Chapter 3

MEASURING HYDROGEL FRICTION WITH A STRESS RHEOMETER

3.1 Introduction

Hydrogels have shown promise in various biomedical devices where soft, low friction surfaces are necessary. Contact lenses are thin, molded hydrogels, and their low friction is necessary for comfort during extended wear.[1, 2] Studies have also shown that thin hydrogel films can reduce friction on the surface of catheters[3] and the inside surface of surgical gloves.[4] Hydrogels are also being studied as possible materials for joint replacements,[5, 6] which has fueled research into making hydrogels that are both very lubricious and very tough.[7-9]

Besides such applied work, several groups have attempted to elucidate a more general understanding of the mechanism of hydrogel friction. There has been no consensus on the best apparatus for measuring hydrogel friction in these model systems, however, and apparatus in the literature fall into three categories: commercial tribometers, homemade tribometers, and rheometers.

The study of hydrogel friction has been dominated by the work of Gong and Osada, and many of their early papers use a commercial tribometer to measure friction on hydrogel

surfaces.[10-12] Hydrogels were loaded into an immobile square frame and placed on top of a substrate which was moved back and forth at a constant velocity. The force needed to maintain the hydrogel at a fixed position while the substrate moved below it was recorded as the friction force, and a weight placed atop the hydrogel allowed friction measurement to be performed at different normal forces. Disadvantages of this method included lack of temperature control and the inability to measure the low friction forces of particularly lubricious systems. In particular, the friction of polyelectrolyte hydrogels against glass was impossible to measure underwater due to the particularly low friction of this system. Only by increasing the drive velocity by an order of magnitude over measurements taken in air could the friction be brought into measurable range.[11]

Home-made tribometers have been used by Ronsin and coworkers to study the friction of gelatin on glass,[13, 14] and by Kawabata and coworkers to study the friction of agar on glass.[15, 16] The apparatus of Ronsin was equipped with a CCD camera to record movies of slip pulses on the interface between the gel and the glass, but operated at low speeds (< 2 mm/sec) and without normal force control. Unlike the work of Gong and Osada and Ronsin, the apparatus used by Kawabata did not allow for the hydrogel to move continually back and forth over the test surface; the gel was pulled only once by a constant force over a set distance. This was a distinct disadvantage of this instrument, since both Gong and Osada and Ronsin report that repeatable data can only be collected after at minimum one run is completed (in the case of Rosin)[13] or after several initial unstable runs (in the case of Gong and Osada).[10] In an alternative to a completely home-made tribometer, Haraguchi and Takada adapted a tensile testing apparatus to measure the friction of hydrogel/clay composite materials against glass.[17] These tests were both limited to low velocities (0.5 mm/sec), and the instrument had the same shortcoming of Kawabata's: it only moved the gel against the contact surface once rather than in a periodic manner.

To overcome the inability of a commercial tribometer to measure the low friction forces of particularly lubricious hydrogel systems, Gong and Oasada adapted a strain rheometer to measure gel friction;[18-20] Zauscher and coworkers used this same technique to measure

friction of thermoresponsive hydrogels[21]. Cylindrical pieces of hydrogel were glued to the upper and lower plates of the rheometer, the gap lowered to create a normal force, and the friction force measured when the lower plate was moved at a constant angular velocity. Besides greater sensitivity to small friction forces, the rheometer also featured better environmental control of the sample using the rheometer's Peltier element.[19] Gong and Osada also showed the equivalence of data taken under constant angular velocity with a rheometer and data taken under constant linear velocity with a tribometer when the angular velocity of the rheometer was converted to an equivalent linear velocity. Unfortunately, there are some problems with using the rheometer to measure friction. Gong and Osada note that the hydrogel pads fixed with cyanoacrylate glues are not stable to high shear stresses.[19] Also, there is no normal force control: the gap is lowered to a set thickness, and the gel relaxes slowly to some steady-state normal force. This relaxation takes approximately an hour to stabilize.[19, 21]

As with Gong and Osada and Zaucher, we also will exploit the sensitivity of a rheometer for the measurement of gel friction, while improving some of the shortfalls of their protocols. Unlike earlier work, we introduce normal force control into the experiment rather than fixing the rheometer gap and waiting for relaxation of the hydrogel to reach a steady state normal stress (Figure 3.1). Besides the obvious benefit of being able to perform experiments under systematically varying normal forces, this normal force control also alleviates the need for prolonged equilibration times. This is especially significant for the study of carbohydrate-based hydrogels, for which their tribological properties have been shown to be a strong function of contact time with the test interface.[15]

Also, we study hydrogels self-assembled on the rheometer and immobilized by means of a cleated tool to prevent the need to attach gels using cyanoacrylate adhesives (Figure 3.1). The temperature control afforded by a commercial rheometer is especially useful in allowing us to apply a hot solution of a thermosetting hydrogel to the preheated rheometer and then cool the rheometer to trigger gelation of the solution. This simple loading protocol allows us to increase the number of different gels that can be tested

(since time to remove cyanoacrylate glue from the rheometer geometry by soaking in acetone is unnecessary between experiments) and alleviate the tearing of the gel away from the rheometer plate noted by Gong and Osada during heavy shear stresses.

