Microscopic Spreading of Nonpolar Perfluoropolyalkylether Film

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무극성 perfluoropolyalkylether 박막의 미시적 퍼짐

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ABSTRACT

The spreading mechanism of nonpolar perfluoropolyalkylehter (PFPE) on carbon surfaces is proposed. For the thin thin-film regime. adsorption-desorption is a main driving force for spreading. and the surface diffusion coefficients increase as the film thickness increases. Two dimensional van der Waals equation is employed to explain the dependency of surface diffusion coefficient on the film thickness. For the thick thin-film regime. the spreading characteristic is determined by the disjoining pressure gradient. The present theoretical analysis explain the dependence of surface diffusion coefficients on film thickness reasonably.

Key words : Microscopic spreading. disjoining pressure. two-dimensional van der Waals equation. perfluoropolyalkylehter

Ⅰ. Introduction

The spreading of liquid films on solid surfaces in the macroscopic regime has been extensively investigated[1]. However. the microscopic spreading behavior is quite different from the macroscopic case. At the microscopic scale for a film thickness less than 10nm. the spreading is governed by the forces originating from the disjoining pressure gradient[2]. The spreading behavior of small drops of polydimethylsiloxane (PDMS) on silica surfaces has been intensively studied by Heslot et al.[3]. Cazabat et al.[4]. Valignat et al.[5]. and Fraysse et al.[6]. Although several theoretical efforts attempt to

explain the experimental observations[2,4]. the understanding of microscopic spreading of liquid film is still unclear. The spreading of ultra-thin. polymer lubricant films on solid surfaces has attracted considerable interests due to its application in the lubrication of magnetic recording media. Novotny[7] has investigated the spreading of polyperfluoropropylene (PPFPO) on silica surfaces using scanning micro-ellipsometry and scanning photoemission spectroscopy. The surface diffusion coefficient increased as the film thickness decreased down to 1nm. and was constant below this value. The spreading characteristics of perfluoropolyalkylethers (PFPE) on silica surfaces has been investigated as a function of initial film thickness. end group functionality. molecular weight. temperature and humidity by Min et al.[8]. O'Connor[9] and Ma[10] using scanning micro-ellipsometry. They

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extract the surface diffusion coefficients from the spreading profiles by employing Matano interface method[11]. In present work. the spreading of nonfunctional PFPE on carbon surfaces was studied. We analyzed the surface diffusion coefficients in two separate regimes. For the thicker regime. a hydrodynamic approach with a slip boundary condition was applied. For the thinner regime. we assumed adsorption-desorption is the main mechanism for spreading. We explain the dependence of surface diffusion coefficients on film thickness systematically.

II. Theoretical Analysis

It is well known that the driving force for microscopic spreading is the disjoining pressure gradient along the spreading direction. For film thickness greater than several monolayers (thick thin-film). conventional hydrodynamics are assumed to be valid[2]. However. for film thickness less than a monolayer (thin thin-film). adsorption and surface pressure play important roles in spreading[4]. In the intermediate range. we assume the hydrodynamic analysis with slip effects is applicable.

If the liquid in the film can be treated as a Newtonian fluid. the Navier-Stokes equation is used as a governing equation of motion for the relatively thick film in the following form[2]:

$$-\eta \frac{\partial^2 v}{\partial z^2} = \frac{\partial \Pi}{\partial x} \qquad (1)$$

where η is the viscosity of liquid. v is the velocity in the x direction. and. For film heights $h \gg h_0$. where h_0 is characteristic mono-layer thickness. conventional hydrodynamics can be assumed to be valid. The following conventional no-slip boundary condition can be applicable to the solid-polymer

interface:

$$v = 0 \qquad \text{at} \qquad z = 0 \qquad (2)$$

And. at the liquid-air interface. the following stress-free condition is applicable:

$$\frac{\partial v}{\partial z} = 0 \qquad \text{at} \qquad z = h \qquad (3)$$

The velocity profile satisfying the above eqs. (1)-(3) is

$$v(z) = -\frac{1}{\eta} \frac{\partial \Pi}{\partial x} \left(\frac{z^2}{2} - hz \right) \qquad (4)$$

The associated volumetric flow rate is given by

$$q = \int_0^h v(z) dz = \frac{1}{\eta} \left(\frac{h^3}{3} \right) \frac{\partial \Pi}{\partial x} \qquad (5)$$

The disjoining pressure for a liquid with non-reactive end group is assumed to be governed by van der Waals interactions of the following form[13]:

$$\Pi = \frac{A}{6\pi h^3} \qquad (6)$$

It is known that thin films flow faster than thick films for a particular gradient in film profile. $\partial h / \partial x$.

