Chapter 5

FRICTION REDUCTION IN A SEMI-INTERPENTITRATING HYDROGEL

5.1 Introduction

Application of a lubricant has been the traditional approach to providing low friction surfaces for medical devices such as endoscopes or catheters that need to be placed in the urinary, tracheal, or gastrointestinal tracts. Lubricants allow for easy insertion and removal of devices, maximize comfort for the patient, and minimize damage to any tissue the device contacts.[1] Application of a lubricant, however, increases the possibility of cross contamination between patients (due to reuse of tubes of lubricant) and mishandling of the medical device (due to the difficulty in holding the slippery surface after lubricant is applied as well as any residual lubricant on the health practitioner's hands). An alternative approach is to develop surface coatings that are inherently lubricious when wet; the ideal surface would have high friction when dry to allow for good handling characteristics and a low friction when wet with bodily fluids to allow for high lubricity[1].

Because of their ability to rapidly swell in water and their high water content when swollen, hydrogels are especially promising for development of such inherently low friction surfaces. A hypothesis to explain the relationship between the physical properties of a hydrogel and the friction force measured between the hydrogel and a solid surface was initially developed by Gong and Osada,[2] and later modified in subsequent articles by themselves[3] and by Ronsin and coworkers.[4] At rest, polymer chains from the hydrogel adhere to the solid surface. The strength of this attraction between the gel and the solid increases over time, making it more difficult to initiate sliding as the interface ages. For movement of the hydrogel to occur, the chains adhering to the surface must stretch and the bond between the polymer and the surface must break. At velocities below a critical velocity, polymer chains from the hydrogel are still able to attach to the sliding solid surface, stretch, and then detach. Friction in this regime arises from energy needed to stretch chains and break their bonds with the surface. As the velocity of the hydrogel increases, the adhesion of chains becomes less frequent and the bonds created less strong. In their studies of the friction of gelatin on glass, Ronsin and coworkers observed slip-stick behavior in this regime,[4] but this has not been observed by other groups.

Above the critical velocity, the interface moves at a velocity too fast to allow adhesion of the polymer chains. The interface is therefore dominated not by the polymers of the hydrogel, but by the solvent. Friction arises due to viscous loss in the thin layer of solvent between the solid surface and the gel. An ideal low-friction hydrogel has a low critical velocity due to low adhesion of hydrogel chains to the contact surface.

Semi-interpenetrating hydrogels of agarose and anionic polymers are promising candidates for low friction biomedical surfaces because of their ability to rapidly swell after dehydration and the mobility of the anionic polymer. While agarose alone can form strong hydrogels at low polymer concentrations (such high water content should make it an excellent candidate for a lubricious surface), the dry gel swells very slowly in contact with water. The introduction of dextran sulfate, however, allows rapid swelling of the dry gel.[5] Besides allowing the gel to swell, mobile charged polymer chains, in principle, may diffuse to the gel surface and act like a lubricant. Studies have shown that dextran sulfate is not immobilized within the pores of agarose, but free to diffuse out of the gel.[5] The mobile, charged polymer should be beneficial for preventing adhesion between agarose and any surface with which the gel is in contact, forcing the gel into the low friction regime in which friction force is dominated by the solvent portion of the gel.

Using a method we developed to test friction with a rheometer,[6] we compare the friction of plain agarose gels with the friction of agarose gels doped with dextran sulfate. The friction of these gels against both hydrophilic, clean glass and hydrophobic, fluorinated glass is examined. Also considered is the effect of changing the dextran sulfate concentration, the effect of gel thickness, and the effect of normal force on the measured friction. We show that our gels exhibiting high friction accord with a scaling relationship proposed by Gong and Osada for gels below the critical velocity, while samples exhibiting low friction fit a power law relationship also observed by Ronsin and coworkers for gels above the critical velocity.

Finally, we look at the effect of replacing dextran sulfate with another polyelectrolyte, hyaluronic acid. Like dextran sulfate, hyaluronic acid is an anionic polysaccharide. Hyaluronic acid is a major component of synovial fluid, thought to be instrumental in the low friction of joints.[7] Unfortunately, hyaluronic acid is also expensive, leading us to develop our material using the much cheaper dextran sulfate and including hyaluronic acid only for final testing. We show that under physiological conditions gels doped with hyaluronic acid behave similarly to those with dextran sulfate—with even greater reduction in friction.

5.2 Experimental

Hydrogel preparation and friction measurement were preformed as described earlier.[5, 6] The only modification to these procedures is the use of glass modified with a fluorinated silane and the testing of gels doped with hyaluronic acid rather than dextran sulfate.

Fluorinated SAMs A modified version of a published protocol[8] was used to modify silicon wafers with fluoro-silanes. Briefly, glass plates cleaned in piranha solution, rinsed with deionized water, and dried in a stream of dry air were submerged in a solution of TFOS in hexane (2.5 %) for five minutes. The surfaces were removed and submerged in dichloromethane for 15 minutes and ethanol for approximately 30 seconds. Excess solvent was evaporated from the surface in a stream of dry air. Control experiments using argon confirmed that the air did not introduce any contaminants.

Semi-Interpenetrating Hydrogels Containing Hyaluronic Acid PBS buffer was prepared so that the total phosphate concentration was 0.018*M* and the sodium chloride concentration was 0.16*M*. The pH was adjusted to 7.2. The pKa of HA is 6.5, so the polymer is charged in this state. Semi-interpenetrating gels containing hyaluronic acid were prepared in the same manner as those gels containing dextran sulfate, except the cold mixture of hyaluronic acid stock solution, dry agarose, and extra buffer was placed on a shaker for fifteen minutes before the solution was heated. This extra mixing was required since the concentrated HA stock solution took longer to dissolve in excess water than the dextran sulfate solution.

5.3 Results

Friction on agarose hydrogels was found to increase with polymer concentration: angular velocity of a clean glass plate on 3% agarose was slower than on 2% agarose due to the increase in friction (Figure 5.1). Preliminary experiments performed on 1% agarose gels showed even less friction than on the 2% gels, but 1% agarose gels were not stable at all normal forces (≤2 N) examined in this paper. 4% agarose gels were impossible to properly test: the hot solution was too viscous to reproducibly spread on the bottom plate of the rheometer. All further friction experiments were therefore performed on 2% agarose hydrogels: the most lubricious hydrogel that was stable at all the normal forces examined.

Friction on gels containing 2% agarose and additional dextran sulfate at 1, 2, or 3% was reduced relative to plain 2% agarose gels (Figure 5.2). The effect of dextran sulfate was nonmonotonic: Agarose hydrogels doped with 2% dextran sulfate showed the lowest friction of the gels examined. Therefore, gels doped with 2% dextran sulfate became the focus of most subsequent experiments. Doping agarose with hyaluronic acid also decreased friction and showed a nonmonotonically dependence on the concentration of the polyanion (Figure 5.3). In the case of the 800k hyaluronic acid, a 1% hyaluronic acid doping gave the most lubricious hydrogel tested.

All tests using the hydrophobic glass were performed using Underwater Protocol 1. The In Air Protocol could not be used to measure the friction of hydrogels against TFOS modified glass due to the formation of bubbles between the hydrogel and the hydrophobic glass, which caused the actual area of contact to be 1) drastically smaller than the full surface area of the gels, 2) irreproducible, and 3) sensitive to imposed normal force.

To unambiguously compare the lubricity of 2% agarose hydrogels with 2% agarose doped with 2% dextran sulfate, a series of experiments were performed using the same piece of glass and the same torque ramping against both types of hydrogel. Underwater Protocol 1 was used for these experiments. These pairs of experiments were repeated with two different pieces of clean glass and two different pieces of TFOS functionalized glass. Against both substrates and at all normal forces tested, the gels doped with 2% dextran sulfate were more lubricious than those without added dextran sulfate (Figure 5.4 and Figure 5.5). A higher maximum torque (T_{max} = 5000 μN·m) was used in the tests against the TFOS functionalized glass compared to the tests against clean glass (T_{max} = 3000 μN·m) due to the higher friction measured against the hydrophobic substrate.

In elastomers, energy loss in the bulk of the material is known to contribute to friction[9]. To evaluate the possible contribution of the bulk mechanical properties to the friction of the hydrogels, a comparison was made between hydrogels of different thicknesses. These experiments were performed using the In Air Protocol against clean glass. As the thickness of 2% agarose gels was decreased, the gels became more lubricious (Figure 5.7). When the same experiments were performed against gels containing 2% agarose + 2% dextran sulfate, there was no clear correlation between gel thickness and lubricity (Figure 5.8).