Finally, since none of the biomedical applications of low-friction hydrogels occur during steady-state conditions, we shift the focus of our work from long, steady-state experiments to short, transient experiments. We use a stress rheometer rather than a strain rheometer to achieve control over the torques applied to the sample. Rather than applying a constant toque, we use a five-minute linear ramping of the torque from zero to a given maximum torque.

As with many other groups, we focus on the friction of hydrogels against glass. We feel glass is an especially appropriate surface for testing hydrogels with an eye towards biomedical applications due to the surface charge of glass. Clean glass has a negative surface charge due to the presence of silanol groups. The body's mucous membranes—the contact surface against which many biomedical devices are used—are also negatively charged. Thus, behavior of hydrogels against glass may be indicative of their tribological characteristics in the body. Besides, glass slides are a ready source of cheap, flat test surfaces.

In this chapter we compare various protocols—both submerged in water and in air—for measuring hydrogel friction using a stress rheometer. We demonstrate both the normal force control that can be achieved on the stress rheometer and the repeatability of the data. While we focus on transient experiments, we do perform one set of steady state experiments so that our data can be compared to that of Gong and Osada for validation.

3.2 Eperimental

Materials. Dextran sulfate sodium salt and agarose were purchased from Sigma and used as received. Dextran sulfate has a nominal molecular weight of 500k. Agarose type 1-B, low EEO was chosen for its high strength and low sulfate group contamination.

Sample Preparation. Stock solutions of dextran sulfate were prepared in twice distilled water with a polymer concentration of roughly 20% by weight. Dextran stock solutions were mixed overnight before use. Dry agarose, dextran stock solution, and water were measured to give ten gram samples of the desired weight percent of polymer: 2% agarose and 0% or 2% dextran sulfate. Samples were alternately stirred for five minute intervals in a heat bath maintained at 95º C and mixed on a vortex mixer. This was repeated three times for a total heating time of 15 minutes. Gels were formed from these liquid samples *in situ* on the rheometer as described below.

Friction Measurement. Friction measurements were performed on a stress rheometer (model AR1000, TA instruments, New Castle, Delaware). A flat 25mm diameter plate was used as the top contact surface, and a 25 mm cleated plate was used to anchor the gel pad the bottom surface of the rheometer. Gels were formed *in situ* on the rheometer (Figure 3.2), eliminating variability associated with cutting and mounting of the gel. The hot polymer solution was pipetted onto the lower plate heated to 45º C. The upper plate was lowered to the desired gap, and the solution was cooled to 25º C. No trimming of the gel was attempted since it was found that any rotation of the upper plate (and it was difficult to trim the gel without causing such rotation) affected the gelation in such a way as to cause a large “diminution” of “lubricity.” Thus, a set volume of gel was pipetted onto the lower plate so that once the upper plate was lowered, the edge of the gel lined up with the edge of the plates. The gel was allowed to equilibrate for 15 minutes at 25º C. (Preliminary time sweeps indicate that the polymer fully gels in approximately nine minutes.) Wet sponges were placed around the plates to minimize evaporation from the gel during equilibration.

After equilibrating 15 minutes, the top plate was lifted and replaced by a clean glass plate (square, 35 mm on each edge) mounted with cyanoacrylate adhesive on a conventional parallel plate fixture. The glass was cleaned with piranha solution prior to use. The minimum amount of superglue needed to fix the glass plate was used, and the assembly

was placed in a humid environment (an overturned beaker placed on a Petri dish of water) to hasten hardening of the glue.

Four different protocols were used for measuring hydrogel friction (Figure 3.3). In the first three protocols, the gel friction was measured underwater. Before the glass place was lowered, a piece of Plexiglas tubing 7 cm in diameter and 3 cm in height was placed on the lower surface of the rheometer to form a reservoir around the hydrogel pad already formed on the rheometer. Vacuum grease (flurorinated lubricant) spread on the bottom edge of the Plexiglass tube created a water-tight seal between the tube and the bottom of the rheometer.

For the first protocol (Protocol 1, Figure 3.3) the reservoir was filled with water, the glass plate lowered so that it was submerged below the water surface; any air bubbles trapped beneath the plate freed by spinning the glass; after the glass plate was still, it was lowered until just touching the gel pad; and the experiment commenced. The next protocol (Protocol 2) differed from Protocol 1 by allowing the gel to equilibrate for thirty minutes under water before the glass plate was lowered into contact with the gel and the experiment commenced. For the final underwater protocol (Protocol 3), the glass plate was lowered into contact with the hydrogel pad before water was added to the reservoir. The experiment commenced as soon as the reservoir was filled with water. For all protocols, the contact between the plate and the gel pad is established by lowering the plate close to the gel surface based on known thickness of the gel and the glass plate and then activating normal force control. The zero of the normal force in Protocol 1 and Protocol 2 is set with the cell filled (which adds a small load to the normal force transducer); in Protocol 3, the normal force is zeroed prior to preparing the gel pad using the lower tool, and the reservoir filled to the specified level. Finally, the friction was also measured with the hydrogel pad surrounded by humid air rather than being submerged (In Air Protocol). The glass plate was simply lowered as soon as the pad was formed.

