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Intelligent Gel
-Surface Properties and Functions of Gels-

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SUMARRY: The sliding friction of various kinds of hydrogels has been studied and it was found that the frictional behaviors of the hydrogels do not conform to Amonton's law $F = \mu W$, which well describes the friction of solids. The frictional force and its dependencies of on the load are quite different depending on the chemical structures of the gels, surface properties of the opposing substrates, and the measurement condition. The gel friction is explained in terms of interfacial interaction, either attractive or repulsive, between the polymer chain and the solid surface. According to this model, the frictional is ascribed to the viscous flow of solvent at the interface in the repulsive case. In the attractive case, the force to detach the adsorbing chain from the substrate appears as friction. Surface adhesion between glass particles and gels measured by AFM showed a good correlation with the friction, which support the repulsion-adsorption model proposed by authors.

Introduction

One of the most important researches of tribology is in the field of bio-systems, in particular, in the human and animal joints. Animal joints have friction coefficients in the range 0.001-0.03, which are remarkably low even for hydrodynamically lubricated journal bearings. However, there are several subjects to be solved. One of them is to explain why the cartilage friction of the joints is so low even in such conditions as that the pressure between the bone surfaces reaches as high as 3-18MPa and the sliding velocity is never greater than a few centimeters per second. Under such conditions, the lubricating liquid layer can not be sustained between two solid surfaces and the common hydrodynamic lubrication does not work.

Animal cartilage consists of a three-dimensional collagen network filled with a synovial fluid. We consider that the role of solvated polymer network existing in extracellular matrix of the cartilage cell as a gel state is critically important in the specific frictional behavior of cartilage. In order to investigate the general features in tribology of solvated polymer matrix, friction of various kinds of hydrogels were investigated. The gel frictions on solid surfaces have been attempted to explain in terms of the adhesion-repulsion model together with the experimental results by AFM.

Experimental Results

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Fig.1a shows the frictional force F in air for the non-ionic synthetic gel, poly(vinyl alcohol) (PVA); partially charged polysaccharide gel, gellan; fully charged polyelectrolyte gel, sodium salt of poly(2-acrylamido-2-methylpropanesulfonic acid) (PNaAMPS) on the glass plate. The friction coefficient, $\mu = F/W$, is calculated and shown in Fig.1b. F is almost constant (gellan gel), slightly increases (PVA gel) and strongly dependent (PNaAMPS) with the load over the observed range of load.

The friction coefficient μ for these gels accordingly shows unique load dependencies, which is quite different from those of solids. μ of PNaAMPS gel is constant over the change of the load, similar to those of rubber, but the value of μ is as low as 0.002, which is two orders of magnitude lower than those of solids. μ of PVA and gellan gels decreases with the increase of load. These results demonstrate that the gel friction does not simply obey Amonton's law of $F = \mu W$, in which μ is a material constant, and shows that the chemical structures of gels have a strong effect on the friction behavior.

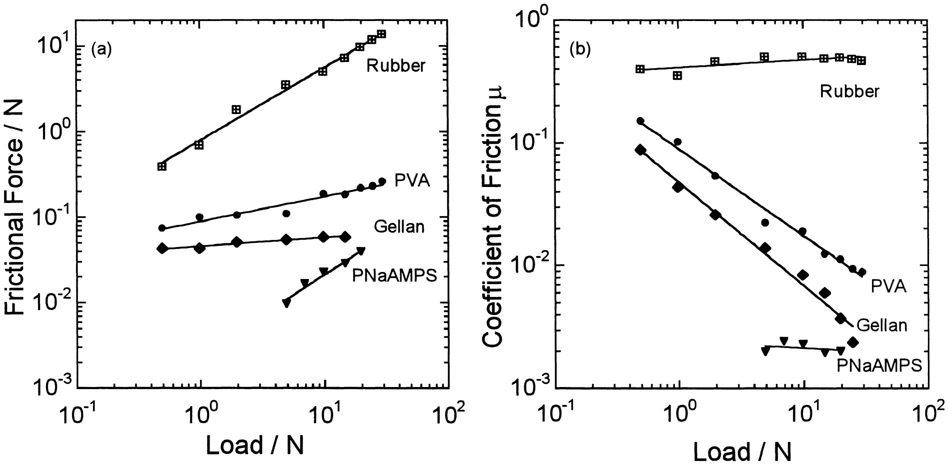

Fig.1 Dependencies of friction(a) and the coefficient of friction(b) on load for various kinds of hydrogels slide on glass surface in air. Sliding velocity: 7mm/min.; Sample contact area: PVA, gellan, and rubber, 3x3cm^2, PNaAMPS, 2x2cm^2. Degree of swelling q: PVA, 17; gellan, 33, PNaAMPS, 15.