To evaluate the performance of semi-interpenetrating hydrogels under physiological conditions, PBS buffer was used rather than water during one set of experiments. Buffer was used both to make the gels and submerge them during testing. It was desired to compare the lubricity of gels doped with dextran sulfate with gels doped with hyaluronic acid. Therefore, gels loaded with 1% HA (the most lubricious composition of HA tested) and 2% dextran sulfate were compared. It was found, however, that the 2% dextran sulfate gels became coarsely grained in buffer. (Although the phase behavior of the agarose/dextran sulfate systems was not studied, solubility of both agarose[10] and dextran[11] has been shown to change with salt concentration. The coarsening of the gel at a lower concentration than occurs in pure water is thus probably due to a salt effect.) Gels with a 1% doping of dextran sulfate were therefore also tested since these gels showed no coarsening under buffer. The gels doped with 1% HA greatly outperformed the gels doped with dextran sulfate (Figure 5.8). Due to the high lubricity of the HA doped gels, a particularly low maximum torque was used in these experiments (T_{max} = 2000 μN·m).

5.4 Discussion

Agarose hydrogels and semi-interpenetrating hydrogels containing agarose and a polyanion follow the theory presented in the introduction: a high friction regime in which friction is dominated by adhesion of polymer chains onto the contact surface and a low friction regime in which friction is dominated by viscous loss in the solvent portion of the hydrogel. To make the connection between our experiments and this theory we show that our data follow the scaling relationship predicted by Gong and Osada in the high friction regime and follow a power law relationship also measured by Ronsin and coworker in the low friction regime. Once the connection between our experiments and this theory of hydrogel friction has been established, we then use the theory to interpret the decreased friction observed when a mobile polyanion is introduced into agarose. Other experiments also consistent with dextran sulfate migrating to the gel/glass interface and acting as a lubricant are also presented. We consider how Gong/Osada/Ronsin theory explains an observation made by ourselves and other groups: the decrease in hydrogel friction underwater. Finally, the significantly improved lubricity of HA compared to dextran sulfate measured in buffer is considered.

Our Data and the Gong/Osada/Ronsin Theory Less lubricious hydrogels in our experiments show a linear relationship between angular velocity and torque. This linear relationship tends to appear in hydrogels without dextran sulfate, during measurements taken using the In Air Protocol, and at higher normal forces. For example, the experiments in Figure 5.3 illustrate the linear relationship between angular velocity and torque measured in the absence of dextran sulfate and at higher normal forces. Linear regression of this data shows an excellent fit for the gels with 0% dextran sulfate (the regression coefficient is between 0.9991 and 0.9996) (Table 5.1). Linear regression is a poor fit, however, for more lubricious gels such as the agarose with 2% dextran sulfate; the regression coefficient drops as low as 0.9505 at 0.5 N normal force (Table 5.1). At higher normal forces, the behavior of the gel doped with 2% becomes more linear. At the highest normal force tested (2 N) the regression coefficient has increased to 0.9893 and the behavior is more similar to that of the plain agarose gels. Also, a linear relationship between the angular velocity and the torque is more likely to occur using the In Air Protocol than any of the underwater protocols (Figure 5.2).

Such a linear relationship between angular velocity and torque is predicted by Gong and Osada in the regime where polymer chains interact strongly with the contact surface.[2] Gong and Osada derive a relationship between friction force (*f*) and velocity (*v*) based on earlier models of elastomer friction:

$$f = \frac{\eta v E^{1/3}}{T^{1/3}} F\left(E, P, b, \varphi, \delta\right) \tag{5.1}$$

where *F* is a function of the elastic modulus (*E*), pressure (normal force per unit area) (*P*), Kuhn length (*b*), polymer volume fraction (*ϕ*), and the dimensionless interaction energy between the polymer and the surface (*δ*). The particular form of *F* depends on the relative magnitudes of ϕ and δ. For our purposes, F is a constant at a given normal force. Additionally, T is the temperature. A linear scaling between friction force and velocity implies a linear scaling between torque and angular velocity, as observed in our experiments. While Gong and Osada's scaling between the f and v matches our data, the full Gong and Osada model predictions cannot capture our experimental observations. Gong and Osada predict that movement occurs at even the smallest applied force. This implies a zero intercept, which clearly contradicts our results. Still, the proper scaling relationship does help validate our view that adhesion between the polymer and the surface is responsible for friction in these high friction experiments.

In the hypothesized regime where the solid surface is moving too fast for chain ends from the hydrogel to adhere to it, Ronsin and coworkers argue in favor of power law relationship between drive velocity and frictional shear stress (σ) based on dimensional analysis. Rather than a layer of pure solvent between the network and the contact surface, Ronsin and coworkers view the interface as a dilute polymer solution.[4] They define a shear rate ($\dot{\gamma}$):

$$\dot{\gamma} = \frac{V}{\xi} \tag{5.2}$$

where V is the velocity of the hydrogel and ξ is thickness of the depletion layer between the polymer and the contact surface. They evoke the model of the c* gel proposed by deGennes in which the mesh size of the gel is equal to the correlation length. Furthermore, ξ is of the order of correlation length. In the case of Ronsin's gelatin—as well as our agarose—ξ must be viewed as a characteristic length of the system rather than the actual mesh size of the gel. To eliminate ξ, the relationship between modulus (G) and mesh size (ξ) for an ideal network is used:

$$G \sim \frac{kT}{\xi^3} \tag{5.3}$$

where k is Boltzmann's constant. Using equations 5.2 and 5.3, a dimensionless viscosity is constructed out of measurable variables:

$$\frac{\eta_{eff}}{\eta_s} = \frac{\sigma}{\dot{\gamma}\,\eta_s} \sim \frac{\sigma}{V\eta_s}\left(\frac{kT}{G}\right)^{1/3} \tag{5.4}$$

where η_{eff} is the effective viscosity and η_s is the solvent viscosity. This dimensionless effective viscosity is plotted against the Weissenberg number (We = $\dot{\gamma}\,\tau_R$), defined as the ratio of the shear rate and a characteristic time (τ_R). The Rouse time is used as the characteristic time, assuming that the polymer blobs in the gap are best modeled by a dilute polymer solution. (The Zimm time would be the more appropriate choice for dilute solutions, but we will stick with the Rouse time since it is the proper choice for polyelectrolytes.)

$$\tau_R = \frac{2\eta_s b^3}{\pi kT} N^2 \tag{5.5}$$

To eliminate the degree of polymerization (N), ideal chain statistics are assumed:

$$N^2 = \frac{\xi^4}{b^4} \tag{5.6}$$

The Rouse time recomes:

$$\tau_R = \frac{2\eta_s \xi^4}{\pi kbT} \tag{5.7}$$

After substitution of the shear rate and τ_R, the We becomes:

$$\mathrm{We} = \frac{2V\eta_s}{\pi b G} \qquad (5.8)$$

The only adjustment to We and η_{eff}/η_s needed to fit our data is the conversion of the linear velocity to an angular velocity:

$$\frac{\eta_{eff}}{\eta_s} = \frac{\sigma}{R\omega\eta_s}\left(\frac{kT}{G}\right)^{1/3} \qquad (5.9)$$

$$\mathrm{We} = \frac{2R\omega\eta_s}{\pi b G} \qquad (5.10)$$

where ω is the angular velocity, and R is the radius of the gel pad. The rim velocity is used for all calculations.

Using these dimensionless groups, the data from Figure 5.4a shows a power law relationship between η_{eff}/η_s and We (Figure 5.9). Similarly, the data taken against TFOS functionalized glass (Figure 5.5a) shows a power law when plotted using the same formalism (Figure 5.10). The power law exponent varies from -0.43 to -0.90 for this data (Table 5.2). Ronsin and coworkers found a slope of -0.6 for gelatin gels, regardless of polymer concentration in the gels. Our power law exponents do show some dependency on the nature of the gel and the contact surface. The average exponents from the 2% agarose gels are lower than those on the gels of 2% agarose + 2% dextran sulfate for all four sets of experiments (Table 5.3). Also, the average exponent for the data taken against TFOS is lower than that taken against clean glass. The fit of our data to the power law relationship of Ronsin offers support for their dimensional analysis treatment of hydrogel friction.