Five linear rampings of the torque from 0 to a maximum torque (either 3000 μN·m, 5000 μN·m or 7000 μN·m) were applied, and the angular velocity of the glass plate was

recorded continuously. The first of the rampings was 2 minutes long, performed with 0.5 N normal force, and was used to establish a reproducible initial condition: in accord with prior literature[10], the shape of the velocity versus torque curve of the first ramping was irreproducible and not characteristic of other rampings. All other rampings were 5 minutes in duration, each performed under successively larger normal force: 0.5, 1, 1.5 and 2N.

Before each loading, the glass plates were cleaned with successive washes in water, saturated sodium chloride solution (to remove any material from the glass surface that may be held on by electrostatic interactions), water, isopropanol (to remove any surface active material), and water. Traces of the angular velocity versus torque were repeatable for measurements taken on the same glass plate (Figure 3.4a).

Friction measurements were sensitive to contamination of the glass surface. Particularly, glass slides where the superglue dried slowly were found to be both less wetting (a non-zero contact angle was observed) and show higher friction than glass sides where the glue dried quickly and the surface was wetting (near zero contact angle). When this trend became evident, plates were screened by visual observation of wetting behavior. If water beaded up on a plate, it was discarded. Also, to keep plates as free from contamination as possible, cyanoacrylate glue was cured in humid conditions to hasten polymerization. Also, the minimum amount of glue possible was used.

Steady State Friction Experiments. Besides the linear torque ramps described above, a few experiments were performed under steady state conditions. These experiments were performed using Protocol 1. After the initial two minute torque ramp, a constant torque was applied for three minutes. For the 2% agarose samples, the first torque applied was 200 μN·m, and subsequently the torque was raised by 100 μN·m increments until the angular velocity exceeded 20 rad/sec. For the 2% agarose and 2% dextran sulfate samples, the first torque applied was 25 μN·m, and subsequently the torque was raised by 25 μN·m increments until the angular velocity exceeded 20 rad/sec.

3.3 Results

Feedback control of the normal force kept its value within 0.1 N of the specified value. The rheometer moves the upper plate up and down to do so. Since hydrogels are soft materials and the sides of the hydrogel pad are open, the gels were able to relax, and the normal force gradually falls for a given fixed gap. In some conditions, this causes the normal force to undergo a saw-tooth type of oscillation: each time the normal force falls to 0.1 N below the set point, the gap is lowered and the normal force jumps to 0.1 N above the set point and the cycle repeats itself (Figure 3.4b).The change in gap thickness over the course of a typical experiment was approximately 50 μm (Figure 3.4c). Normal force control was less effective at high angular velocity. For this reason, most data are reported at angular velocities less than 2 rad/sec.

Steady state experiments were performed on agarose in order to calculate friction coefficients. The friction coefficient, μ, is defined as the ratio of the friction force to the normal force. For a 2% agarose hydrogel, five steady state angular velocities were recorded for torques between 200 μN·m and 600 μN·m (Figure 3.5a). The next highest torque (700 μN·m) caused the velocity to exceed the limit programmed into the rheometer (10 rad/sec). This experiment was also attempted on a gel containing 2% agarose and 2% dextran sulfate (a material discussed in Chapters 4 and 5). This material was more lubricious than 2% agarose, and a steady state angular velocity could not be measured, even using lower torques increased at smaller intervals (Figure 3.5b). The data from the steady state experiment on 2% agarose was used to calculate a friction coefficient. The friction coefficient for 2% agarose was an increasing function of angular velocity (Figure 3.6). For comparison, data collected using Protocol 1 on agarose during a transient experiment (Figure 5.4) was also used to calculate the friction coefficient at the same angular velocities measured during the steady state experiments. The friction coefficient calculated from transient data is higher than that calculated from steady state data, but also increases with increasing angular velocity.

Four different protocols were used to test hydrogel friction. To compare these protocols, each of the four protocols was tested using a given piece of clean glass on 2% agarose and 2% dextran sulfate gels (Figure 3.6). Then the suite of experiments was repeated with a different piece of glass. That is, using a given glass plate, a gel pad is prepared and tested by Protocol 1, another pad is prepared and tested by Protocol 2, etc. The entire set of experiments is then repeated with a different glass plate, again held fixed for that set of experiments. Measurements in air produced qualitatively greater friction than protocols in water. In Chapter 5, we discuss the behavior under air and under water in terms of the model of Gong and Osada and Ronsin. The similarity of measurements taken using Protocol 1 and Protocol 3 convinced us that we were not measuring the effects of a squeeze film of water between the glass plate and the gel. All further experiments were therefore performed using Protocol 1 or the In Air Protocol.