In the general case. the continuity equation is written as.

$$\frac{\partial h}{\partial t} = -\frac{\partial q}{\partial x} \qquad (7)$$

By combining eqs. (6) and (7). we obtained the following surface diffusion equation:

$$\frac{\partial h}{\partial t} = \frac{A}{6\pi\eta} \frac{\partial}{\partial x} \left[\left(\frac{1}{h} \right) \frac{\partial h}{\partial x} \right] \qquad (8)$$

which is also expressed as

$$\frac{\partial h(x, t)}{\partial t} = -\frac{\partial}{\partial x}\left[D_s(h)\frac{\partial h(x, t)}{\partial x}\right] \qquad (9)$$

where the quantity   can be interpreted as a thickness-dependent surface diffusion coefficient.

It is assumed that the molecular weight effect on surface diffusion coefficient is implied in η. The dependency of zero shear viscosity on the molecular weight has the following forms[14],[15]:

$$[\eta]_0 \propto M \qquad (M < M_c) \qquad (10.a)$$

$$[\eta]_0 \propto M^{3.4} \qquad (M < M_c) \qquad (10.b)$$

whrere M_c is the critical molecular weight. Therefore. we can assume that the dependency of the surface diffusion coefficient on the molecular weight has the form of $D_s \propto M^{-1 \sim -3.4}$. The molecular weights of our sample are quite small. So we expect that $D_s \propto M^{-n}$. $n \approx 1$.

For the sub-monolayer regime. the velocity v_m can be written as[4]

$$v_m = -\frac{V_M}{\alpha}\frac{\partial \Pi}{\partial x} \qquad \text{for} \qquad h < h_0 \qquad (11)$$

where V_M is the molecular volume. α is the friction coefficient between the molecule and the surface. Π is the disjoining pressure and h_0 is the monolayer thickness. This relationship is quite similar to Darcy law for flow through the porous media. The resistance term of this relationship. α/V_M. corresponds to that of Darcy's law η/K. There are some models for the friction coefficient. α [16]. however. rigorous models have not been developed. The corresponding sub-monolayer surface diffusion coefficient D_M is

$$D_M = -\frac{V_M}{\alpha}h\frac{\partial \Pi}{\partial h} \qquad (12)$$

For thin films. the two-dimensional pressure $P(h)$ is commonly used for describing monolayers. This pressure is correlated with the disjoining pressure as follows[17]:

$$P(h) = -h\Pi(h) + \int_0^h \Pi(h)\,dh \qquad (13)$$

Therefore. the sub-monolayer surface diffusion coefficient is expressed as:

$$D_M = \frac{V_M}{\alpha}\frac{\partial P}{\partial h} \qquad (14)$$

For the ultra thin film $(h \to 0)$. $P(h)$ is given by the two dimensional perfect gas law. as follows:

$$PS = kT \qquad (15)$$

where S is the molecular area. The equivalent film thickness can be expressed as:

$$h = \frac{V_M}{S} \qquad (16)$$

By combining the eqs. (14) ~ (16). the limiting value for D_M can be obtained as:

$$D_0 = D_M(h \to 0) = kT/\alpha \qquad (17)$$

This value corresponds to the diffusion coefficient of an isolated molecule on the surface. For the thicker case. we employ the two-dimensional van der Waals equation as the equation of state for the thin film[17].