Dextran Sulfate as a Lubricant Unlike other groups examining gel friction, we introduced a polymer into the gel that was free to diffuse out of the network. We hypothesized that a mobile polymer would give the gel a self-lubricating surface. Indeed, at all normal forces examined, at each imposed torque, the angular velocity of a glass plate is greater on the gel with dextran sulfate than it is on agarose without dextran sulfate. While this data supports the idea that dextran sulfate improves hydrogel lubricity, it can not exclude the possibility that the effect be due to the increase in electrostatic repulsion between the glass and the gel. Introducing dextran sulfate into agarose increases the charge density of the gel. Since glass caries a negative surface charge, this charge increases electrostatic repulsion between the gel and the glass. In turn, increased repulsion can lessen gel friction by increasing any gap (ξ) present between the glass and the gel (Figure 5.11).[12] To test whether lubricity persists when electrostatic repulsion between the gel and the solid is eliminated, glass plates were functionalized with a fluorinated hydrocarbon. This treatment raises the contact angle of the glass surface to 105°,[13] a high contact angle consistent with elimination of surface charge. Even with surface charged eliminated, dextran sulfate still lowers friction when doped into agarose (Figure 5.5). In the absence of charge repulsion, the dextran sulfate still acts as a lubricant. Charge repulsion can also be eliminated by high ionic strength. Agarose gels doped with dextran sulfate and hyaluronic acid were tested in buffer with a Debye length of 1.3 nm. Long range repulsion between the hydrogel and the glass is not possible in such buffer, but both dextran sulfate and hyaluronic acid still act as lubricants. In particular, hyaluronic acid still showed remarkable lubricity under these conditions.

Since the mobile polymer in the semi-interpenetrating hydrogel is charged, a large repulsion exists between different chains. This repulsion drives the polymer to distribute itself over as large an volume as possible, inevitably driving some polymer to diffuse to the gel/glass interface. Dextran sulfate molecules present at the interface will sterically hinder agarose from absorbing to the surface of the solid. By reducing interaction of network chains with the contact surface, dextran sulfate hastens the transition between the high friction regime and the low friction regime. Even if attraction existed between the dextran sulfate and the contact surface, it would not contribute strongly to friction because dextran sulfate is not bound to the agarose network.

Hydrogel friction was greater against TFOS surfaces than against clean glass. When friction against a clean glass plate was tested against agarose, a maximum torque of 3000 μN·m was used (Figure 5.4). To achieve similar angular velocities using a fluorinated glass plate against agarose, the maximum torque was increased to 5000 μN·m (Figure 5.5). Since agarose is sparsely charged, and agarose + dextran sulfate is highly charged, there is undoubtedly a decrease in electrostatic repulsion when the contact surface is changed from clean glass to TFOS. This decrease in repulsion can explain the observed increase in friction. Gong and Osada also compared the friction of gels against glass and Teflon and saw friction forces increase one order of magnitude against the Teflon.;[14] they ascribed the increase in friction against Teflon as being due to dominance of attractive van der Waals forces between the polymer and the surface in the absence of electrostatic repulsion.[14] Certainly, when the contact surface is changed, differences in several forces (van der Waals, hydrogen bonding, as well as "hydrophobic" forces) may occur that alter the interaction between polymer, solvent, and the contact surface. While electrostatic repulsion alone is sufficient to explain the trends in our data, other forces may contribute to the observed friction.

The mobility of dextran sulfate explains the observation in Chapter 3 that when dextran sulfate is given time to leach out of the gel, friction is increased. Protocol 2 gave angular velocity versus torque traces that consistently showed higher friction than the other two underwater protocols (Figure 3.6). During this protocol, the gel pads were equilibrated underwater for thirty minutes before the glass plate was lowered and the experiment commenced. The amount of dextran sulfate able to diffuse out of the gel pad during those thirty minutes is substantial: when cylinders of gel—with dimensions (1.1 cm in height, 1.5 cm in diameter) much larger than the 1 mm thick gel pad used in friction experiments—were placed underwater, approximately 25% of the dextran sulfate in the cylinders was lost during the first thirty minutes of the experiment.[5] Once the glass plate is lowered during Protocol 2 and the experiment commences, less dextran sulfate is available to act as a lubricant than in the protocols where no underwater equilibration occurred and friction increased. With the reduced amount of dextran sulfate, the friction increases.

Based on the physical picture we have presented for lubrication in the presence of dextran sulfate in the gel, one would expect friction to be governed by phenomena very near the surface for dextran sulfate containing gels; this is borne out in the observed effects of the thickness of the gel pad on friction. When bulk processes (dissipation) contribute to friction, the magnitude of friction decreases as thickness decreases. Indeed, friction measured on the 500 μm pad of agarose was less than that measured on a 750 μm pad or a 1000 μm pad (Figure 5.6). In the high friction regime, this dependence on bulk properties can arise from the deformation of the gel as polymer chains from the network adhere to the contact surface. All but one of the traces measured during this experiment show a linear dependency of angular velocity on torque, indicative of the high friction regime. When the same experiment is performed on gels doped with 2% dextran sulfate, the tendency to measure higher friction on thicker gels disappears (Figure 5.7). Without bulk deformation due to network chains adhering to the glass, the dependency of friction on gel thickness is lost. Also, the traces are no longer linear, consistent with the low friction regime. Dextran sulfate present at the gel/glass interface would prevent the absorption of agarose chains onto the glass. Without absorption, friction is limited to interfacial viscous loss, and the dependence on gel thickness disappears.

Implications of the Gong/Osada/Ronsin Theory for Friction Under Air Versus Water Hydrogel friction measured underwater is lower than friction measured in air[14] We considered the possibility that decreased friction measured underwater (Figure 3.6) is due to a squeeze film formed when the test surface is lowered through water into contact with the hydrogel. However, angular velocity traces were nearly identical whether the glass is lowered onto a gel underwater (Protocol 1) or whether the reservoir was filled with water after contact between the test surface and the gel had already been made (Protocol 3) (Figure 3.6). Meniscus forces, which can greatly increase friction between solids in air but disappear when the interface is submerged,[15] are unlikely to occur in hydrogels due to the close fit between the soft, compliant gel and the contact surface.

Changes in the very outer layer of the gel may create an interface that favors interaction between the polymer chains in the gel and the contact surface rather than the solvent or the free chains in the gel and the contact surface. In relation to the physical picture of Gong/Osada/Ronsin, it is noteworthy that the three “underwater protocols” in figure 3.6 are all associated with a velocity versus force trajectory that is highly nonlinear and the “in air protocol” gives an approximately linear increase of velocity with force. The former is consistent with Ronsin’s view of a thin solution-like layer, while the latter, linear behavior accords with Gong and Osada’s model of network strands interacting with the surface. Perhaps the near surface structure of a hydrogel in contact with air is rich in polymer segments, particularly those that are uncharged and relatively nonpolar. Certainly, highly charged chains would not be enriched at the gel/air interface. We note that in Protocol 3 (Figure 3.3) contact between the glass plate and the gel is established under air, yet the history is “erased” by subsequently filling the cell with water. We hypothesize that rapid restructuring of the contact occurs when water in introduced, leading to a contact very similar to that for contact established underwater, Protocol 1, since the velocity versus force is virtually indistinguishable (Figure 3.6).

Hyaluronic acid and buffer. In buffer, gels doped with HA showed superior lubricity to gels doped with 1% dextran sulfate. The difference in lubricity between gels doped with dextran sulfate and gels doped with HA might be due to differences in the ability of the two polymers to be compressed. The Kuhn length of dextran is 3-3.6 nm,[17] while the Kuhn length of HA is 8 nm.[18, 19] The free energy cost of confining a polymer of given length (*N*) and Kuhn length (*b*) to a pore of given diameter (*D*), or a gap between parallel plates separated by a distance (D), scales as:

$$F \approx kT\left(\frac{bN^{\nu}}{D}\right)^{1/\nu} \qquad (5.9)$$

where ν is the scaling exponent of the polymer.[20] At the same normal force, the gap between plates will be larger for HA than dextran sulfate since HA is longer and less flexible. If this gap is seen as ξ between the glass and the gel (Figure 5.11), the lubricity at a given normal force will be higher for HA.

5.5 Conclusion

To our knowledge, this chapter presents the first studies of friction on a hydrogel that contains mobile, linear chains. Friction on this hydrogel accords with the theory of Gong, Osada, and Ronsin, demonstrating the scaling relationship between angular velocity and torque predicted by Gong and Osada in a high friction regime and obeying the power law relationship of Ronsin in a low friction regime. We have shown that the free chains are able to diffuse out of the hydrogel and believe that this mobile polymer acts as a lubricant at the interface, disrupting interaction between the agarose network and the contact surface. While electrostatic repulsion between the hydrogel and the contact surface is shown to be partially responsible for this reduction in friction, the addition of dextran sulfate also increases lubricity against neutral surfaces.

