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Friction of zwitterionic hydrogel by dynamic polymer adsorption

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ABSTRACT

A simplified model describing the sliding friction of hydrogel on solid surface by dynamic adsorption of the polymer chains is proposed on the basis of polymer adsorption-repulsion theory. This dynamic adsorption model is used to analyze the friction results of zwitterionic hydrogels sliding over glass substrates with different substrate wettability, hydrogel swelling degree, ionic strength and pH of bath solution. The adsorption time τ_b of polymer strands is found to decrease with the increase in sliding velocity or the Weissenberg number as a result of stretching. The adsorption time τ_b^0 and the adsorption energy U_{ads} at stress-free condition, which are characteristic for each friction system, are also estimated. Roughly, a master curve is observed for the normalized adsorption lifetime τ_b/τ_b^0 and the Weissenberg number, with less dependence on the adsorption energy and the bulk properties of the gels in the observed experimental conditions. Thus, the dynamic adsorption model successfully correlates the frictional behavior of hydrogels with the adsorption dynamics of polymer strands, which gives insight on the molecular design of hydrogels with predefined frictional properties for biomedical applications.

I. INTRODUCTION

The sliding friction of hydrogels in aqueous solution has recently been drawing a great scientific attention for the excellent features [1-12] of hydrogels similar to the internal organs in our body. Understanding the surface frictional properties of hydrogels is necessary to understand the sliding mechanism in biological system as well as to design low friction biomedical devices and implants. Among many hydrogels the polyzwitterionic hydrogels, which have both cationic and anionic groups in each repeating unit of the polymer, have the excellent anti-biofouling properties [13-22] and biocompatibility, which makes the zwitterion-based hydrogels better candidate for bio-applications.

Recently, the sliding friction of carboxybetaine type zwitterionic hydrogels, poly(N-(carboxymethyl)-N,N-dimethyl-2-(methacryloyloxy) ethanaminium, inner salt) (PCDME), against glass substrates were investigated in aqueous solutions [23]. The PCDME hydrogels showed high frictional stress on glass in water with weak dependence on normal pressure as long as the two sliding surfaces were in complete contact. The results performed in solutions with varied ionic strength revealed that the high friction on glass substrates has an electrostatic origin. The electrostatic potential measurement revealed that the PCDME gels have an isoelectric point at pH 8.5. Since

the glass substrates carrying negative charges in pure water, the gel and the glass have electrostatic attraction in water. Study on the effect of pH has shown that below pH 8.5, attraction between the positively charged gels and negatively charged glass gives high friction, while above pH 8.5, the electrical double layer repulsion between two negatively charged surfaces gives low friction. From these results it is concluded that although the PCDME gels behave like neutral gels in the bulk properties, their surface properties sensitively change with pH and ionic strength of the medium. These results of PCDME hydrogel friction are in consistence with many previous results of hydrogels that also showed the similar dependence on interfacial interaction [24-27].

The friction of a hydrogel having adhesive interaction with the substrate is from two contributions: the elastic stretching of adsorbed polymer strands, which was named as elastic friction (σ_{el}) and the viscous resistance of solvent (σ_{vis}) [25]. On an adhesive surface, the polymer strands of a hydrogel are dynamically adsorbed and desorbed. An adsorbing strand is stretched when the substrate is in motion relative to the gel. The elastic force of the polymer strand increases with the deformation and the strand gets detached from the substrate at a certain elastic deformation and the stress appears as the frictional stress. In the framework of Schallamach's theory of forced desorption of rubber friction [28], the elastic friction for hydrogels has been theoretically predicted

in an adsorption-repulsion theory for hydrogels [25]. In this work, we try to analyze the experimental results of PCDME hydrogels using a simplified dynamic adsorption model that is developed on the basis of polymer adsorption-repulsion theory [25].

The paper is organized as follows. First, a simplified dynamic adsorption equation for the friction of hydrogel sliding over a smooth solid substrate is constructed. Then, four sets of the experiment results of the PCDME hydrogels are analyzed with the dynamic adsorption equation, and the adsorption time of the polymer strand and its dependence on the sliding velocity are discussed. From the normalized adsorption lifetime in relative to that at the equilibrium state and the Weissenberg number, the effect of the sliding velocity on the polymer strand adsorption dynamics is discussed.

II. EXPERIMENTS

Materials

N-(Carboxymethyl)-N,N-dimethyl-2-(methacryloyloxy)ethanaminium, inner salt (CDME), a courtesy from Osaka Organic Chemical Industry, Ltd., Japan, was used as received. 2-Oxoglutaric acid (Wako Pure Chemical Industries, Ltd.), Sodium hydroxide (NaOH, Wako Pure Chemical Industries, Ltd.), Hydrochloric acid (HCl, Wako Pure Chemical Industries, Ltd.) and Sodium chloride (NaCl, Wako Pure Chemical Industries,

Ltd.) were used as received. N,N'-Methylenebis(acrylamide) (MBAA, Wako Pure Chemical Industries, Ltd., Japan) was recrystallized from ethanol.

Synthesis of hydrogels

PCDME gels were prepared by radical polymerization initiated by UV irradiation [29].

Gels with different water content and swelling degree were prepared by varying the crosslinker density C_{MBAA} . The aqueous solutions containing 3M of monomer (CDME), 0.01 to 0.5mol% of crosslinker (MBAA) and 0.1mol% of initiator (2-oxoglutaric acid) were prepared. Here, the mol% is in relative to the monomer concentration. The precursor solution was poured into a reaction cell consisted of two parallel glass plates separated by a silicone spacer of 2 mm in thickness. The reaction cell was irradiated by UV (365 nm) from both sides for 8 hours under argon atmosphere.

After polymerization, the glass plates were removed and the obtained sheet-shape gels were immersed in a large amount of water for sufficiently long time to reach swelling equilibrium and to wash away the residual chemicals. Extreme care was taken during the synthesis to obtain a microscopically smooth surface of the gel.

