

Lubrication by Thin Liquid Films of Aqueous Polymer Solutions

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(Received July 6, 1985)

ABSTRACT: Lubrication properties of eight water-soluble polymers were studied by measuring the static friction coefficients μ_s of thin liquid films of these polymer solutions between glass surfaces. Thin liquid films of polymer solutions definitely enhance lubricity even at $C_p = 0.01$ g/100 ml and reduce the μ_s values of glass-water-glass interfaces to the extent of 20 to 30%, depending on their chemical structures. Above a concentration of 0.2 g/100 ml, μ_s becomes constant. Vinylic polymers usually have higher μ_s than polysaccharides and their derivatives.

KEY WORDS Water-Soluble Polymers / Tribology / Adsorption of Polymers / Lubrication / Static Friction Coefficient /

The friction between two solid surfaces originates from molecular attractive force which acts between the two surfaces. The action of a liquid lubricant is that, by being adsorbed on the solid surfaces, lubricant molecules (1) prevent from adhesion of the two solid surfaces and (2) replace the friction between the two surfaces by the friction between the liquid films formed by adsorption of the lubricant molecules on the surfaces. Thus, lubrication is an important surface phenomenon.¹ For boundary lubrication, Bowden and Tabor² proposed a contact model shown in Figure 1(a). The frictional force F is given by

$$F = A\{\alpha S_m + (1 - \alpha)S_f\} \quad (1)$$

where A is the area which supports loading, α is the surface fraction of the solid-to-solid type contact of shear strength S_m , and $1 - \alpha$ is the fraction of the film-film contact of shear strength S_f . Since the load W is expressed as $W = AP_m$, where P_m is a characteristic yield pressure, the friction coefficient μ is expressed by

$$\mu = \frac{F}{W} = \alpha \frac{S_m}{P_m} + (1 - \alpha) \frac{S_f}{P_m} \quad (2)$$

or

$$\mu = \alpha \mu_m + (1 - \alpha) \mu_e \quad (3)$$

where μ_m is the friction coefficient between the solid-solid contact part and μ_e is the friction coefficient of the thin liquid films. Since μ_e is less than μ_m it is necessary to decrease α in order to reduce μ , and this is usually achieved by the addition of a low molecular weight additive (lubricant) to liquids. The preferential adsorption of the lubricant in comparison with the liquid becomes pronounced and thus reduces α considerably.

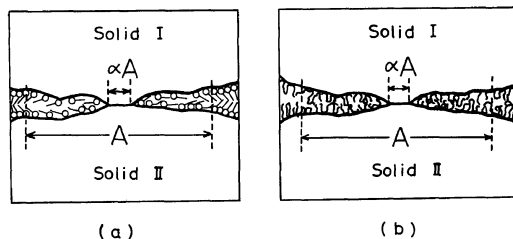


Figure 1. Model for boundary lubrication. (a) Case of low molecular weight lubricant. (b) Case of adsorbed polymer layer.

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Table I. Constants of the viscosity equation $[\eta] = KM^b$ and solvents for each polymers

Sample	$K \times 10^4$	b	Solvent	Temp/°C	References
PAAm	3.09	0.67	Water	25	7
PVA	4.28	0.64	Water	30	8
PVP	0.41	0.85	Water	25	9
Pullulan	1.79	0.67	0.1 N NaCl aq.	25	6
MC	3.19	0.79	0.1 N NaCl aq.	25	10
HEC	0.953	0.87	Water	25	11
HPC	8.69	0.65	0.1 N NaCl aq.	25	10
HPMC	3.72	0.77	0.1 N NaCl aq.	25	10

It is now well known that macromolecules can easily be adsorbed onto inorganic surfaces as well as metallic surfaces from dilute solutions.³ Therefore, it is expected that adsorbed macromolecules can also act as lubricating additives by reducing α with polymer adsorption as shown in Figure 1(b). Moreover, in a good solvent, interaction between two adsorbed polymer layers is repulsive and this should also reduce μ .