The gel showed a much lower friction in water. Fig.2 shows the results in water measured at a velocity of 90mm/min, which is more than one order of magnitude larger than that in Fig.1 in order to obtain a friction force large enough to be measurable. The friction of PVA gel showed slightly stronger load dependence than that in air. The frictional force of poly(2-acrylamido-2-methylpropanesulfonic acid) (PHAMPS) gel is much lower with two load dependence profiles: it shows strong load dependence at low load, and less strong load dependence at high load that is similar to behavior of PVA. Such a load dependence of friction observed by PHAMPS gel was reversible.

However, if PHAMPS is allowed to slide on a Teflon plate, the friction-load profile remarkably changes. As shown in fig.2, the behavior of PHAMPS on Teflon is similar to that of PVA on glass showing a monotonous increase with the load but with a much higher value. These data demonstrate that besides the chemical structure of the gel, the surface property of the opposing substrate are crucial in friction and the interaction of the gel network with the substrate should be taken into consideration.

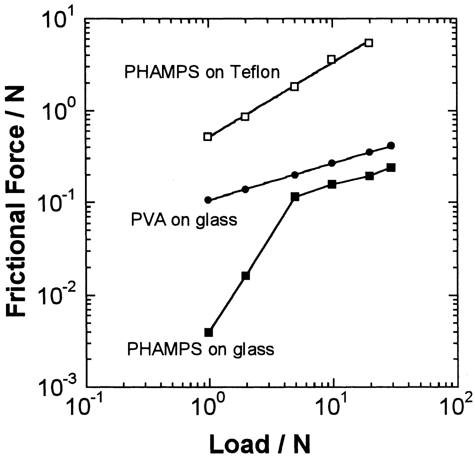

Fig.2 Load dependence of gel friction in water. Sliding velocity: 90mm/min., gel size: PVA, 3x3x0.8cm^3; PHAMPS, 3x3x0.6 cm^3. Degree of swelling: PVA, q=10; PHAMPS, q=15.

Repulsion-Adsorption Model

The gel friction can be explained in terms of polymer-solid surface repulsion and adsorption. When a polymer gel is placed in contact with a solid wall, the polymer chain would be either repelled from or adsorbed on the solid wall depending on the strength of the interaction between them in relative to the solvent. In the former case, a solvent layer is formed at the interface and the viscous flow of this solvent layer will make a dominant contribution to the frictional force. In the latter case, however, the adsorbing chain will be stretched when the solid surface is in motion relative to the gel. The elastic force increases with the deformation and detaches the adsorbing polymer chain from the substrate, thus it will in turn appear as the frictional force. According to this consideration, we have tried to deduce the friction theoretically.

1) Repulsive substrate

The viscous flow of the solvent layer at the interface should obey Newton's law and that of solvent in the polymer network can be expressed by the Debye-Brinkman equation[3] where the effect of polymer network is represented by a distributed force. By solving the Debye-Brinkman equation together with the Newton equation, the hydrodynamic lubrication between a repulsive solid surface and a gel is obtained[4]

$$f = \frac{\eta v}{\xi_g + \sqrt{K_{gel}}} \tag{1}$$

where η is the viscosity of solvent, v is the sliding velocity, ξ_g is the solvent layer thickness or the repelled distance of the gel from the solid surface against the normal pressure P, K_{gel} is the permeability of the gel. This result indicates that the equivalent non-slippery boundary of a gel surface is located at a depth of $\sqrt{K_{gel}}$ from the surface.

ξ_g can be determined from the interfacial free energy. The work done by the solid surface to repel the gel from the surface against the normal pressure should be equal to the increase in the interfacial free energy A, that is,

$$A - A_0 \cong P\xi_g \tag{2}$$

where A_0 is the interface energy between the substrate and the pure solvent. Supposing that the interfacial free energy between the gel and the substrate is the same as that between a polymer solution with a corresponding concentration and the substrate,

$$A - A_0 \cong \Pi_0 \xi \tag{3}$$

from the scaling theory[5]. Here Π_0 is the osmotic pressure and ξ is the correlation length of the polymer solution. On the other hand, K_{gel} can be related to ξ as $\xi \cong \sqrt{K_{gel}}$. From the above results, the friction for the repulsive substrate is

$$f \cong \eta v (E/T)^{1/3} \frac{(P/E)}{1+(P/E)/(1+P/E)^{1/3}} \tag{4}$$

in consideration of the deformation of the gel under the pressure P. Here E is the elastic modulus of the gel.