Preparation of counter surface

Cover glasses (Micro cover glass, C050701; Matsunami glass Ind. Ltd., Japan) were used as counter surface for friction test. The glasses were treated with hydrophobic binding silane (H1, H1, H2, H2-Perfluorodecyletrychlorosilane). In this treatment the glasses were cleaned with detergent, soaked in alkali solution for 1 hour and washed with water. After drying with air blow, they were kept in UV/O₃ chamber for extra cleaning. Then the glasses were exposed to the vapor of silane binding polymer in another vacuum chamber. Different exposure time gave different hydrophobicity of the glasses. The contact angle to water (droplet size 2.0 μ L) of these glasses was determined by contact angle meter (Drop Master 300, Kyowa interface science Co. Ltd., Japan) as shown in Table 1.

Measurements

The degree of swelling of the gels in water, q , defined as $q = (\text{swollen weight})/(\text{dry weight})$, was calculated by obtaining the respective weights of the samples using moisture balance (MOC-120H, Shimadzu Co.). The dry samples were obtained by heating the gels at 120°C until they reached a constant weight.

The Young's moduli E of water-equilibrated gels were calculated from the slope of tensile stress-strain curves measured by using a tensile tester (Instron 5965, Instron Co.). The tensile tests were carried out with gel samples cut into a standard dumbbell shape (20 mm in length and 4 mm in width). The tensile strain rate was 10% length/min. The mesh size of the network ξ is estimated [30] from $E = 3k_B T/\xi^3$. The parameters for the hydrogel samples are summarized in Table 2.

The friction of hydrogels against glass surfaces was measured using a rheometer (ARES-G2, TA INSTRUMENTS.) that works in a constant compressive strain mode at 25°C. The rheometer was equipped with a home-made optical system, which allows the *in situ* observation of the frictional interface [31]. The images of the frictional interface were recorded by a digital video camera (HDR CX550, Sony). The equilibrium swollen gels were cut into a disk-shape of $R=7.5$ mm in radius and glued on the lower surface of coaxial disk-shaped plate of rheometer with cyanoacrylate instant adhesive agent (Toa Gosei Co., Ltd.). As the counter surface for friction, the cover glass was attached onto the bottom surface of a prism. The prism was connected to the upper plate of the rheometer. The counter surface was allowed to approach the gel surface in liquid until the normal load reaches a prescribed value to form full interfacial contact, and then the contact was equilibrated for 15 minutes. The liquid was the

same with that the gel previously swelled. During measurement the gel attached to the lower plate rotates at a pre-defined angular velocity. Due to the friction, the load cell connected to the counter surface experiences a torque.

For the measurement of frictional stress with successive velocity change, the SRST (steady rate sweep test) mode of the rheometer was chosen [23]. In this mode, the lower plate of the rheometer rotated the gel at an angular velocity (ω) that was increased stepwise from 10^1 rad/s to 10^3 rad/s, each lasted for 40 seconds, without separation of the two surfaces. At each angular velocity, the average torque (T) of last 20 seconds was adopted as friction torque. In this measurement geometry, the linear sliding velocity, $v = \omega r$, varied along the radius of the sample. The total torque is related to the shear stress σ as [11]-

$$T(\omega) = \int_A \sigma(r) r dA = \int_0^R 2\pi \sigma(\omega r) r^2 dr = \frac{2\pi}{\omega^3} \int_0^{\omega R} \sigma(u) u^2 du \dots\dots\dots (1)$$

Then we have

$$\frac{d(\omega^3 T(\omega))}{d\omega} = 2\pi \omega^2 R^3 \sigma(\omega R) \dots\dots\dots (2)$$

Assuming that

$$T(\omega) = A\omega^\alpha \dots\dots\dots (3)$$

Then the friction stress

$$\sigma(v = \omega R) = \frac{(\alpha+3)T(\omega)}{2\pi R^3} \dots\dots\dots (4)$$

Here, A and α are constants determined by the experiment. Eq. (4) is the same with that obtained by Chaudhury [32], though the approaches to derive the equation are slightly different. Theoretical model predicted that the value of α varies from 1 to -0.7

[11, 25], much smaller than 3. So we simply set $\alpha = 0$ in the calculation of the friction stress in this work. We adopted the linear velocity as the value at the outer most part of the disc-shape gel, that is, $v = \omega R$.

III. THEORETICAL BACKGROUND

When a hydrogel is in contact with a smooth, adhesive solid surface, thermodynamically reversible adsorption will take place and at equilibrium the rate of adsorption and desorption will be equal. Following the adsorption-repulsion theory [25], let us consider a polymer strand adsorbed on the surface with an average lifetime τ_b^0 . In the case of a simple thermally activated process, τ_b^0 should depend on the temperature following the Arrhenius law [25]-

$$\frac{1}{\tau_b^0} = \frac{1}{\tau_0} \exp\left(-\frac{U_{ads}}{k_B T}\right) \dots\dots\dots (5)$$

Here U_{ads} is the adsorption energy of one polymer strand, τ_0 is a pre-exponential factor, k_B and T are Boltzmann constant and temperature, respectively. When the solid surface slides in relative to the gel, the adsorbing strand will be stretched (Scheme 1). This induces an additional elastic energy that counteracts the adsorption energy U_{ads} .

As a result, the adsorbed time under stressed condition τ_b is shortened,

$$\frac{1}{\tau_b} = \frac{1}{\tau_0} \exp\left(-\frac{U_{ads}-U_{el}}{k_B T}\right) \dots\dots\dots (6)$$

Here U_{el} is the elastic energy of the stressed strand at the breaking point. So τ_b and τ_b^0 are correlated with

$$\frac{1}{\tau_b} = \frac{1}{\tau_b^0} \exp\left(\frac{U_{el}}{k_B T}\right) \dots\dots\dots (7)$$

For the most simple case, we assume that each polymer strand only form one adsorption point, then, the elastic energy of a strand of size ξ at small stretching ($v\tau_b/\xi < 1$) is [25,30],

$$\frac{U_{el}}{k_B T} = \frac{3}{2} \left(\frac{v}{\xi}\right)^2 \tau_b^2 \dots\dots\dots (8)$$

By combining Eq. 7 and 8, we have,

$$\tau_b^0 = \tau_b \exp\left[\frac{3}{2} \left(\frac{v}{\xi}\right)^2 \tau_b^2\right] \dots\dots\dots (9)$$

For a specific system (fixed gel, substrate, bath solution, temperatre), U_{ads} and therefore τ_b^0 , are constant, independent of the sliding velocity. Eq. (8) and (9) indicate that the elastic energy U_{el} at breaking of polymer adsorption is intertwined with the adsorption energy U_{ads} .