Using hyaluronic acid, a very biocompatible polyelectrolyte, in place of dextran sulfate provides even better lubricity under physiological conditions. This finding, along with observations that agarose doped with a polyelectrolyte rapidly swells makes us optimistic that this gel may have clinical use. Experiments adhering thin films of this gel to relevant materials (such as surgical steel or polymer tubing), dehydrating the gel, and then testing the lubricity in contact with moist tissue would be particularly interesting.

5.6 Figures and Tables

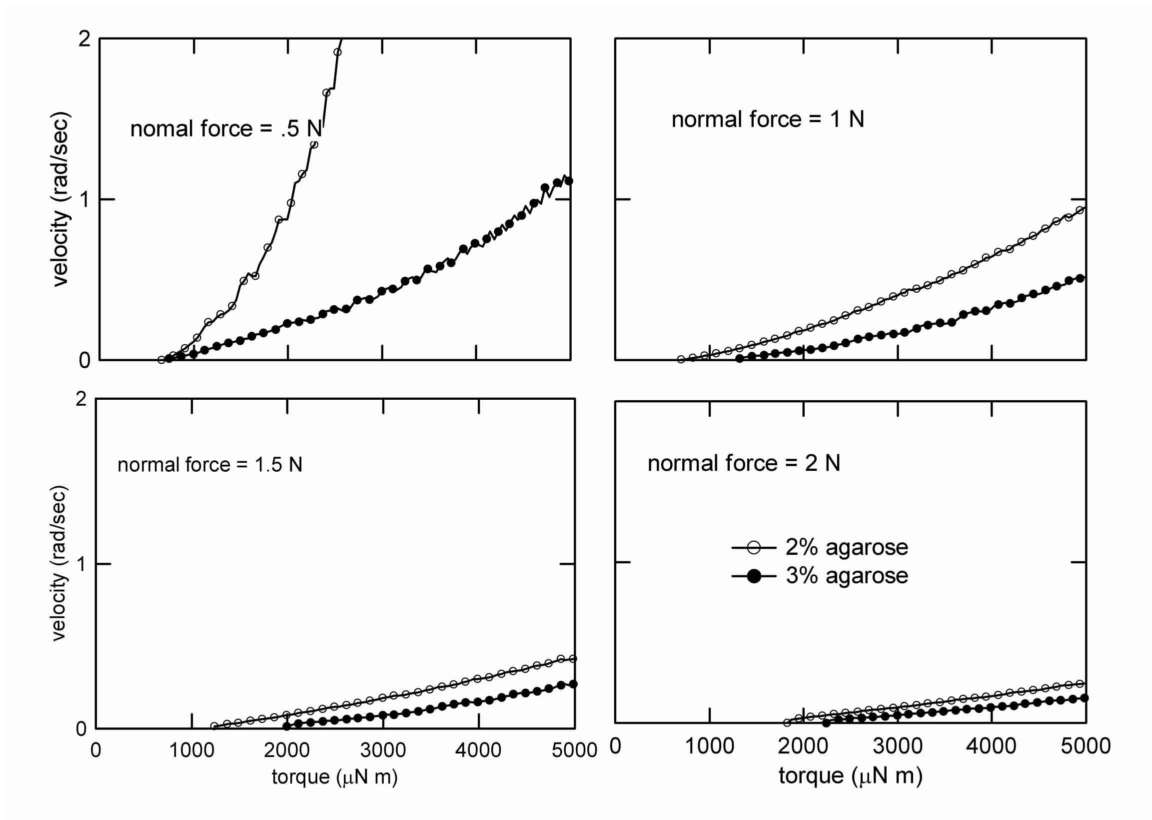

Figure 5.1 Comparison of velocity of glass plate on 2% and 3% agarose gels. Measurements were taken using the In Air Protocol.

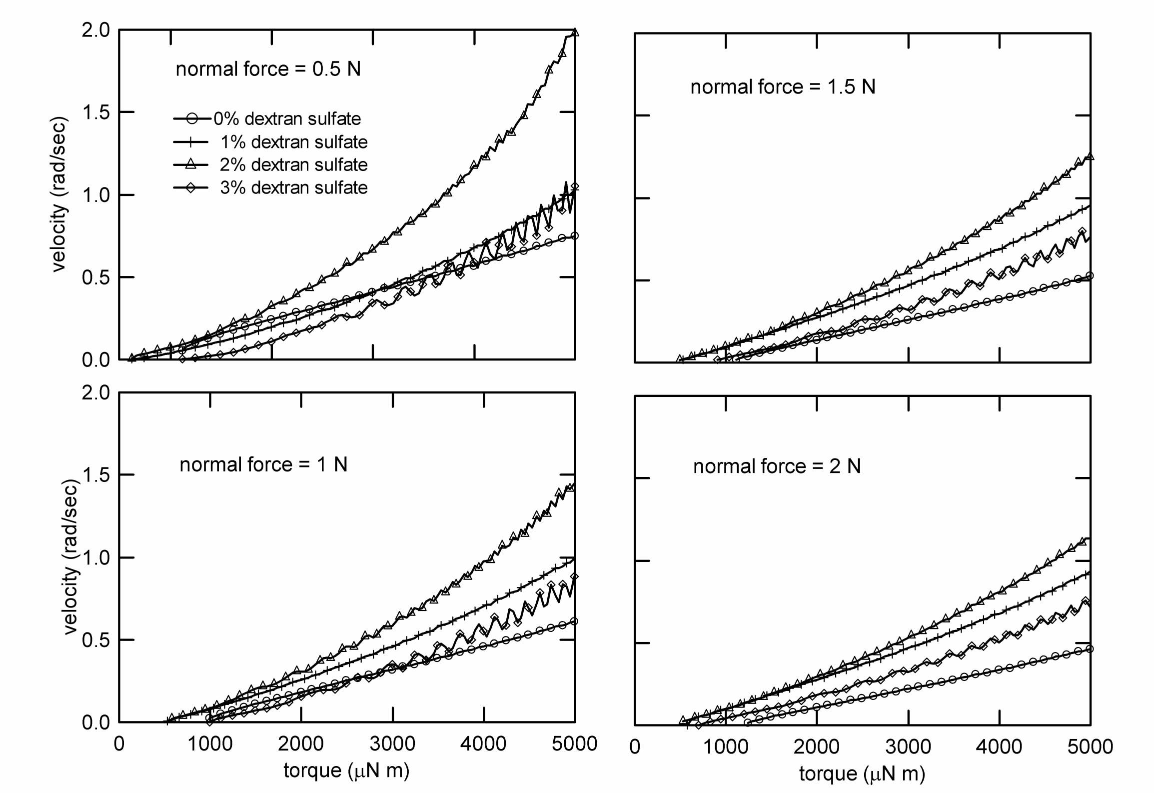

Figure 5.2 Effect of dextran sulfate composition in a semi-interpenetrating hydrogel in which the matrix is composed of 2% agarose. Measurements were taken using the In Air Protocol. Contact surface was a clean glass plate.