Using the In Air Protocol, friction measurements taken with normal forces increasing in successive rampings were compared to those taken with normal forces decreasing in successive rampings. On 2% agarose hydrogels, the angular velocity versus torque traces were nearly identical regardless if the data were taken from high-to-low normal force or low-to-high normal force (Figure 3.7b). Only data taken at a normal force of 0.5 N showed a discrepancy of more than 0.1 rad/sec at the maximum torque of 7000 μN·m between the two different protocols. When this same experiment was performed on hydrogels containing 2% agarose and 2% dextran sulfate, the angular velocity versus torque traces showed substantial differences between the high-to-low normal force protocol and the low-to-high normal force protocol (Figure 3.7a). The most extreme difference observed is for the normal force of 2 N, for which the angular velocity 7000 μN·m (the maximum torque) was almost 3-fold greater in the high-to-low protocol than in the low-to-high protocol. In Chapter 5 we argue that the history dependence arises from the migration of dextran sulfate to the gel's surface.

3.4 Discussion

Screening of the wettability of the glass plates used as contact surfaces was necessary to improve repeatability of friction measurements. Decreased wettability of the glass plate was observed to correlate with increased friction between the glass plate and the hydrogel pad. Gong and Osada also measured an increase in friction when changing from a glass contact surface (low contact angle) to a Teflon contact surface (high contact angle).[11] Our own measurements (Chapter 5) confirm this increase in hydrogel friction on surfaces with poor wettability. The mechanism for this decrease in lubricity on surfaces with poor wettability will be discussed in Chapter 4.

Using feedback control, normal force could be maintained constant during tribological measurements. The invariance of angular velocity versus torque curves to whether normal forces were successively increased or decreased during measurement of friction on 2% agarose surfaces indicates no alteration of gel structure occurred by the applied normal force. Most significantly, this normal force control was achieved with a 1 minute equilibration time rather than the long (~1 hour) equilibration time used by other groups.

Coefficient of friction values calculated from steady state experiments can be used to validate our experiments by comparing our data with that of Gong and Osada. Gong and Osada look at friction on 2% Konjac gels (another carbohydrate hydrogel without a large change density) in the same range examined during our steady state experiments: 10 mm/min to 400 mm/min.[10] As with our results, the coefficient of friction (μ) increases linearly with velocity in this range. At 10 mm/min, Gong and Osada measure $\mu = 0.02$ on Konjac, while we measure $\mu = 0.04$ on agarose. At 400 mm/min, Gong and Osada measure $\mu = 0.09$ on Konjak, while we measure $\mu = 0.015$ on agarose. The slight discrepancy between experiments can partially be attributed to a difference in normal force per unit area, i.e., pressure. Gong and Osada make measurements at 2.2×10^3 Pa, while our measurements are taken at a pressure of 1.0×10^3 Pa. Gong and Osada show that coefficient of friction decreases as pressure is increased, which would make our slightly higher measurements in line with theirs at higher pressures.

Coefficients of friction calculated from steady state experiments were found to differ substantially and consistently from coefficients of friction calculated from transient experiments (Figure 5.8). Friction coefficients calculated from transient experiments on the same gel using the same protocol give consistently greater coefficients of friction. Friction measured using steady state experiments may underestimate the friction that would be observed during real-world, transient biomedical applications.

The coefficient of friction for a hydrogel cannot be viewed as a general material property but as a characteristic of the specific circumstances (velocity, normal force, and sample history) during which it was measured. For solids, the coefficient of friction is a useful measure of material properties because it is weakly dependent on velocity and normal force for many systems.[22] In contrast, the coefficient of friction for hydrogels is a function of both normal force and velocity. Figure 3.9 shows data plotted as the coefficient of friction versus linear velocity (raw data, Figure 5.4) for agarose against glass. At a given normal force, the coefficient of friction is a strong function of velocity, varying as much as an order of magnitude over the range of velocities studied. Furthermore, the coefficient of friction for hydrogels decreases as normal force is increased. Since hydrogels are soft materials that can mate to asperities on the contact surface, the actual area of contact and the apparent area of contact are equal. This means that increasing normal force does not increase the area of contact (and thus friction) as it does in solid materials. In solids, the increase in normal force causes a proportional increase in friction force due to an increase in actual contact area. Due to the less than linear increase of friction force with normal force, hydrogels would be attractive materials in applications with high normal loadings if their mechanical weakness can be overcome. One place where the weakness of hydrogels has been overcome is in animal joints: very low coefficients of friction (0.03-0.001) are achievable under large normal pressures (3-18 MPa)[23].