The maximum elastic stress f_{el} of a polymer strand at stretching of $r=v\tau_b$ is [25]-

$$f_{el} \approx \frac{k_B T r}{\xi^2} = \frac{k_B T v \tau_b}{\xi^2} \dots\dots\dots (10)$$

Let us suppose m numbers of polymer chains per unit area are in adsorbed state during sliding and the cumulative elastic stress can be given by-

$$\sigma_{el} \approx \frac{m k_B T v \tau_b}{\xi^2} \dots\dots\dots (11)$$

Here, $m = m_0 \left(\frac{\tau_b}{\tau_b + \tau_f} \right)$, $m_0 \approx 1/\xi^2$ is the total number of polymer chains per unit area, and $\frac{\tau_b}{\tau_b + \tau_f}$ is the fraction of chains that are in adsorbed state where τ_f is the time to form adsorption of the polymer strand (self-healing time). Therefore, the frictional stress due to the stretching of adsorbed polymer is-

$$\begin{aligned} \sigma_{el} &= \frac{1}{\xi^2} \frac{\tau_b^2}{(\tau_b + \tau_f)} \frac{k_B T v}{\xi^2} \\ &= \left(\frac{k_B T}{\xi^3} \right) \left(\frac{v}{\xi} \right) \tau_b \frac{\tau_b}{(\tau_b + \tau_f)} \dots\dots\dots (12) \end{aligned}$$

Equation (12) represents the friction due to the stretching of adsorbed polymer strands per unit area. Since $(k_B T/\xi^3)$ is equivalent to the shear modulus G [30], and $(v/\xi)\tau_f$ is the Weissenberg number W_e , which is a parameter represents the shear rate in relative to the relaxation rate of the polymer strand during sliding, we can rewrite Eq. (12) in terms of G and W_e as-

$$\sigma_{el} = G W_e \frac{(\tau_b/\tau_f)^2}{(\tau_b/\tau_f) + 1} \dots\dots\dots (12)'$$

As the W_e increases with the sliding velocity, and τ_b decreases with the velocity due to stretching effect, σ_{el} will exhibit a maximum value at certain velocity. In addition to the elastic friction, the liquid medium at the interface gives the viscous resistance σ_{vis} and also contributes to frictional stress of a hydrogel sliding over a solid surface. The viscous term has an equivalent liquid layer thickness of the hydrogel mesh size. So the overall frictional stress can be represented as -

$$\sigma = \sigma_{el} + \sigma_{vis} \dots\dots\dots (13)$$

Where

$$\sigma_{vis} = \frac{2}{3} \frac{\eta v}{\xi} \dots\dots\dots (14)$$

Here η is the viscosity of solvent (water), and the numerical factor 2/3 in equation (14) comes from the geometry of the measurement system [23]. So the elastic friction (σ_{el}) can be obtained by subtracting the viscous resistance of lubricant (σ_{vis}) from the total friction (σ).

$$\sigma - \sigma_{vis} = \sigma_{el} = GW_e \frac{(\tau_b/\tau_f)^2}{(\tau_b/\tau_f)+1} \dots\dots\dots (15)$$

The shear modulus of the hydrogel G is measurable and the mesh size ξ , and therefore the Weissenberg number, can be estimated from G . If we know τ_f , then we can estimate the variation of the adsorption time τ_b with the sliding velocity from the friction using Eq. (15). In the following section, we simply assume that τ_f equals to the characteristic relaxation time of the gel $\tau = \eta/G$ [33], which is equivalent to the Zimm motion relaxation time of the polymer strand, and estimate τ_b from the friction stress σ at various sliding velocity using Eq. (15).

IV. RESULTS AND DISCUSSION

As described previously [23], the friction of PCDME hydrogel against smooth glass substrate is governed by the electrostatic interaction and therefore a change in

substrate wettability, ionic strength or pH of the medium will change the energy of adsorption, U_{ads} . Here the friction study was carried out with different conditions where the interfacial electrostatic interaction was varied systematically and the effects were correlated with the mechanism proposed in the previous section.

Effect of substrate wettability

If we assume that the electrostatic attraction causes the adsorption of polymer chains on the glass substrate, which in turn gives the frictional stress, a decrease in the wettability of glass substrate would decrease the frictional stress. To study the effect of substrate wettability on frictional stress, glass substrate with different wettability was prepared by coating them with hydrophobic silane binding agent in various extents. The process blocks the SiO^- groups and reduces the wettability of the surface. Frictional tests were then carried out using these glass substrates keeping the hydrogel and other friction parameters in identical condition. Frictional stress, σ for different glass substrates having varied wettability against sliding velocity, v is shown by a log-log plot in Figure 1a. Its linear plot is shown in supporting information (Figure S1). It is observed that the friction stress is higher on glass substrates of lower contact angle to water. When the water contact angle θ_w of the glass is above 90° , the friction

decreases rapidly. The results indicate that the electrostatic attraction is screened by the hydrophobic coating of glass.

To extract the elastic adsorption component from the overall friction, the ratio of the elastic friction stress to the shear modulus of the gel, σ_{el}/G , was estimated from the friction stress using equation (13) and (14), where σ and v are obtainable from the friction test, ξ and G from measuring the bulk properties of the hydrogel. Figure 1b shows the relationship between σ_{el}/G and the Weissenberg number, $W_e=(v/\xi)\tau_f$. It is worth mentioning that some data at high velocity end were removed in Figure 1b since the σ_{el}/G value went to negative due to the dominant effect of viscous resistance term when the velocity becomes very high. On relatively hydrophilic substrates, σ_{el}/G reaches a maximum at a certain velocity. The shear-thickening in the low velocity indicates that the adsorption time τ_b of the polymer strands in this region is less perturbed by the stretching, while the shear-thinning in the high velocity indicates that τ_b decreases with the sliding velocity in this region due to enhanced stretching of the adsorbed chain (forced desorption). Furthermore, the maximum value of σ_{el}/G decreases with the increase of θ_w . Especially when $\theta_w > 90^\circ$, σ_{el}/G decreases rapidly.