$$\left(P + \frac{a}{S^2}\right)(S - b) = kT \qquad (18)$$

where a and b are the cohesion parameter and excluded area. By combining eqs. (13) and (17). and neglecting higher order terms. the following relation is assumed to be good approximation of the surface diffusion coefficient for the sub-monolayer

regime:

$$D_M = \frac{kT}{\alpha} \left[\frac{1}{(1 - bh/V_M)^2} - \frac{2a}{kTV_M} h \right] \quad (19)$$

It is well-known that the parameters. a and b have the relation of $a \propto kT\sigma^2$ and $b \propto \sigma^2$. where molecular diameter σ and the molecular area S_M has the relation of $\sigma^2 \propto S_M \approx V_M/h$. For the sub-monolayer regime. molecules have relatively flat conformation[12], so can be assumed to be independent of molecular weight. In this case. if we neglect the higher order terms of bh/V_M the above relation for the surface diffusion coefficient in the sub-monolayer region is expressed as

$$D_M = \frac{kT}{\alpha} [1 + \gamma h] \quad (20)$$

where γ is a constant that is independent of molecular weight. The molecular weight dependence on surface diffusion coefficients is implied in α. If it is assumed that the friction factor coefficient between surface and molecule. α. is proportional to the area which the molecule contacts the surface. the dependency of surface diffusion coefficients in this regime depends on the molecular conformation on solid surfaces.

Novotny et al.[18] suggested that the surface conformation of polyperfluoropropylene oxide (PPFPO) is different from the bulk conformation. A two-layer model with interfacial and bulk layers was proposed: The interfacial layer. with a thickness of 1-2 monolayers. has the molecular chains preferentially extended along the surface. The remaining second layer has a normal bulk polymer conformation. According to their suggestion the friction coefficient. α. is nearly proportional to molecular weight of each polymer. so the surface diffusion coefficient shows the relation of

$$D_s \propto 1/M_n.$$

III. Comparison with Experiments

The polymeric liquid used in this work is PFPE Z. which has the following chemical structure:

$$CF_3 - [(OCF_2 - CF_2)_n - (OCF_2)_m] - OCF_3$$
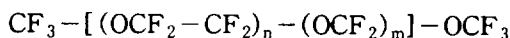
where $n/m \approx 2/3$. The spreading profile of PFPE Z on an amorphous carbon surface was measured by using scanning micro-ellipsometry[10]. To extract the surface diffusion coefficients. the Matano Interface method[11] which extracts the thickness-dependent diffusion coefficient directly from the film profile was employed. Since the spreading is measured in the direction perpendicular to the film boundary. the spreading process is described by a one-dimensional diffusion equation as:

$$\frac{\partial h(x, t)}{\partial t} = \frac{\partial}{\partial x} \left[D_s(h) \frac{\partial h(x, t)}{\partial x} \right] \quad (9)$$

where $h(x, t)$ is the thickness of the film at a distance x from the initial film boundary at time t. and $D(h)$ is the thickness-dependent diffusion coefficient. The integration of eq. (10) under the sharp initial film boundary condition gives:

$$D_s(h) = -\frac{1}{2} \left(\frac{dx}{dh'} \right)_{h' = h} \int_0^h x dh' \quad (21)$$

with the condition:

$$\int_0^h x dh' = 0 \quad (22)$$

Equations (21) and (22) allow $D_s(h)$ to be calculated from an experimentally measured spreading profile.
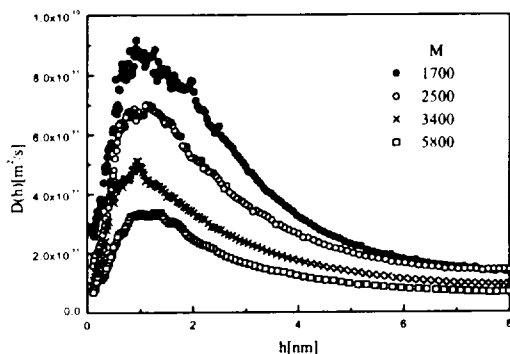
Fig. 1 shows the diffusion coefficient $D_s(h)$ as a