3.5 Conclusion

A stress rheometer allowed us to simulate the transient stresses experienced by hydrogels in biomedical applications. Friction was evaluated using a linear ramping of the torque

rather than the steady state shear rate experiments performed by other groups. A normal force control loop was used during these experiments in contrast to the constant gap conditions used by earlier groups. Finally, self assembled hydrogels were used to circumvent the need to glue hydrogels to the rheometer. In the subsequent two chapters we will investigate a novel hydrogel material (Chapter 4) and then use the methods developed in this chapter to investigate the tribologial properties of these novel materials (Chapter 5).

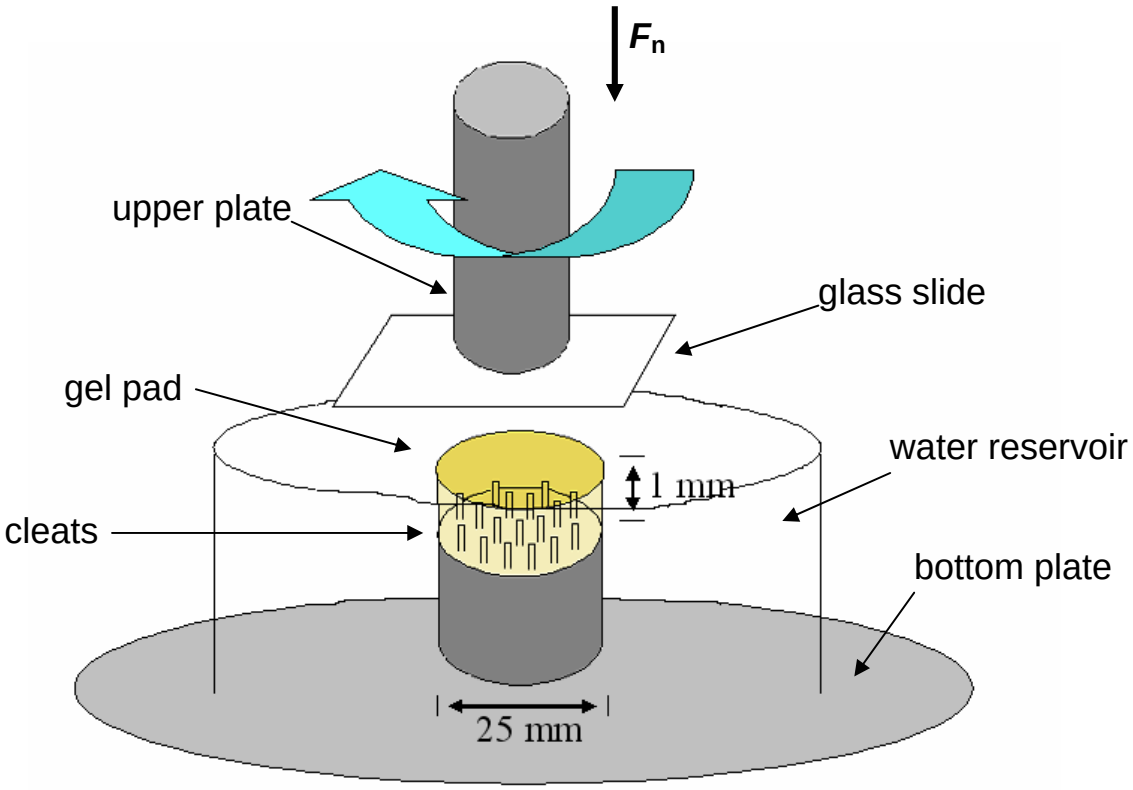

Figure 3.1 Schematic of rheometer modification used to measure hydrogel friction. Like Gong and Osada, the sample is kept hydrated using a bath surrounding the specimen, and the torque and angular velocity are acquired using the rheometer. Going beyond prior methods, the hydrogel is held using cleated tools, avoiding potential modification by adhesives, and the normal force, $\boldsymbol{F}_{\mathbf{n}}$, is recorded and controlled throughout each experiment. The cleated tool has a regular array of protrusions (450 μm wide, 600 μm long on a square grid pattern 900 μm center-to-center) machined into the aluminum. The gel pad is 1000 μm thicker than the length of the cleats and is formed in situ (Figure 3.2) to provide secure anchoring to the lower tool.