The adsorption lifetime τ_b at different sliding velocity was calculated using equation (15), and plotted against the Weissenberg number, W_e (Figure 1c). As expected, τ_b

decreases with the increase in W_e , indicating that the adsorption time of polymer strand becomes short at enhanced stretching. At low velocity limit, the τ_b tends to saturate to a steady value, which should be related to the velocity-independent lifetime τ_b^0 at equilibrium adsorption. It should be mentioned that the lowest τ_b values thus estimated are in the order of 1 μ s, which is very close to the characteristic relaxation time τ of the gels (Table 2). This is reasonable since when τ_b is shorter than τ , no adsorption occurs and the friction is due to lubrication. This self-consistency in turn confirms the validity of using the characteristic relaxation time τ of the gels as the re-adsorption time in the dynamic model.

We found that the τ_b^0 value estimated using Eq. (9) was almost constant, independent of Weissenberg number in the low W_e range. This result indicates that the dynamic adsorption model proposed in this work catches the essence of the hydrogel friction on adhesive substrate. Figure 2 shows τ_b^0 against the contact angle of the substrate θ_w . A sudden drop of τ_b^0 was observed at $\theta_w = 90^\circ$, indicating that the adsorption energy due to the electrostatic attraction is substantially screened by the hydrophobic treatment of the substrate surface.

To estimate the adsorption energy U_{ads} per polymer strand, we need to know the pre-exponential factor τ_0 in Eq. (5). If we simply assume that τ_0 equals to the characteristic

time τ , then U_{ads} is about $4k_B T$ for the hydrophilic substrate, as shown in Figure 2. As the adhesion energy per unit area W_{adh} is equal to the product of the adsorption energy per strand U_{ads} and the areal density of the adsorbing strands at zero velocity $m = \tau_b^0 \xi^2 / (\tau_b^0 + \tau_f) \simeq \xi^2$, we can estimate the adhesion energy of the gel in water, which is equals to the negative value of the spreading coefficient S between the gel and the substrate [11].

$$W_{adh} = -S = U_{ads} / \xi^2 \dots\dots\dots(16)$$

For $U_{ads} = 4k_B T$ and $\xi = 13.4$ nm (Table 2), the adhesion energy W_{adh} is estimated about ~ 0.1 mJ/m². Future work is required to confirm this assumption by measuring the adhesion energy of the gel to the substrate in water.

The normalized adsorption lifetime τ_b / τ_b^0 against Weissenberg number, W_e , was calculated and shown in Figure 3. It was found that all the curves calculated from the friction results with different substrate wettability almost superimpose into a single curve (Figure 3). Since τ_b / τ_b^0 is related to the elastic energy U_{el} by $\ln(\tau_b / \tau_b^0) = -U_{el} / k_B T$, the result of Figure 3 suggests that in the observation range, the stored elastic energy U_{el} during friction, roughly, only depends on the Weissenberg number, with little dependence on the adsorption energy $U_{ads} / k_B T$.

Chaudhury *et al* [34] showed that the dissipation of elastic energy at the breaking point is related to the sliding velocity as $U^{1/2} \approx \text{Inv}$. In the present study, a plot of $[\ln(\tau_b^0/\tau_b)]^{1/2}$ vs Inv (Figure 4) also showed linear relationships for different surface pairs, demonstrating the validity of the relation. Furthermore, all the curves give approximately similar slope within the experimental resolution. This can be understood as that the average spring constant is the same as long as the swelling degrees of the hydrogels are the same.

Effect of swelling degree

To explore the effect of swelling degree of hydrogels on the friction, a series of PCDME hydrogels were synthesized with different crosslinking densities (Table 2). This difference in crosslinking density gives different chain lengths between the crosslinking points and swelling degrees, which determine the elastic modulus, mesh size and polymer chain density at the gel surface. The hydrogels with different swelling degree were slid over an untreated glass substrate (Table 1, G2-1) under the same normal pressure. Previous studies have shown that for the adhesive friction, the normal pressure does not have any significant effect on the friction as long as the surfaces are in complete contact [23, 31]. So we can discuss the frictional behavior due to the

combined effect of elastic modulus, mesh size and polymer chain density at the gel surface.

Figure 5a shows the log-log plot of friction-velocity curve for different swelling degrees, q . The experiments were performed at a more wide velocity range than that of Figure 1, and three characteristic behaviors are observed depending on the q values. For the low q samples ($q=16.0-22.1$), the friction increases and then decreases with velocity. At more high velocity, the friction increases with the velocity again. These behaviors are basically the same to that observed in Figure 1. This result indicates that at low and intermediate velocity, the elastic friction due to adhesive interaction is dominant while at the high velocity end, the hydrated lubrication dominates the friction mechanism. For the high q sample ($q=59.3$), the friction decreases and then increases with the velocity. This behavior indicates that the hydrated lubrication mechanism dominant the friction except at the lowest velocity end. For the intermediate q sample ($q=34.5$), it shows intermediate friction behaviors of the low q and high q samples.

For the PCDME gels, it was experimentally observed that the shear modulus scales with the swelling degree as $q \sim G^{-2.15}$ [29]. So the re-adsorption time τ_f scales with the network modulus as $\tau_f = \tau = \eta/G \sim q^{2.15}$. When the swelling degree q is very large, it takes

a very long time for the highly hydrated polymer strand to form adsorption with the substrate, so the elastic friction term becomes very small, and we could hardly observe the adsorption behavior even in the lowest velocity end of this study. That is, the transition from adsorption to hydration depends on the competition between adsorption kinetics and the sliding velocity.