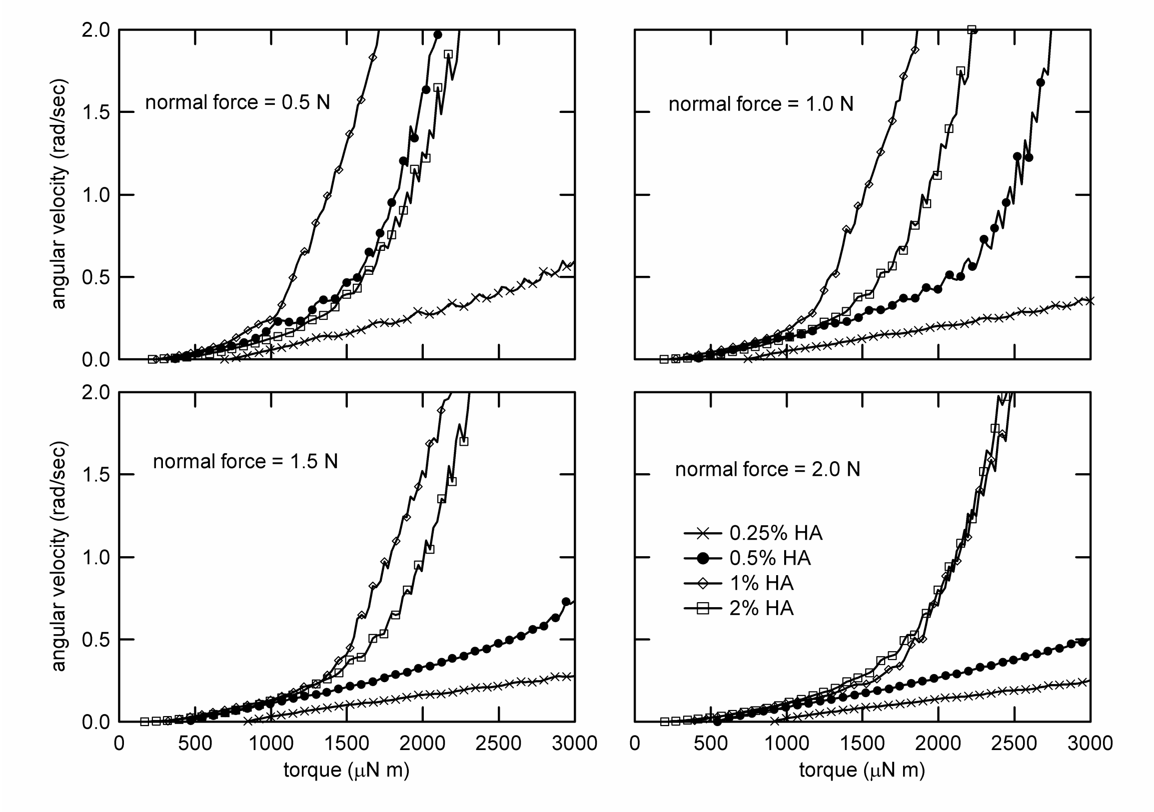

Figure 5.3 Effect of 800k hyaluronic acid composition in a semi-interpenetrating hydrogel in which the matrix is composed of 2% agarose. All measurements were taken using the same clean glass plate. The In Air Protocol was used. Gels were made with buffer rather than water.

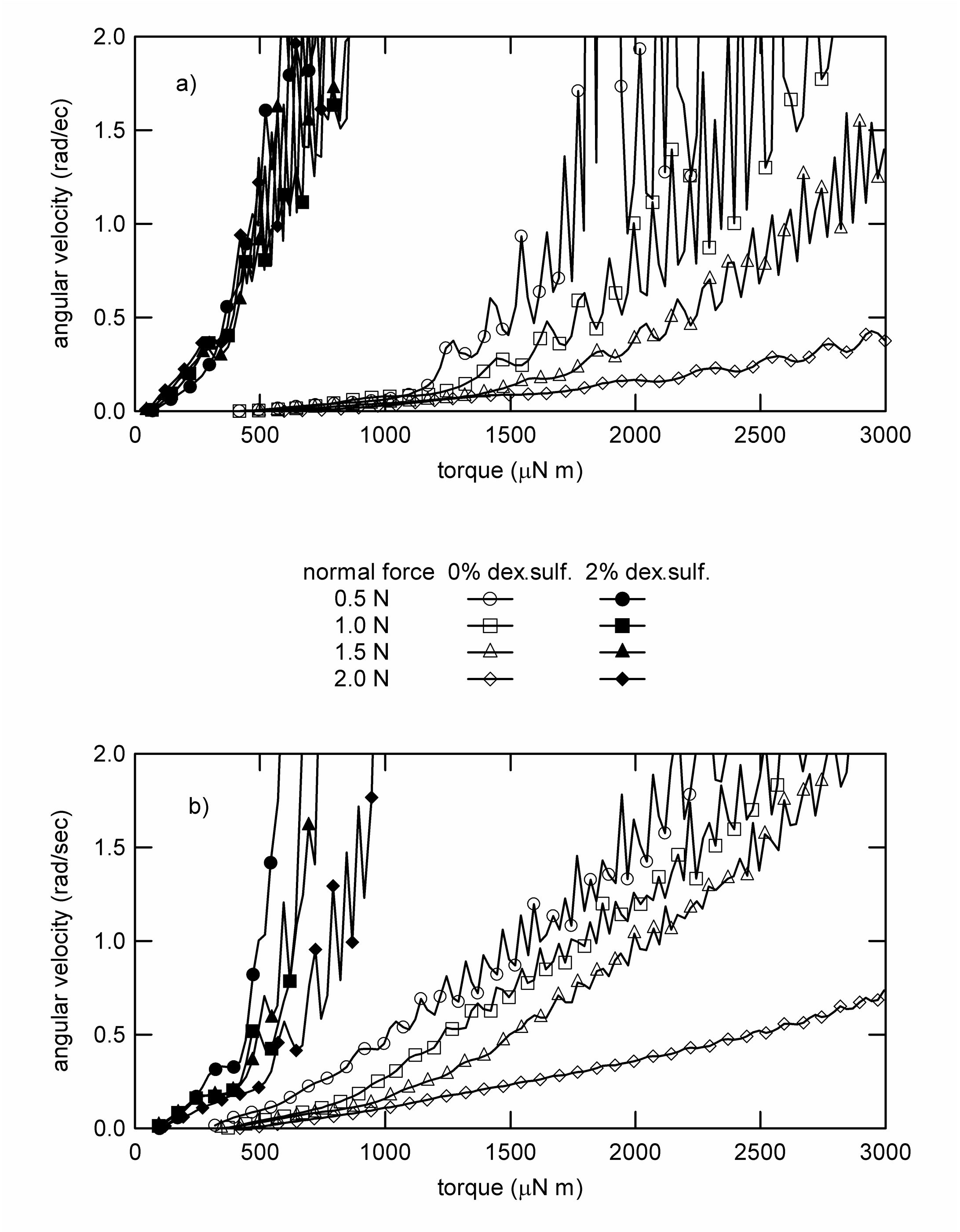

Figure 5.4 Velocity of clean glass on 2% agarose hydrogels (open symbols) and semi-interpenetrating 2% agarose and 2% dextran sulfate hydrogels (filled symbols). All measurements are taken under water using Protocol 1. Matching shapes indicate measurements taken at the same normal force. Each piece of glass is used for two measurements, once on each type of hydrogel. a) Glass slide #1. b) Glass slide #2.