The lubricating action of dilute polymer solutions, especially those of biological macromolecules, is quite important in living processes such as the lubrication of joints. Tachibana⁴ measured the static friction coefficients of gelatin and albumin solutions between glass surfaces, and observed the lubricity of these protein solutions. Recently, certain synthetic water-soluble polymers were found to act as lubricants, especially in the molding processes in fine ceramic industry. However, no report has been published on the friction coefficient of water-soluble polymers in dilute solutions. The purpose of this paper is to measure the static friction coefficients μ_s for various types of water-soluble polymers and examine the μ_s values obtained in the light of their chemical structures.

EXPERIMENTAL

Samples

Eight water-soluble non-ionic polymers were used in this work. Poly(acrylamide) sample (PAAm) was prepared by radical poly-

Table II. Molecular characteristics of samples

Sample	$[\eta]/\text{dl g}^{-1}$	$M_v/10^4$	DS ^a	MS ^b
PAAm	2.95	87.1		
PVA	0.40	4.4		
PVP	1.60	25.2		
Pullulan	0.85	30.7		
MC	1.83	5.73	1.76	—
HEC	2.16	10.1	—	1.8
HPC	1.26	7.3	—	3.0
HPMC	13.8	85.9	1.89	0.27

^a Degree of substitution (DS) is the number of sites at which modification is made in an anhydroglucose unit.

^b Degree of molar substitution (MS) is the total number of propylene oxide or ethylene oxide molecules which reacted with one glucose unit.

merization with ammonium persulfate and *N,N,N',N'*-tetramethylethylenediamine as the initiators in MacIlvaine buffer solution (pH=4.7) to prevent hydrolysis of the amide unit in the monomer. The sample was dissolved in distilled water and was fractionated by the addition of methanol as precipitant at 25°C. The adequate fraction was used as the sample in this work. Poly(vinyl alcohol) sample (PVA, 88% hydrolyzed) was purchased from Katayama Kagaku Co., Japan, and the nominal molecular weight was reported as $M = 4 \times 10^4$. Poly(vinylpyrrolidone) sample (PVP, designated as K90) was purchased from Tokyo Kasei Co., Japan, and precipitated from aqueous solution by the addition of acetone. Methyl cellulose (MC, Metolose SM25) and hydroxypropyl-methyl cellulose (HPMC, Metolose 60SH4000) were supplied

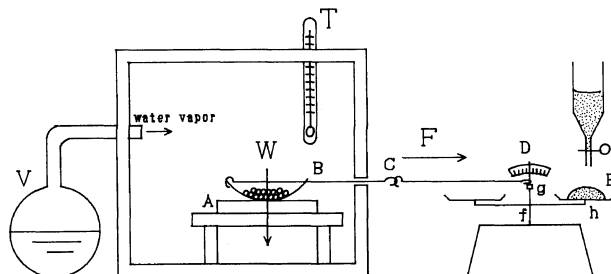


Figure 2. Schematic representation of the apparatus for static friction coefficient measurement. *T* is a thermoregulator. For the other symbols, see the text.

by Shin-Etsu Chemical Co., Japan. Hydroxyethyl cellulose (HEC, CELLOSIZO WP3L) was purchased from Union Carbide Corp., U.S.A. Hydroxypropyl cellulose (HPC, designated as HPC-L) was purchased from Nippon Soda Co., Japan. These four cellulose derivatives were purified by dissolving them in cold water, precipitating in acetone or methanol and washing the precipitates by dried methanol. Pullulan (PF30) was supplied by Hayashibara Biochemical Laboratories, Inc., Japan. The purification and fractionation were reported in previous papers.^{5,6} Each polymer sample was dried overnight in vacuo at room temperature. Intrinsic viscosities $[\eta]$ were measured on an Ubbelohde-type viscometer. The kinetic energy correction was always negligible.

The molecular weight of each polymer was determined by intrinsic viscosity measurement. The solvents and viscosity-molecular weight equations used were listed in Table I. The degree of substitution of methoxy groups of MC and HPMC and the number of propylene oxide and ethylene oxide molecules reacted with one glucose unit (degree of molar substitution) of HPMC, HPC and HEC were determined by the Zeisel-gas chromatography method.^{12,13} The results of molecular characterization of samples are shown in Table II.