Figure 5b shows the relationship between σ_{el}/G and the Weissenberg number. Very clear maximum of σ_{el}/G is observed for each curve, even for high swelling degree samples. The value of σ_{el}/G drops rapidly at high W_e . The corresponding relationship between the adsorption time τ_b estimated from Eq. (15) and the Weissenberg number is shown in Figure 5c. τ_b shows a decreasing tendency with the increase of the Weissenberg number. Furthermore, there is a slight increase in τ_b with the increase of swelling degree q . This tendency is also observed in the τ_b^0 as shown in Figure 6. If we assume that the pre-exponential factor τ_0 is a constant and independent of q , this leads to an increase in adsorption energy U_{ads} with the polymer strand length. This is in agreement with the Lake-Thomas theory that the energy to break the adsorption of polymer strand increases with the chain length [35]. However, if we assume $\tau_0=\tau_f$, then U_{ads} slightly decreases with q (Figure 6) since τ_f becomes long with the increase in q .

Further study on the adhesion behaviors of the gels with varied q is necessary to clarify these discussions.

Figure 7 shows a plot of τ_b/τ_b^0 vs. $(\nu/\xi)\tau_f$. For hydrogels with different swelling degree q , roughly a master curve is also observed for the relation of the τ_b/τ_b^0 vs. Weissenberg number. This indicates that the energy stored in the polymer chains at the desorption point is also not very sensitive to the structure or polymer strand size (ξ). Furthermore, when the Weissenberg number is less than 0.005, the stretching effect is negligible and the polymer strand adsorption is not perturbed from its equilibrium state.

Effect of ionic strength and pH of the medium

Our previous study [23] showed that frictional stress of similar PCDME hydrogels over glass substrate decreases with the increase in ionic strength of the medium. The screening effect of the ions was accounted for the lowering of friction. The energy of electrostatic interaction in presence of ion-atmosphere is screened by the factor of $(1 - rC^{1/2})$ according to [36] -

$$U \sim U_0(1 - rC^{1/2}) \dots\dots\dots (17)$$

Here, r is a constant and C is the ionic strength of the medium. Here, we analyzed the frictional behavior of PCDME hydrogel ($q=20.1$) over a glass substrate of $\theta_w=45^\circ$ under different ionic strengths. From the raw data (Figure S2) obtained from reference 23, the equilibrium adsorption lifetime τ_b^0 is calculated and plotted against $C^{1/2}$ in Figure 8. The adsorption energy $U_{ads}/k_B T$ is also estimated assuming $\tau_0=\tau_f$. The straight lines for τ_b^0 or $U_{ads}/k_B T$ follow equation (17), which validates our assumption and again confirms the presence of ion screening during friction.

Being zwitterionic in nature, the PCDME hydrogel exhibits different frictional behaviors [23] at different pH. In previous study it was found that the frictional stress remains unchanged at lower pH and as the pH is increased the friction starts to decrease after a transition point around pH 9, which is the isoelectric point of PCDME hydrogel (Figure S3). The difference in electrostatic potential of hydrogel and the glass substrate was accounted for the pH dependence. The pH-dependence of equilibrium adsorption lifetime τ_b^0 and the adsorption energy $U_{ads}/k_B T$ was also calculated from the friction data [23], and the results are shown in Figure 9. A sudden drop in τ_b^0 and $U_{ads}/k_B T$ is observed after pH 9.8, which is in agreement with the pH effect explained in reference 23.

The plots of normalized adsorption lifetime against Weissenberg number for various ionic strengths and pH are shown in Figure 10a and 10b, respectively. Again we found that all the data are almost collapsed to a single curve, with no systematic dependence on the adsorption energy, in similar to Figure 3.

According to the adsorption-repulsion theory, τ_b/τ_b^0 is a function of Weissenberg number and the adsorption energy [25],

$$\tau_b/\tau_b^0 = \phi\left[\frac{v\tau_f}{\xi} \exp\left(\frac{U_{ads}}{k_B T}\right)\right] \dots\dots\dots (18)$$

This means that if we plot all of the τ_b/τ_b^0 data against $\frac{v\tau_f}{\xi} \exp\left(\frac{U_{ads}}{k_B T}\right)$, a master curve should be observed. However, we could not observe such a master curve when all the data were plotted in such a figure. Instead, as shown in Figure 11, which summarized the normalized adsorption lifetime against Weissenberg number for varied ionic strength, pH, substrate wettability, and swelling degree, roughly all the data fall on a single master curve, regardless of the changes in adsorption energy and bulk hydrogel properties. This discrepancy between the model and the analyzed result probably comes from a relative narrow varying range of the adsorption energy and mesh size used in this study.

V. CONCLUSIONS

In summary, the frictional stress appeared from sliding of PCDME hydrogels against glass substrates follows a simple dynamic adsorption model. The model is valid for a wide variety of interface characteristics. The frictional stress developed from the sliding of hydrogel over a solid substrate under water is due to the combined effect of adsorption energy, elastic energy of polymer strands and viscous drag of the lubricant. These individual effects can be calculated using the model. The adsorption of polymer strands on the substrate is governed by the electrostatic interaction, which was reduced by coating the glass substrate with hydrophobic silane binding agent. It was found that the decrease in friction with the increase in substrate wettability is related to a decrease in the adsorption energy of polymer strands. Moreover, the decrease in frictional stress with the increase in swelling degree revealed that the friction is strongly related to the water content and areal density of the polymer at the interface. The dissipated elastic energy of a polymer chain during sliding is related to the Weissenberg number. From the normalized adsorption lifetime and Weissenberg number a master curve can be constructed. The curve indicates that the elastic energy dissipation during friction is less dependent of surface as well as bulk properties but strongly depends on the Weissenberg number, which is governed by the sliding velocity. The proposed model with the obtained results might provide a better

understanding to the frictional properties of polymeric soft and wet materials and might be useful for designing low-friction biomaterials.