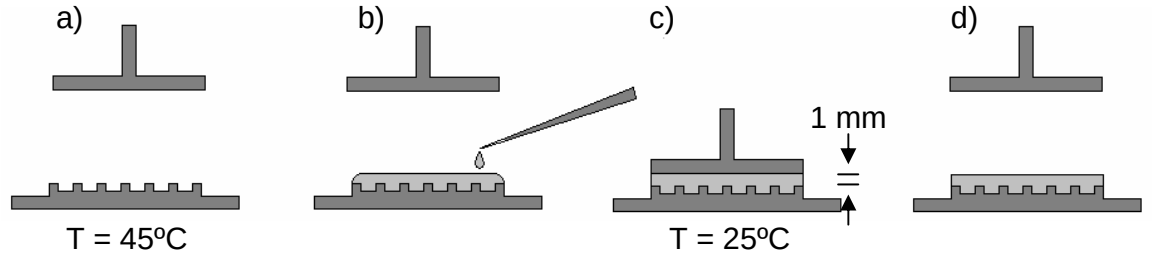

Figure 3.2 Preparation of gel pad on rheometer for friction measurement. a) The bottom, cleated tool of the rheometer geometry is heated to 45º C. b) A known volume of hot agarose solution is pipetted onto the cleats. c) The upper plate is lowered to a gap of 1 mm measured from the top of the cleats. Once the upper plate reaches this gap the temperature is lowered to 25º C. The pad is allowed to gel at 25º C for fifteen minutes. d) A spatula is inserted around the edge of the gel pad to loosen adhesion between the gel and the plate, and the plate is slowly raised. No trimming of the sample edge is required because the volume of the pipetted solution is measured to precisely fill the tool geometry.

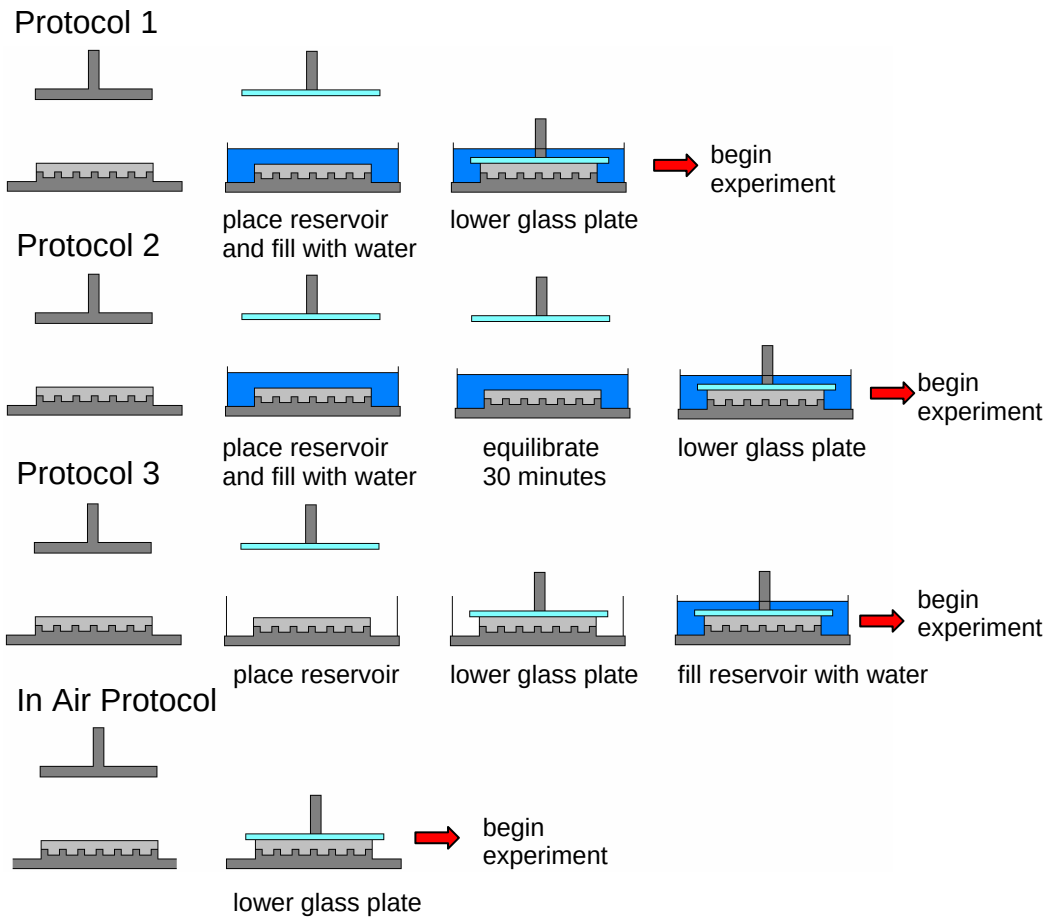

Figure 3.3 Schematic representation of protocols used for friction measurement.