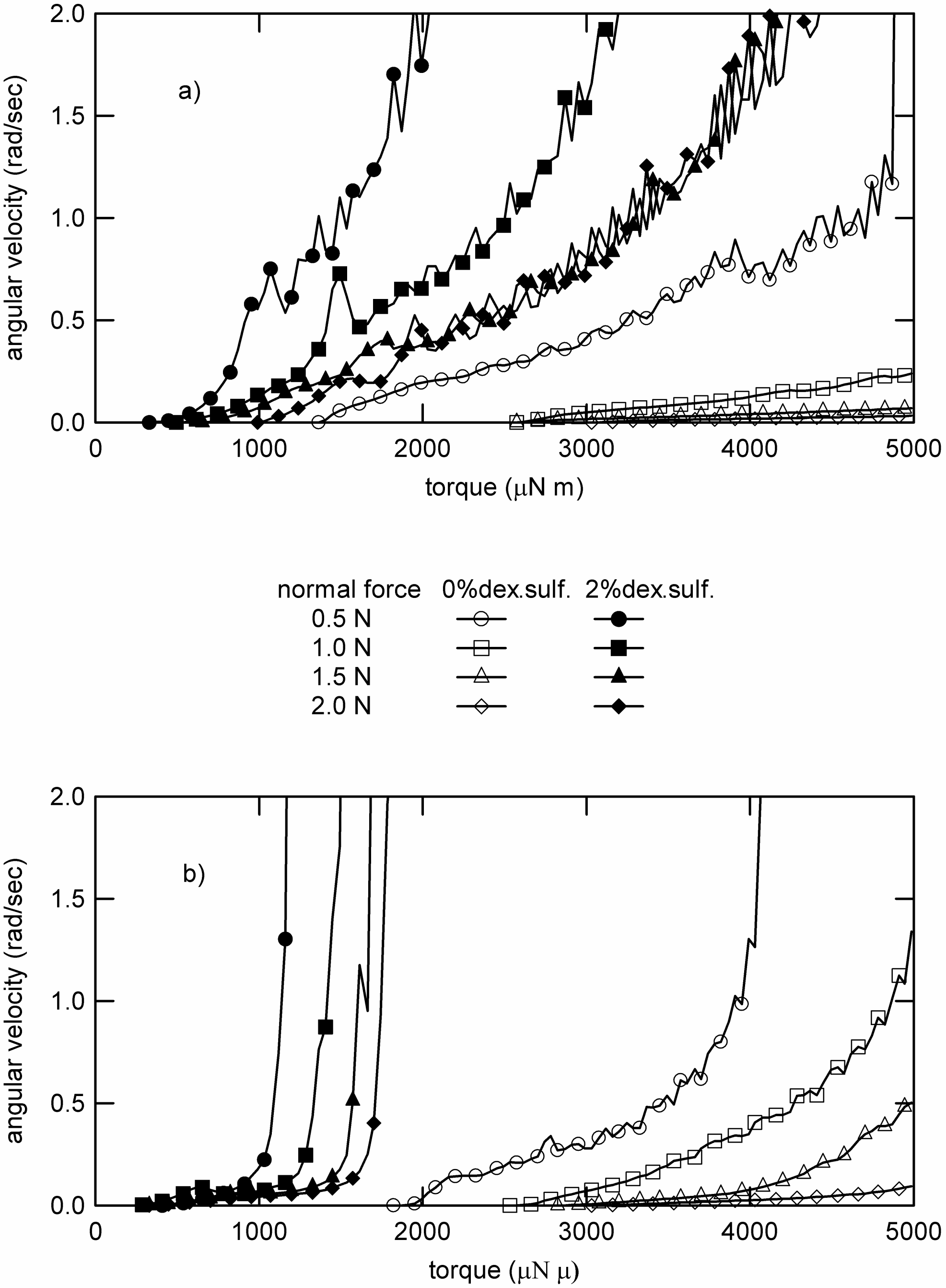

Figure 5.5 Velocity of TFOS modified glass on 2% agarose hydrogels (open symbols) and semi-interpenetrating 2% agarose and 2% dextran sulfate hydrogels (filled symbols). All measurements are taken under water using Protocol 1. Matching symbols indicate measurements taken at the same normal force. Each piece of glass is used for two measurements, once on each type of hydrogel. a) Glass slide #1. b) Glass slide #2.

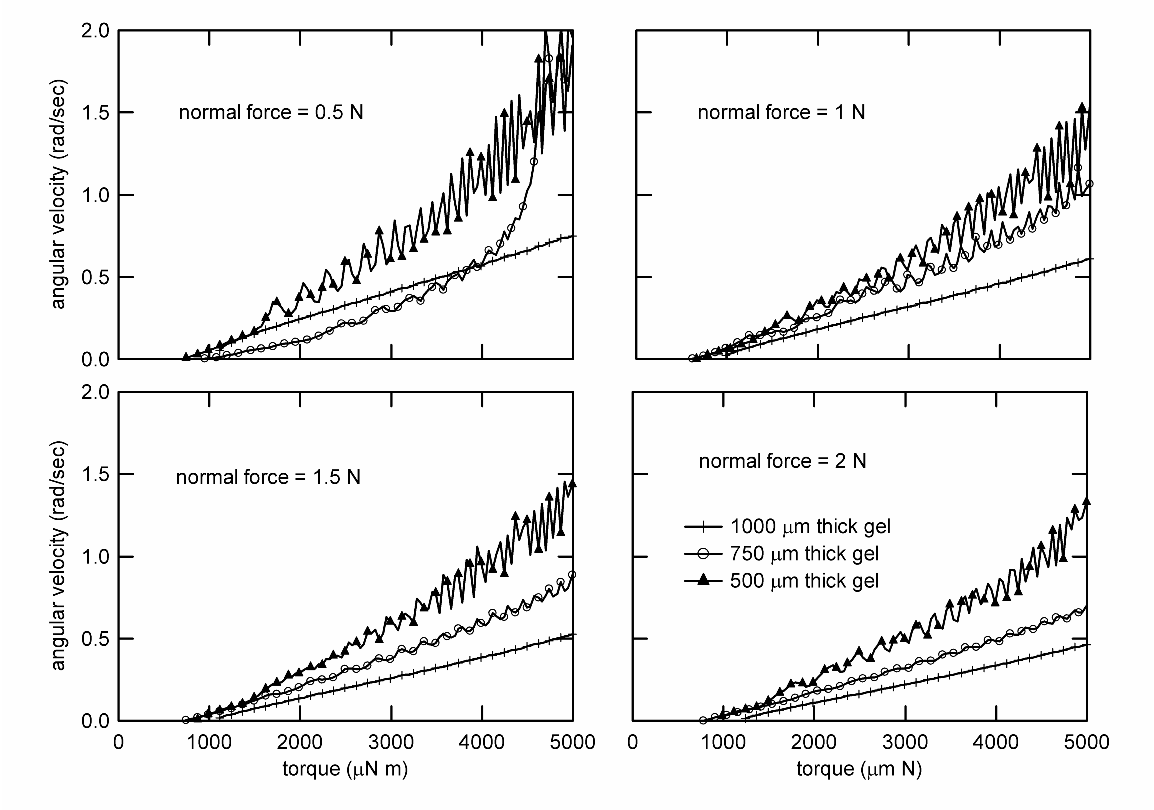

Figure 5.6 Effect of change of gel thickness on tribology: gel was 2% agarose. All three experiments were run using the In Air Protocol and using the same piece of glass as the contact surface. It was also attempted to measure friction on a gel 250 mm thick, but the thin layer of gel was too delicate to prepare without ripping.

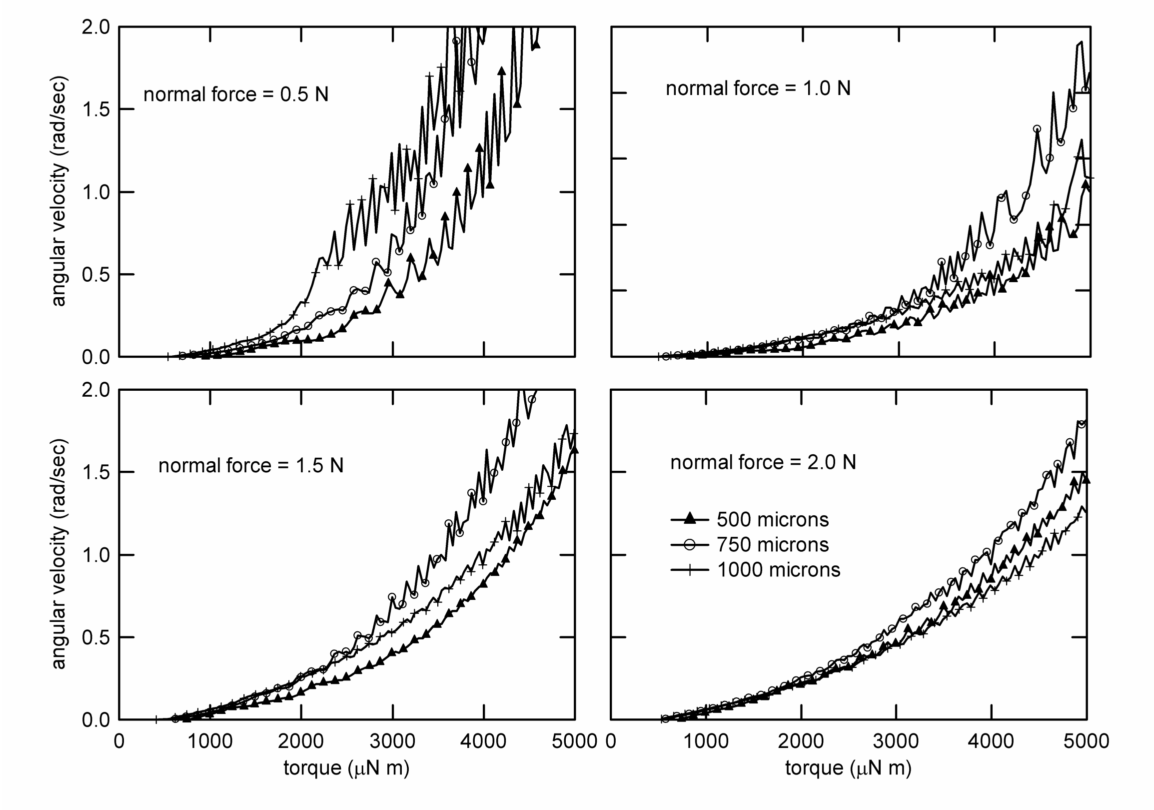

Figure 5.7 Effect of change of gel thickness on tribology: gel was 2% agarose and 2% dextran sulfate. All three experiments were run using the In Air Protocol and using the same piece of glass as the contact surface.