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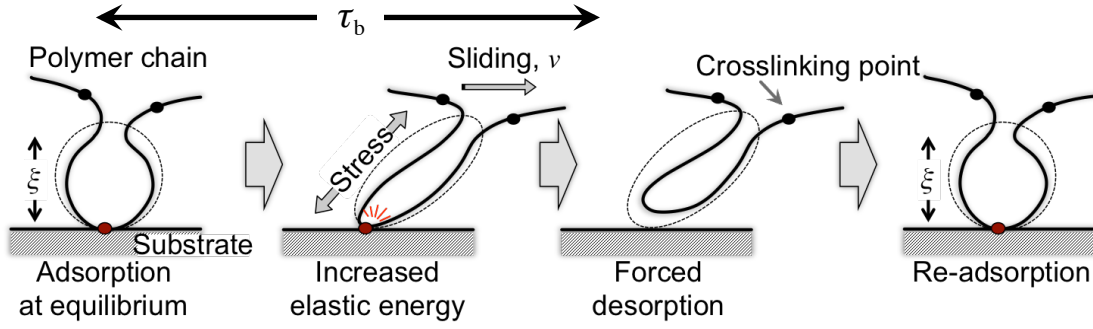
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Schemes and Figures



Scheme 1. Simplified representation of polymer chain adsorption and desorption dynamics during sliding of a hydrogel over a substrate.

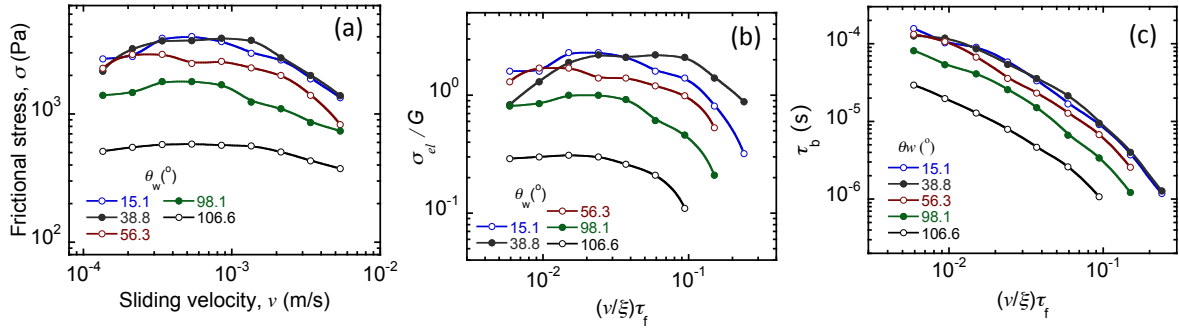


Figure 1. Dependence of frictional behavior of PCDME gel on glass substrates with varied wettability. (a) Overall frictional stress σ vs. sliding velocity, (b) Ratio of elastic component of frictional stress σ_{el} to shear modulus G vs. Weissenberg number $W_e = (v/\xi)\tau_f$, (c) Adsorption time τ_b vs. Weissenberg number. The adsorption time τ_b was estimated from the results of Figure 1a using Equation (15). Contact angles of glass substrates to water θ_w are shown in figure. Hydrogel: PCDME (S-16.0). Substrates: G1 and G3 series, Normal pressure: 2.75 kPa.

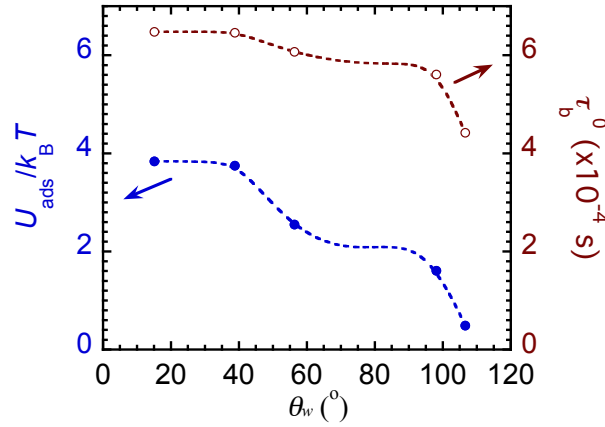


Figure 2. Change in the adsorption lifetime τ_b^0 (right-Y) of a polymer chain with the decrease in wettability of glass substrates. The normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) was estimated from τ_b^0 assuming that the pre-exponential factor τ_0 in Eq. (5) equals to the characteristic time τ of the gel. Hydrogel: PCDME (S-16.0), Substrates: G1 and G3 series, Normal pressure: 2.75 kPa.

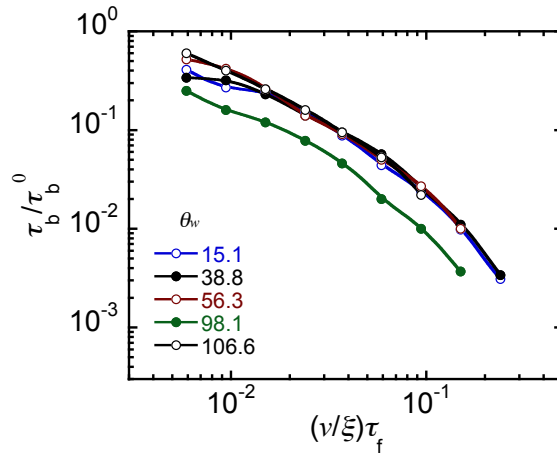


Figure 3. Change in normalized adsorption lifetime with respect to the Weissenberg number $W_e=(\nu/\xi)\tau_f$, of polymer chain on different substrates having varied wettability. Hydrogel: PCDME (S-16.0), Substrates: G1 and G3 series, Normal pressure: 2.75 kPa.

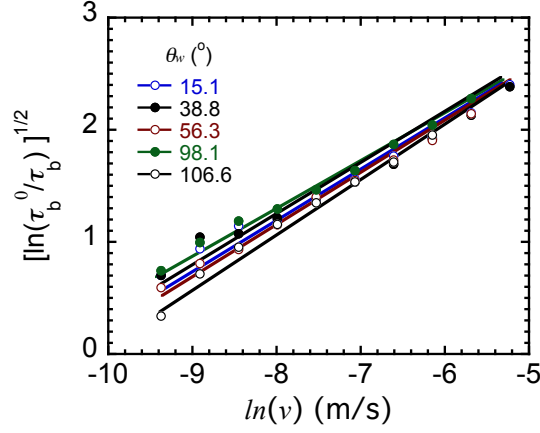


Figure 4. Velocity dependence of the elastic energy $U_{el}/k_B T = \ln(\tau_b^0/\tau_b)$ of a polymer chain for a hydrogel sliding over substrates having different wettability. The plot follows the model described by Chaudhury *et al* [34].