Twice distilled water was used as solvent. Watch glasses and optical flat plate glasses, supplied from Central Glass Co., Japan were first dipped into a warm $\text{H}_2\text{SO}_4\text{-HNO}_3$ (1:1

vol. ratio) mixture, then thoroughly washed in distilled water and dried in a dust free box.

Static Friction Coefficient

Static friction coefficients for thin liquid films of aqueous polymer solutions between glass surfaces were measured by Sameshima's apparatus¹⁴ shown in Figure 2. *A* is a glass plate (10 cm \times 10 cm \times 0.5 cm) and *B* is a watch glass ($\phi=9$ cm), which acts as a slider and its weight *W* is adjusted by putting lead shots in it. *C* is a thin steel wire one end of which is hitched to the cutting of the watch glass *B*. The other end of *C* is connected to the pointer *D* of a prescription balance. Both *A* and *B* are located in a thermostated transparent plastic box. Water vapor was supplied from a vaporizer *V* to keep the saturated vapor pressure at a specified temperature in the box, and the vapor pressure was checked by a hygrometer placed in the box.

An aqueous polymer solution (0.15 ml) of a specified concentration was placed between *B* and *A*. Fine sand was poured as a small stream from a reservoir *R* onto the right pan *E*.

Addition of sand is continued until the pan at the right moves downward, the pointer inclines to the right side and the slider *B* moves to the right. The weight of sand is measured. When the weight of sand is *s*, the length between *f* and *g* is *l*, and the distance between *f* and *h* is *l'*, then the force *F* acting on the slider *B* is given by

$$F = s \frac{l'}{l} \quad (4)$$

The static friction coefficient μ_s is given by

$$\mu_s = \frac{F}{W} \quad (5)$$

For a specified polymer concentration and W , at least eleven measurements of F were performed and then the averaged F value was used in eq 5.

RESULTS AND DISCUSSION

As examples, Figure 3 shows the static friction coefficient μ_s of five aqueous polymer solutions (concentration: 0.1 g/100 ml) as a function of weight W . At less than $W = 120$ g, μ_s increases with a decrease in W ; however, when W is more than 120 g, μ_s becomes constant. According to the famous Coulomb's experiment,¹⁵ F is expressed as

$$F = A + \mu_1 W \quad (6)$$

where A is a constant and μ_1 is a friction coefficient. Then μ_s is given by

$$\mu_s = \frac{F}{W} = \mu_1 + \frac{A}{W} \quad (7)$$

Equation 7 indicates that when vertical force, W in this case, is very small, μ_s becomes very large and with increasing W , it approaches asymptotically to a constant value μ_1 . In Figure 4, F is plotted against W according to eq 6 and from the slope, we can determine μ_1 with the least square method. Even at present, the physical meaning of the constant A is obscure, but it is independent of W and is called the adhesion force. Moreover, when W is larger than around 120 g, the values of the second term (A/W) on the righthand side of eq 7 become smaller. μ_1 is thus practically equal to μ_s .

In the following, we employed the μ_1 values as μ_s for different polymer concentrations. The experimental errors in μ_s values at a relevant

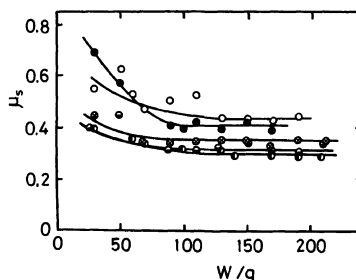


Figure 3. Static friction coefficient μ_s vs. weight W plots for the five polymer solutions. Polymer concentration: 0.1 g/100 ml. \circ , PAAm; \otimes , PVP; \bullet , MC; \bullet , HEC; \bullet , HPMC.

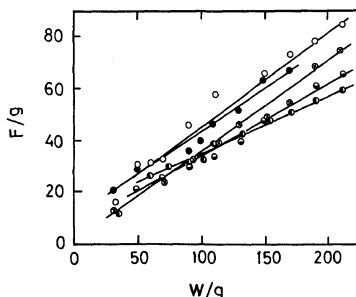


Figure 4. Force F vs. W plots for the five polymer solutions. Symbols are the same as in Figure 3.