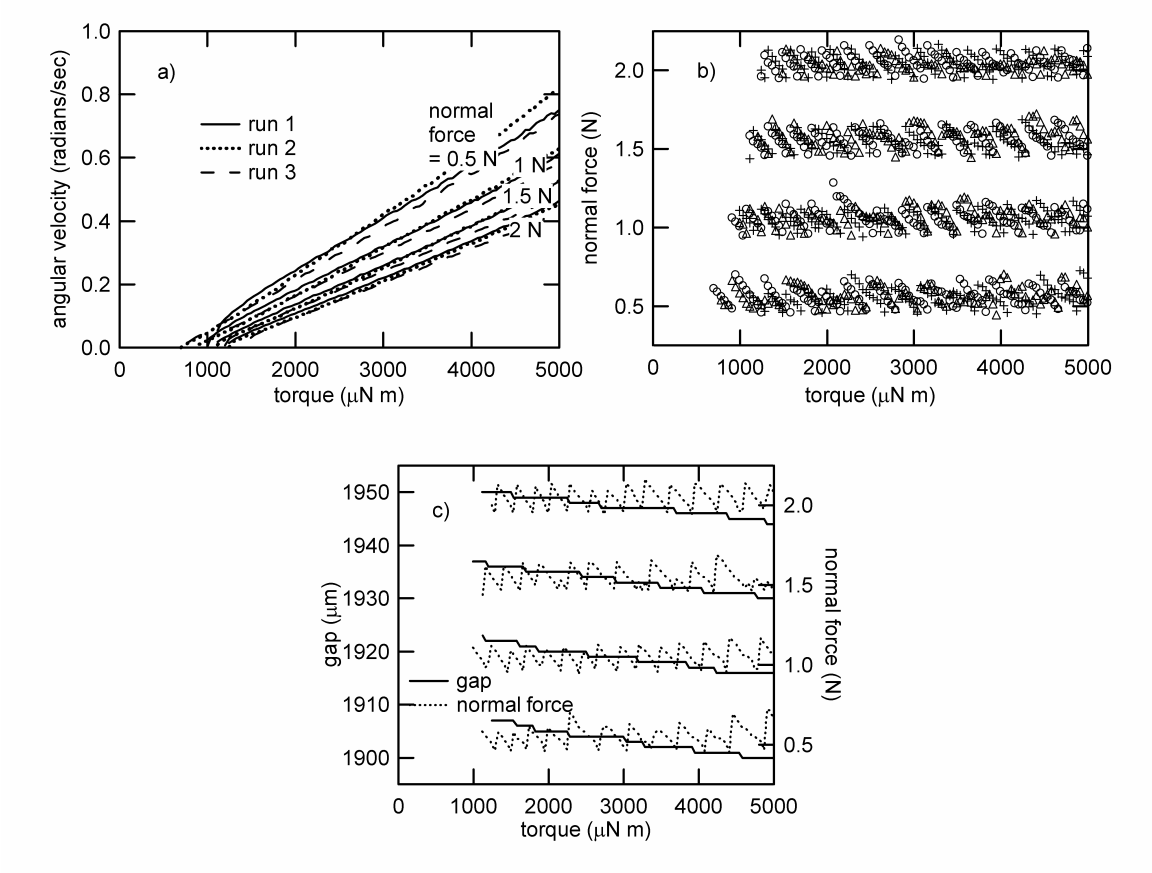

Figure 3.4 Repeatability and normal force control of tribology experiments. Angular velocity of a glass plate against a 2% agarose hydrogel was measured in air. Note that the rheometer only collects data when movement is occurring—thus the lack of gap and normal force data when the angular velocity is zero.

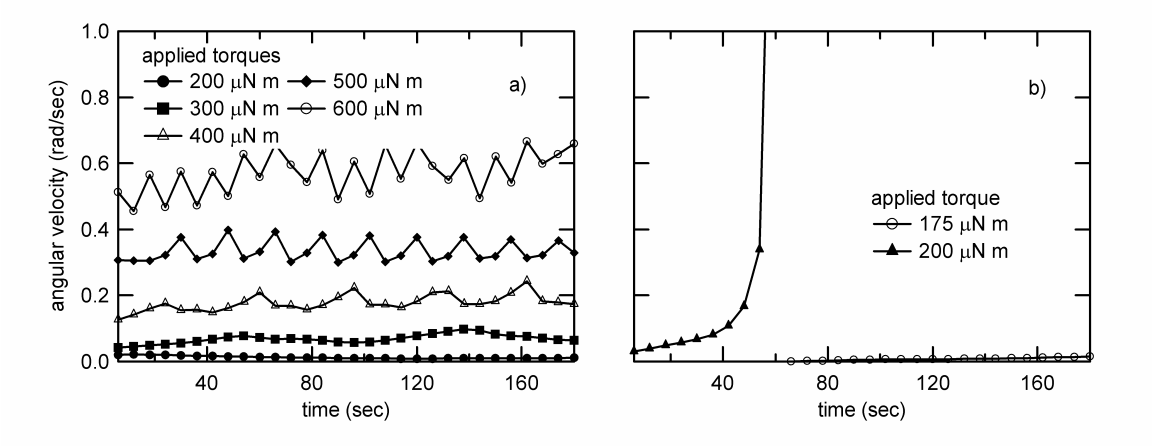

Figure 3.5 Measurement of steady state friction on agarose hydrogels using Protocol 1. a) 2% agarose and b) 2% agarose and 2% dextran sulfate. Data taken at a normal force of 0.5 N (pressure = 1.0×10^3 Pa).