2) Attractive substrate

The friction mechanism in this case is quite similar to what occurred when rubber slides against a hard substrate. That is, the friction is due to the polymer chain detachment. We can follow the outline of the model proposed by A. Schallamach for the case of dynamic rubber friction. The dynamic friction per unit area due to adsorption can be expressed as[7]

$$f \cong \frac{Tv\tau_f}{R_F^4} \frac{(\tau_b/\tau_f)^2}{(\tau_b/\tau_f+1)} \tag{5}$$

where τ_b and τ_f are the average life-times of the polymer chain in the adsorbing state and in the free state, respectively. R_F is the radius of the polymer chain. The adsorption and desorption are attributed to thermal fluctuation. The stretching of the chain would favor desorption, that is, it would lower the energy difference between the adsorbing state and the free state by a value of F_{el}, which is the elastic energy of one stretched chain. So the transition rate from the adsorbing state to the free state becomes

$$\rho = \tau_f^{-1} \exp[-(F_{ads} - F_{el})/T] \qquad (6)$$

The above relation suggests that the adsorption time τ_b is a function of the deformation rate, or the sliding velocity. Under the normal pressure P, the adsorption energy would increase and it is found

$$F_{ads} \cong \begin{cases} T\phi^{-1/2}\delta(1+P/E)^{1/3} & for \quad \delta << \phi^{1/2} \\ T\phi^{-5/4}\delta^{5/2} & for \quad \delta >> \phi^{1/2} \end{cases} \qquad (7)$$

here, $T\delta$ is the effective attraction energy between a monomer unit and the surface in respect to the solvent and ϕ is the volume fraction of the polymer. Different with that of a rubber friction, the hydrodynamic component also exists in this case. The total friction for the attractive substrate of weak adsorption at small pressures is

$$f = \eta v(E/T)^{1/3}[\frac{1}{2} + (1+\frac{3}{2}\delta\phi^{-1/2})(1+P/E)^{1/3}] \qquad (8)$$

Discussion

Fig.3 shows the calculated curves of the relations between the friction and the normal pressure for a gel sliding on solids. The theoretical analysis showed that when the interaction between a gel and a substrate is repulsive, the frictional force is small with a linear dependence on the load. In the case of the attraction, the frictional force is high with weak load dependence if the attraction is not very strong. With the increase in the attraction, the friction increases and the load dependence becomes stronger. Comparing the observed frictional force in Fig.1 and Fig.2 with the theoretical prediction, we have found that the frictional forces of PNaAMPS gel and PHAMPS gel sliding on a glass substrate is quite low with strong pressure dependence. This suggests that the interaction between the PNaAMPS or PHAMPS gel with the glass surface is repulsive. The load dependence and the higher friction values of PVA gel on glass substrate and the PHAMPS gel on Teflon substrate suggest the attractive interaction.

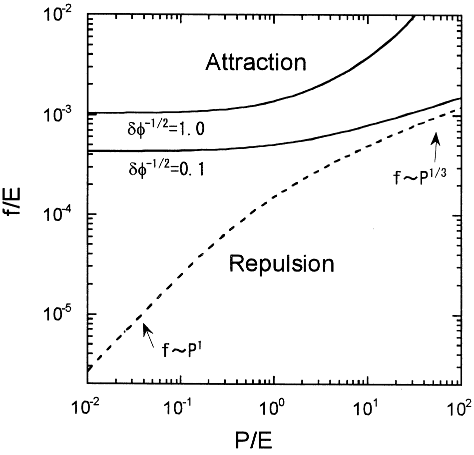

Fig.3 Pressure dependence of the frictional forces for gels sliding on a repulsive substrate (dotted line) as well as on attractive substrates with various $\delta\phi^{-1/2}$ (solid lines). $v=10^{-4}$m/s, ϕ=0.04, a=3×10^{-10}m, E=10^5Pa, $\eta=10^{-3}$Ns/m^2, T=4.14×10^{-21}J (300K).

In order to confirm the above prediction, the adhesive forces of these gels with the glass surface have been measured using the colloidal probe AFM. We found that PVA gel exhibits a large adhesive force in out-ward measurement examining the adhesive force, and gellan gel has a weak repulsion while PHAMPS gel and PNaAMPS gel show a strong electrostatic repulsion with the substrate. The repulsions are apparently due to the interaction between anions on the gel network and on the glass surface since it has negative Zeta potential in pure water. The weak repulsion between gellan and the glass could be attributed to the low charge density of $-COO^{-}$ in the gellan gel.

The results of AFM measurement well coincides with that of the frictional force which increases in an order of PNaAMPS<gellan<PVA. That is, the stronger the repulsion, the lower the friction. These results are in agreement with the modelling in which the predominant effect of the polymer-substrate interaction was postulated.

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