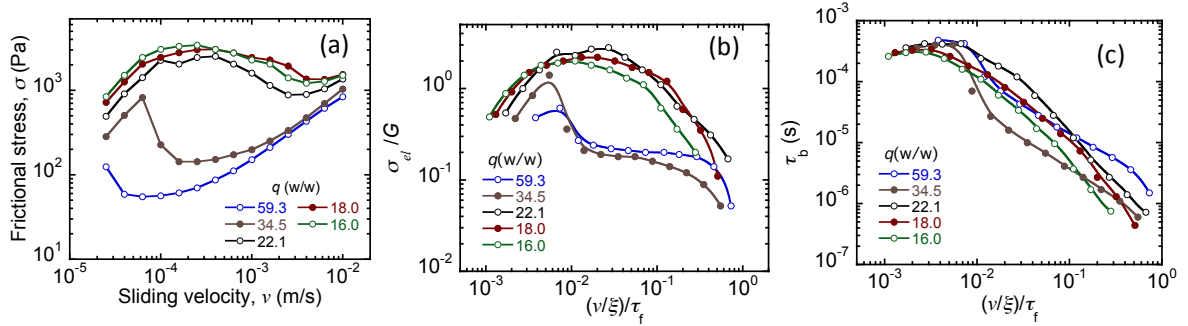


Figure 5. Dependence of frictional behavior of PCDME hydrogel on swelling degree q . (a) Overall frictional stress σ vs. sliding velocity v , (b) Ratio of elastic component of frictional stress σ_{el} to shear modulus G vs. Weissenberg number $W_e = (v/\xi)\tau_f$, (c) Adsorption lifetime τ_b vs. Weissenberg number W_e . The adsorption time τ_b was estimated from the results of Figure 5a using Equation (15). Swelling degree q of the hydrogels is shown in figure. Hydrogel: PCDME(S-59.3 to S-16.0). Substrates: G2-1, Normal pressure: 2.75 kPa.

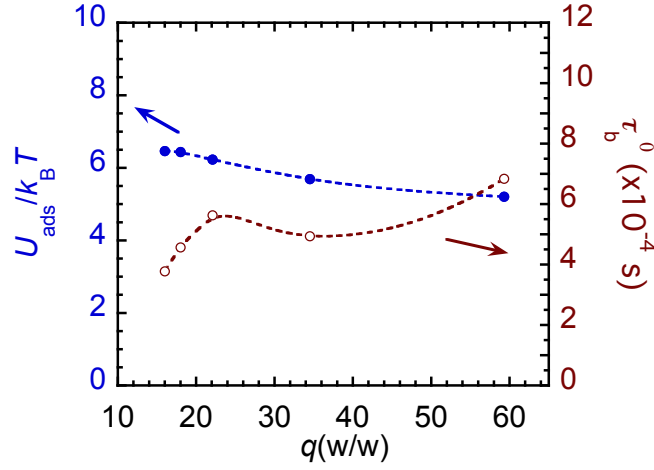


Figure 6. Change in normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) and adsorption lifetime τ_b^0 (right-Y) of a polymer strand with change in the swelling degree q . The normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) was estimated from τ_b^0 assuming that the pre-exponential factor τ_0 in Eq. (5) equals to the characteristic time τ of the gel. PCDME(S-59.3 to S-16.0). Substrates: G2-1, Normal pressure: 2.75 kPa.

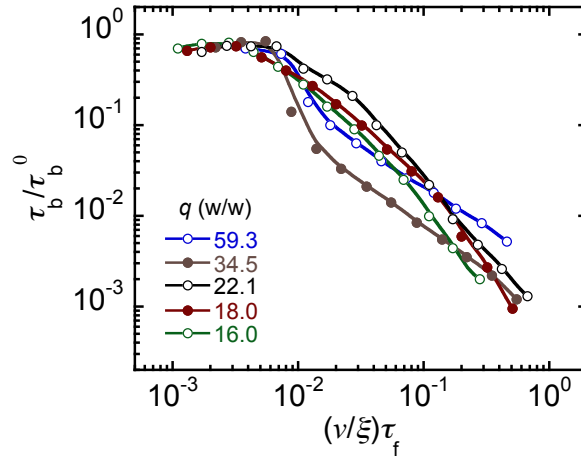


Figure 7. Change in normalized adsorption lifetime with respect to the Weissenberg number of polymer chain of hydrogels with different swelling degrees. Hydrogel: PCDME (S-22.1 to S-16.0), Substrates: G2-1, Normal pressure: 2.75 kPa.

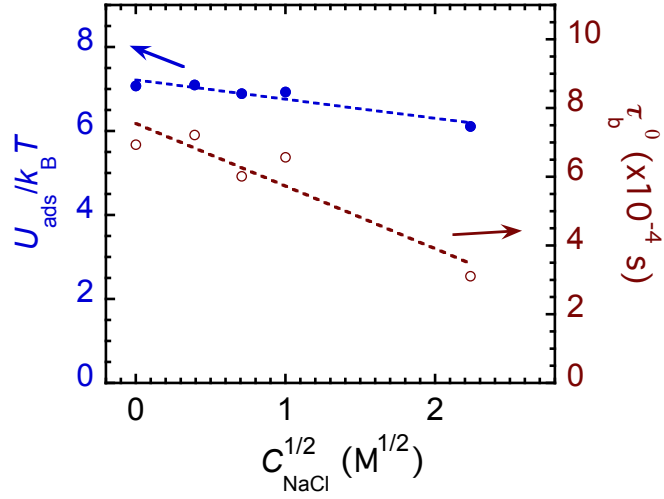


Figure 8. Change in normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) and adsorption lifetime τ_b^0 (right-Y) of a polymer chain with change in the ionic strength at pH 6.8. The normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) was estimated from τ_b^0 assuming that the pre-exponential factor τ_0 in Eq. (5) equals to the characteristic time τ of the gel. Hydrogel: PCDME with swelling degree of 20.1. Substrate: glass with contact angle of 45° . Normal pressure: 5.5kPa. The original data are from reference 23.