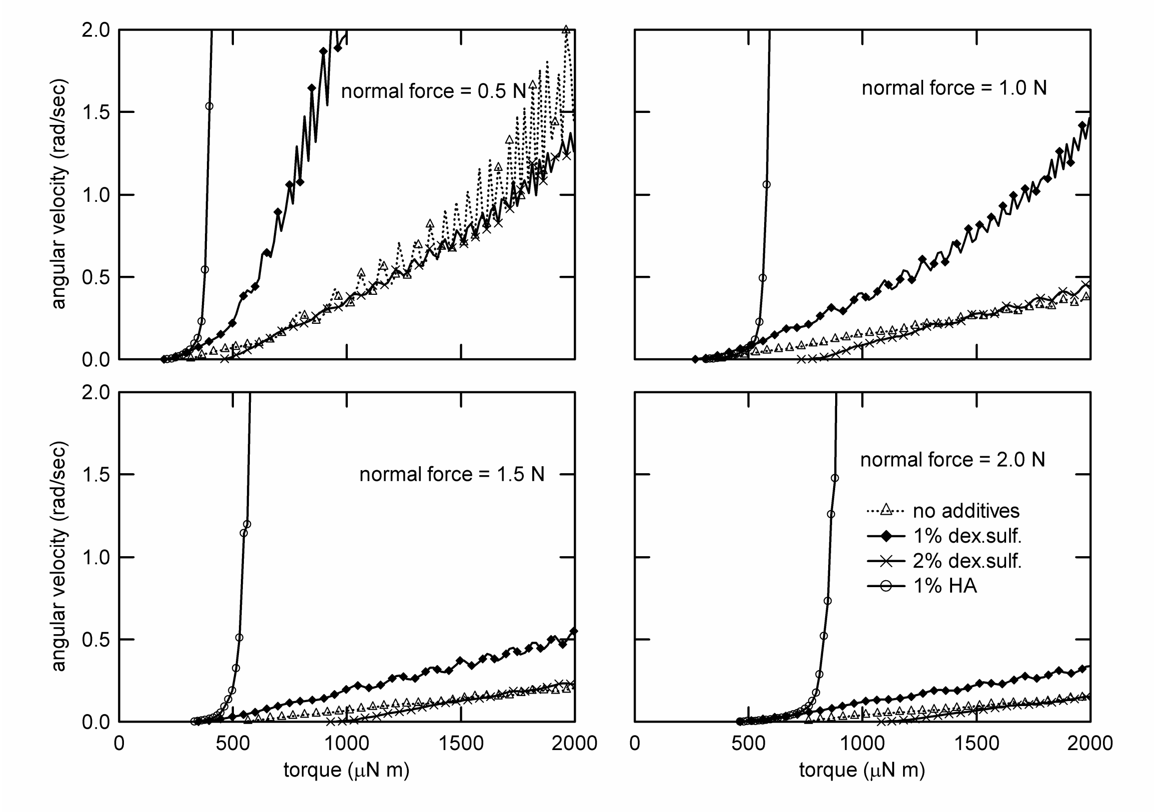

Figure 5.8 Comparison of 2% agarose gels doped with 60k dextran sulfate or 800k hyaluronic acid. All data was taken against the same clean glass plate. Protocol 1 was used under buffer rather than water. Buffer, rather than water, was also used to prepare the gels.

% dextran sulfate	normal force [N]	slope [rad/μN m sec]	intercept [rad/sec]	R^2
0	0.5	0.0002	-0.1009	0.9991
	1	0.0001	-0.1042	0.9996
	1.5	0.0001	-0.1182	0.9994
	2	0.0001	-0.1262	0.9994
1	0.5	0.0002	-0.2385	0.9978
	1	0.0002	-0.1604	0.9906
	1.5	0.0002	-0.1293	0.9944
	2	0.0002	-0.1184	0.9960
2	0.5	0.0004	-0.4684	0.9505
	1	0.0003	-0.2862	0.9774
	1.5	0.0003	-0.2145	0.9850
	2	0.0002	-0.1824	0.9893
3	0.5	0.0003	-0.3940	0.9563
	1	0.0002	-0.2563	0.9755
	1.5	0.0002	-0.1968	0.9849
	2	0.0002	-0.1550	0.9889

Table 5.1 Results of least squares linear fit of data shown in Figure 5.2. Hydrogels are 2% and doped with between 0% and 3% dextran sulfate. Data was taken using the In Air Protocol.

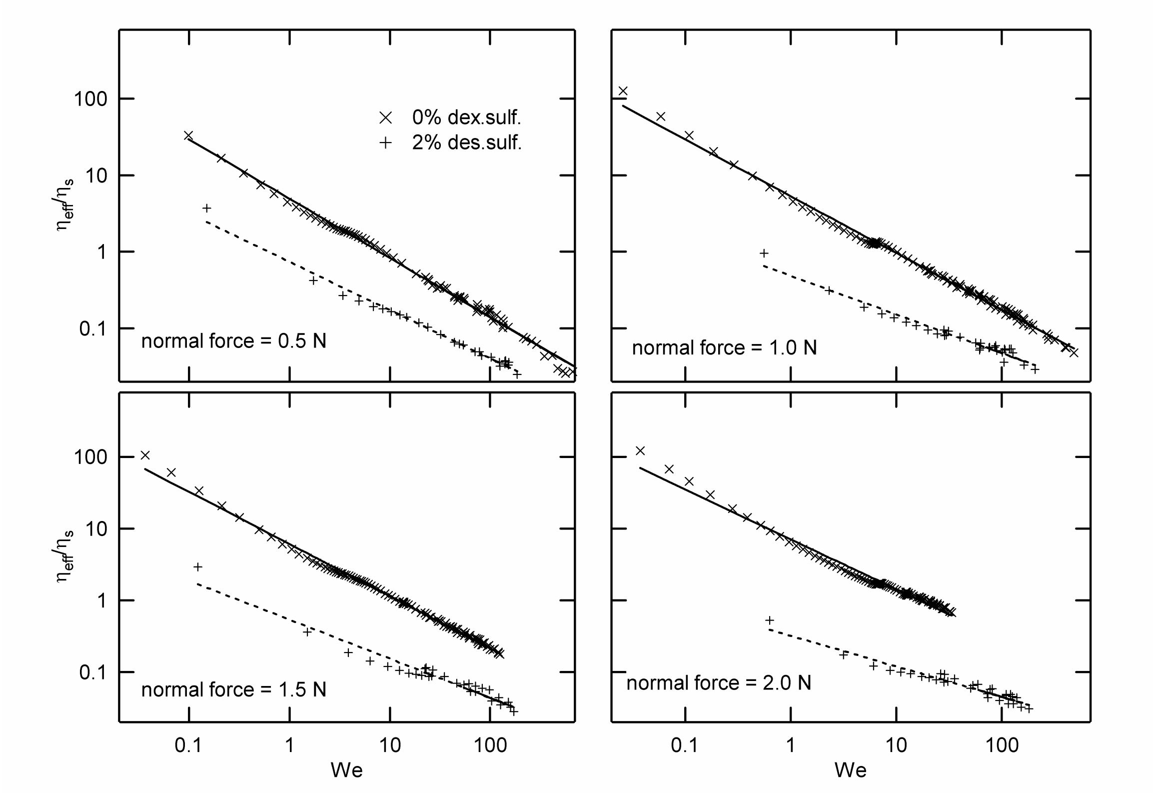

Figure 5.9 Friction of 2% agarose hydrogels and 2% agarose doped with 2% dextran sulfate hydrogels plotted as dimensionless effective viscosity versus Weissenberg number (same data as Figure 5.4a). Data was taken against clean glass using Underwater Protocol 1.