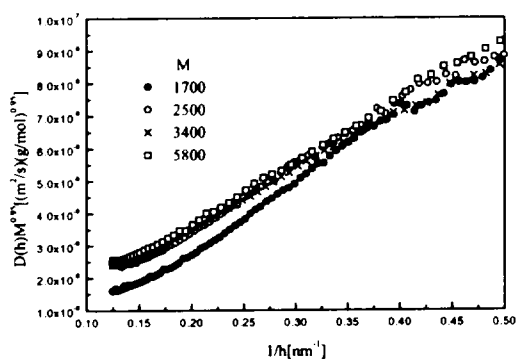Fig. 1 Experimental data of surface diffusion coefficient of PFPE-Z[10]

Fig. 2 Comparison between the present analysis with experimental data of Ma[10] for thick thin-film regime
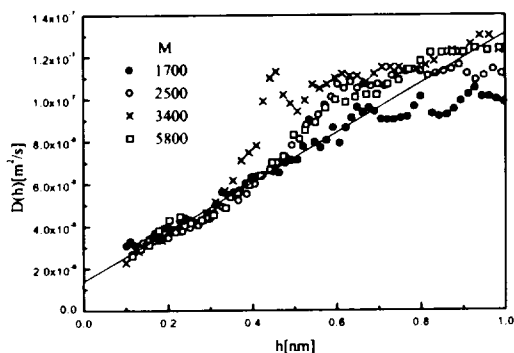

Fig. 3 Comparison between the present analysis with the experimental data of Ma[10] for thin thin-film regime

function of film thickness for various molecular weights. $D_s(h)$ reaches a maximum value at a thickness of 1nm. Thereafter, it decreases monotonically, and follows a relationship, $D_s(h) \approx 1/h$, for a higher film thickness. These trends are consistent with the eqs. (9) and (10). Therefore, it is assumed that van der Waals interaction is the dominant driving force for PFPE Z on an amorphous carbon surface for film thickness greater than a mono-layer. The results of least squares fitting of experimental data to $D_s(h) = (A/6\pi h \eta)[1/h]$ are summarized in Fig. 2.

For the sub-monolayer regime, $D_s(h)$ increase as the film thickness increase as shown in Fig. 1. Novotny[7] suggested that $D_s(h)$ should remain constant, however our experimental results are inconsistent with his suggestion. Cazabat et al.[4] discussed the relation between various adsorption-desorption isotherms and surface diffusion coefficients. They show that the surface diffusion coefficient for sub-monolayer regime is a function of film thickness. We correlate the experimental results based on eq. (20) in Fig. 3. As shown in this figure, eq. (20) represents the experimental data, especially for thinner regime. The slope seems independent of molecular weight for a thinner regime. As the film thickness increase, the experimental data deviate from eq. (20). Therefore, it seems that the higher order terms should be considered for a thicker regime.

IV. Conclusion

The spreading characteristic of PFPE Z was analyzed theoretically and experimentally. The slip boundary condition instead of conventional no-slip boundary condition was applied in thick-thin film regime (hydrodynamic analysis), and this modification explained the experimental results more reasonably. The surface diffusion coefficient had the maximum

value at $h \approx 1nm$ and decreased as $D_s \propto 1/h$ for the thicker regime. The two-dimensional virial equation was employed to analyze thin-thin film (sub-monolayer) regime. In thin-thin film regime the surface diffusion coefficients was roughly proportional to film thickness and inversely proportional to molecular weight.

요 약

탄소 표면 위에서 무극성 perfluoropolyalkylehter (PFPE)의 퍼짐 기구를 제시하였다. 단분자층 이하 영역에서는 흡착-탈착이 퍼짐에 대한 주 구동령이고, 표면 확산 계수는 박막의 두께가 증가할수록 증가하였다. 이 영역에 대해서는 표면 확산 계수의 박막 두께에 대한 의존성을 설명하기 위하여 2차원 van der Waals식을 적용하였다. 다분자층 영역에서는 퍼짐 특성은 disjoining 압력 구배에 의하여 지배되었다. 본 연구의 이론적 해석결과는 표면 확산 계수의 박막 두께에 대한 의존성을 합리적으로 설명한다.

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