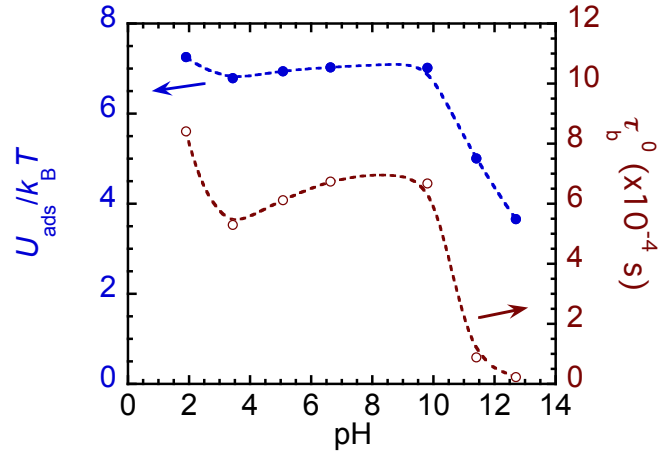


Figure 9. Change in normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) and adsorption lifetime τ_b^0 (right-Y) of a polymer chain with the change in pH of the medium. The normalized adsorption energy $U_{\text{ads}}/k_B T$ (left-Y) was estimated from τ_b^0 assuming that the pre-exponential factor τ_0 in Eq. (5) equals to the characteristic time τ of the gel. Ionic strength 0.1 M, Hydrogel: PCDME with swelling degree of 20.1. Substrate: glass with contact angle of 45° . Normal pressure: 5.5kPa. The original data are from reference 23.

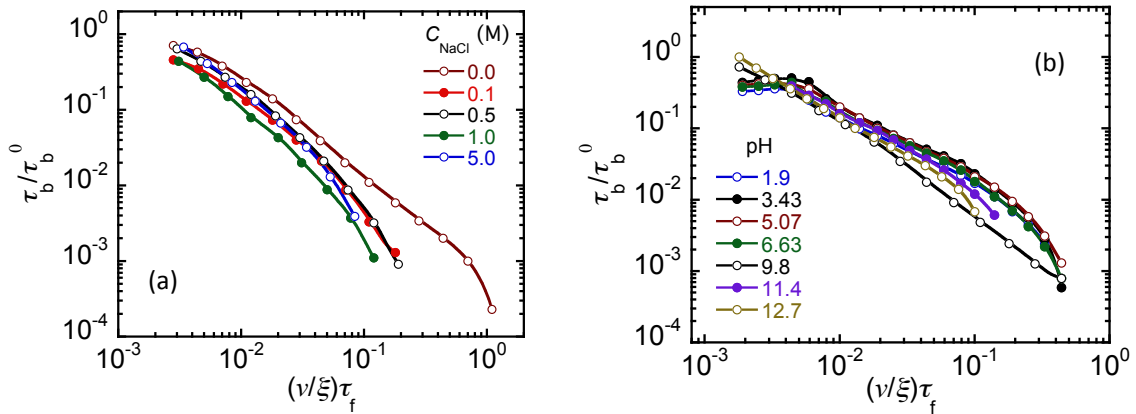


Figure 10. Change in normalized adsorption lifetime with respect to the Weissenberg number of polymer chain under different (a) ionic strength and (b) pH. Hydrogel: PCDME with swelling degree of 20.1. Substrate: glass with contact angle of 45° . Normal pressure: 5.5kPa. The original data are from reference 23.

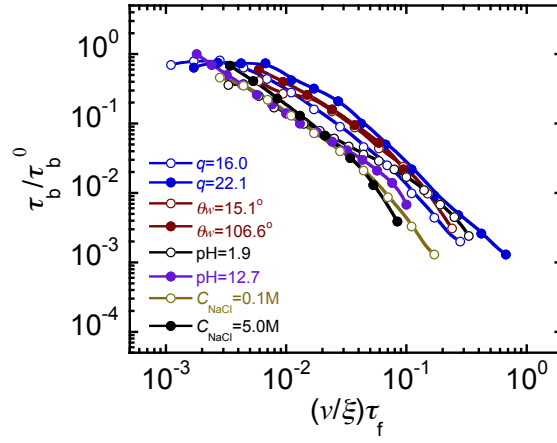


Figure 11. Summary for the changes in normalized adsorption lifetime with respect to the Weissenberg number for friction measured under varied ionic strength, pH, substrate wettability, and swelling degree. Roughly, a master curve is observed.

Tables

Table 1. Contact angle to pure water θ_w of glass substrates after different treatment.

Substrate code	Treatment	θ_w at pH 6.8 (°)
G1-1	Alkali soaked	15.1
G1-2		38.8
G2-1	As received	45.0
G3-1	Hydrophobic silane	56.3
G3-2		98.1
G3-3		106.6

Table 2. Synthesis compositions, swelling ratio q , Young's modulus E , mesh size ξ , and the characteristic relaxation time τ of PCDME hydrogels at equilibrium swelling state in water.

Sample code	C_{CDME} (M)	C_{MBAA} (mol%)	q (w/w)	E (kPa)	ξ (nm)*	τ (μ s)**
S-59.3	3.0	0.01	59.3	0.8	24.9	3.75
S-34.5		0.025	34.5	1.8	19.0	1.67
S-22.1		0.05	22.1	2.7	16.6	1.11
S-18.0		0.075	18.0	4.1	14.4	0.64
S-16.0		0.1	16.0	5.1	13.4	0.59

*Mesh size of the network was estimated from $E = 3k_B T / \xi^3$.

** The characteristic time was estimated from $\tau = 3\eta / E$.

Graphic for manuscript

