. This seems to be caused by the anchoring effect. In the high load system friction is largely dependent on the polar group but not on the outermost surface property.

5 REFERENCES