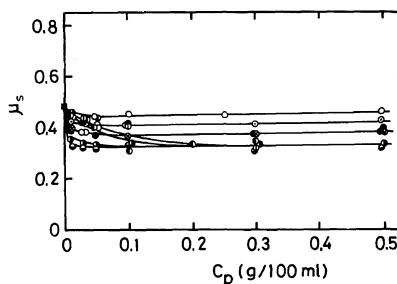


Figure 5. Polymer concentration dependence of μ_s of the eight polymer samples. \blacksquare , solvent (H_2O); \circ , PAAm; \otimes , PVP; \circ , PVA; \circ , Pullulan; \bullet , MC; \bullet , HEC; \bullet , HPC; \bullet , HPMC.

polymer concentration were less than 5%. Next, μ_s values of the eight polymer samples were plotted against the polymer concentrations in Figure 5. Except for pullulan and HEC, μ_s steeply decreases by the addition of polymers, notably even at 0.01% polymer solutions. It decreases from $\mu_s = 0.500 \pm 0.010$ of

Table III. Static friction coefficients μ_s of thin liquid films of polymer solutions

Polymer	μ_s	Backbone	Functional groups
PAAm	0.445 ± 0.010	$(-\text{CH}_2-\text{CH}-)_n$	R = $-\text{CONH}_2$
PVA	0.390 ± 0.007	$(-\text{CH}_2-\text{CH}-)_n$	R = $-\text{OH}$
PVP	0.350 ± 0.012	$(-\text{CH}_2-\text{CH}-)_n$	R = $-\text{N} \begin{array}{l} \text{O} \\ \parallel \\ \text{C}-\text{CH}_2 \\ \\ \text{CH}_2-\text{CH}_2 \end{array}$
MC	0.387 ± 0.012	Poly(β -1,4-glucose)	R = $-\text{OH}, -\text{OCH}_3$
HEC	0.307 ± 0.005	Poly(β -1,4-glucose)	R = $-\text{OH}, -\text{OC}_2\text{H}_4\text{OH}$
Pullulan	0.329 ± 0.011	Poly(β -1,4 and β -1,6-glucose)	R = $-\text{OH}$
HPC	0.322 ± 0.008	Poly(β -1,4-glucose)	R = $-\text{OH}, -\text{OC}_3\text{H}_6\text{OH}$
HPMC	0.312 ± 0.008	Poly(β -1,4-glucose)	R = $-\text{OH}, -\text{OCH}_3, -\text{OC}_3\text{H}_6\text{OH}$

the water film to $\mu_s = 0.31 \sim 0.45$ and then becomes constant irrespective of polymer concentration. It is clear that all water-soluble synthetic polymers as well as pullulan have lubricating action.

Table III shows a comparison of the μ_s values of various polymer obtained by averaging the values for polymer concentrations of more than 0.2 g/100 ml. In general, depending on their chemical structures, it appears that vinylic polymers have slightly higher μ_s values than polysaccharides and their derivatives except methylcellulose. Probably, the polysaccharide chains have a flat conformation on the glass surface and this may be favorable for reducing μ_s values.

In most experiments of polymer adsorption onto solid surfaces, the adsorption isotherm steeply increases first with increasing bulk polymer concentration and reaches a plateau region, while the shape of the μ_s vs. polymer concentration curve is just a mirror image of the shape of the adsorption isotherm. Therefore, to obtain more information about the molecular mechanism of lubricating action of these polymers, it is necessary not only to determine the adsorption isotherms onto glass surfaces but measure the thickness of the adsorbed layer; these studies are now in progress.

In conclusion, thin liquid films of water-soluble polymers definitely have lubricity and

reduce the μ_s values of glass-water-glass interface as much as 20 to 30%, depending on their chemical structures.

Acknowledgments. The fellowship given by Shinetsu Chemical Co., Ltd. is greatly appreciated. We also thank Messrs Y. Onda, S. Nakamura, and K. Hayakawa for their comments.

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