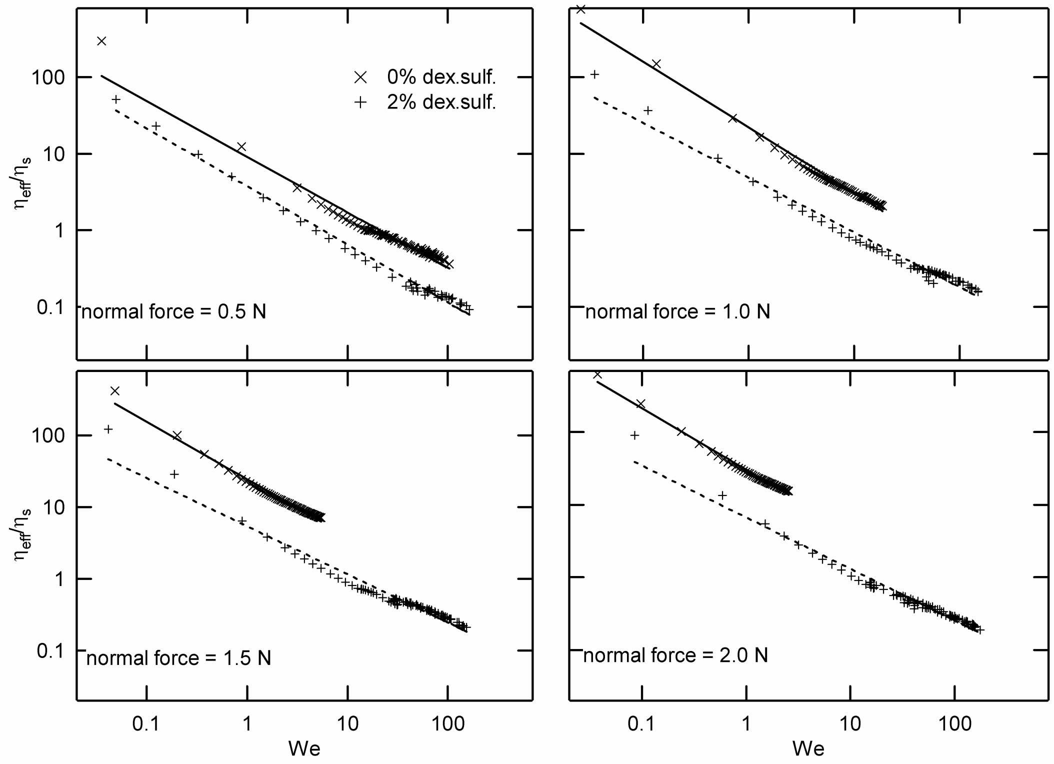

Figure 5.10 Friction of 2% agarose hydrogels and 2% agarose doped with 2% dextran sulfate hydrogels plotted as dimensionless effective viscosity versus Weissenberg number (same data as Figure 5.5a). Data was taken against TFOS modified glass using Underwater Protocol 1.

contact surface	hydrogel	normal force (N)	power law exponent	prefacter	R^2
clean glass #1	0% dextran sulfate	0.5	-0.77	4.92	0.994
		1.0	-0.74	5.33	0.995
		1.5	-0.73	6.11	0.995
		2.0	-0.70	7.14	0.981
	2% dextran sulfate	0.5	-0.63	0.744	0.986
		1.0	-0.50	0.485	0.959
		1.5	-0.54	0.537	0.948
		2.0	-0.43	0.321	0.938
clean glass #2	0% dextran sulfate	0.5	-0.53	1.51	0.979
		1.0	-0.63	2.76	0.984
		1.5	-0.64	3.24	0.987
		2.0	-0.59	3.79	0.956
	2% dextran sulfate	0.5	-0.72	1.05	0.983
		1.0	-0.50	0.638	0.940
		1.5	-0.53	0.659	0.954
		2.0	-0.54	0.858	0.967
TFOS #1	0% dextran sulfate	0.5	-0.73	9.13	0.955
		1.0	-0.86	22.2	0.988
		1.5	-0.80	24.6	0.985
		2.0	-0.85	30.4	0.988
	2% dextran sulfate	0.5	-0.76	3.74	0.989
		1.0	-0.72	4.91	0.977
		1.5	-0.67	5.45	0.960
		2.0	-0.71	6.70	0.972
TFOS #2	0% dextran sulfate	0.5	-0.88	15.7	0.992
		1.0	-0.89	21.4	0.997
		1.5	-0.90	25.8	0.999
		2.0	-0.89	29.4	0.998
	2% dextran sulfate	0.5	-0.84	4.63	0.998
		1.0	-0.70	3.54	0.949
		1.5	-0.74	5.03	0.982
		2.0	-0.73	5.46	0.979

Table 5.2 Results of power law fit of dimensionless effective viscosity against Weissenberg number for data presented in Figure 5.4 and Figure 5.5.

contact surface	hydrogel	average power law exponent
clean glass #1	0% dextran sulfate	-0.73
	2% dextran sulfate	-0.53
clean glass #2	0% dextran sulfate	-0.60
	2% dextran sulfate	-0.57
TFOS #1	0% dextran sulfate	-0.81
	2% dextran sulfate	-0.71
TFOS #2	0% dextran sulfate	-0.89
	2% dextran sulfate	-0.75

Table 5.3 Average of power law exponents at the four normal forces meaured using the same surface and same hydrogel.

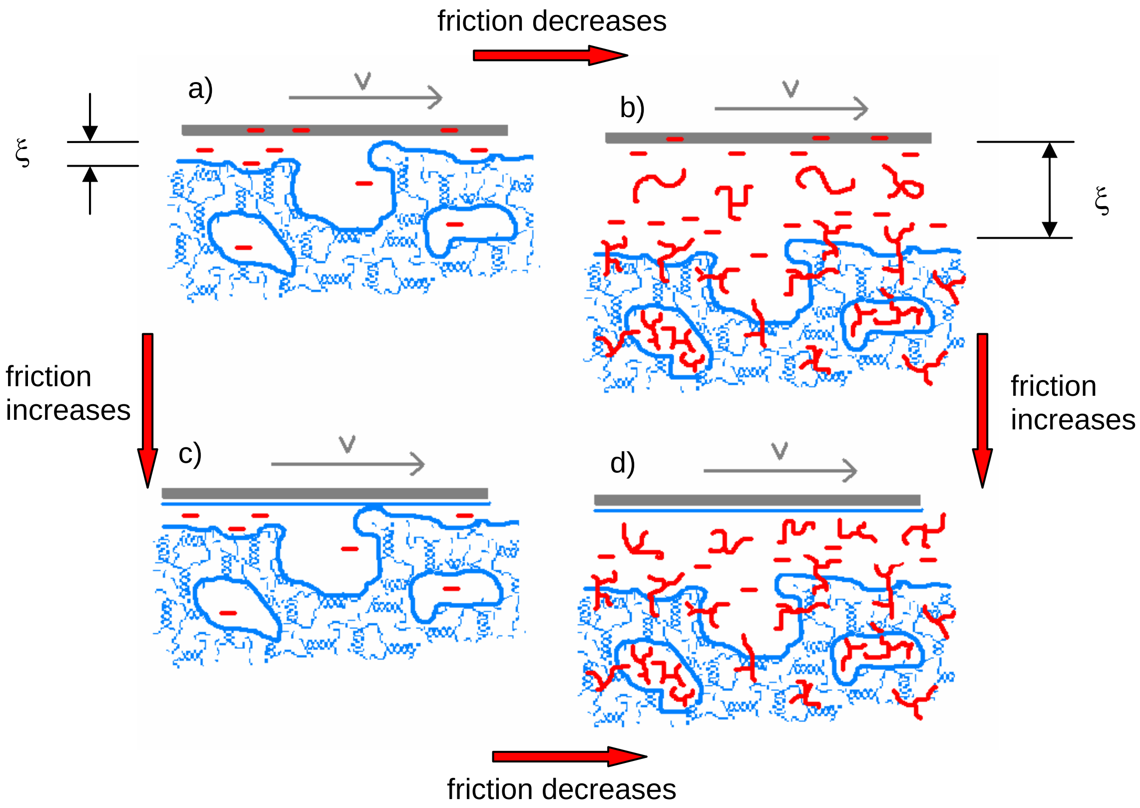

Figure 5.11 Hypothesis regarding the increase in lubrication produced by addition of dextran sulfate to agarose hydrogels. a) When a clean glass plate (negatively charged) moves against agarose (sparse anionic groups), there is minimal electrostatic repulsion between the gel and the surface. Direct contact between the glass and the nearly-neutral agarose chains in the gel may occur. b) When dextran sulfate is present, mutual electrostatic repulsion may drive the polyanion to diffuse to the interface and prevent direct interaction between the agarose and the glass. The increase in charge density of the gel may increase repulsion between the glass and the gel and, therefore, increase the layer free of agarose at the interface. This case represents the lowest friction measured during our investigation. c) When the glass slide is treated with TFOS, its interface is uncharged, no electrostatic repulsion occurs between the gel and the surface. Friction increases compared to that against a clean glass plate. d) Doping of dextran sulfate still increases

lubricity against the TFOS-treated glass, however, because dextran sulfate can still impede interactions between agarose and the contact surface.

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