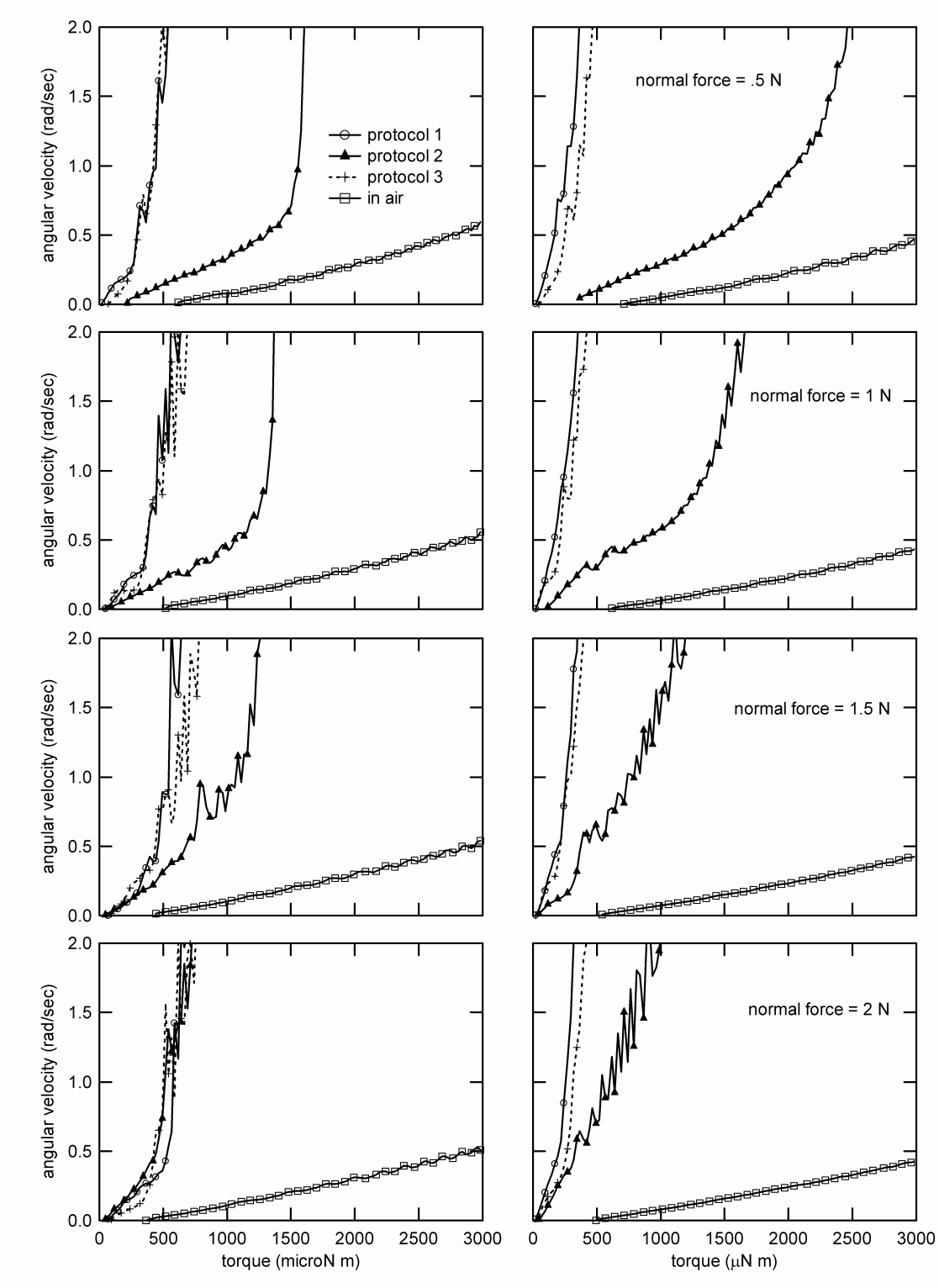
protocol 1
protocol 2
protocol 3
in air
normal force = .5 N
normal force = 1 N
normal force = 1.5 N
normal force = 2 N
angular velocity (rad/sec)
torque (microN m)
torque (μN m)
0.0
0.5
1.0
1.5
2.0
0
500
1000
1500
2000
2500
3000

Figure 3.6 Comparison between different protocols for tribology measurements on a semi-interpenetrating hydrogel composed of 2% agarose and 2% dextran sulfate. Protocol 1: The reservoir is filled with water, the glass plate is lowered, and the experiment immediately started. Protocol 2: The reservoir is filled with water, the gel is allowed to equilibrate for 30 minutes, the glass plate is lowered, and the experiment started. Protocol 3: The glass plate is first lowered and pressed on the gel with a 0.5 N normal force, the reservoir is filled, and the experiment started. The same glass plate is used for all figures in the right column. A second glass plate was used for all figures in the left column.

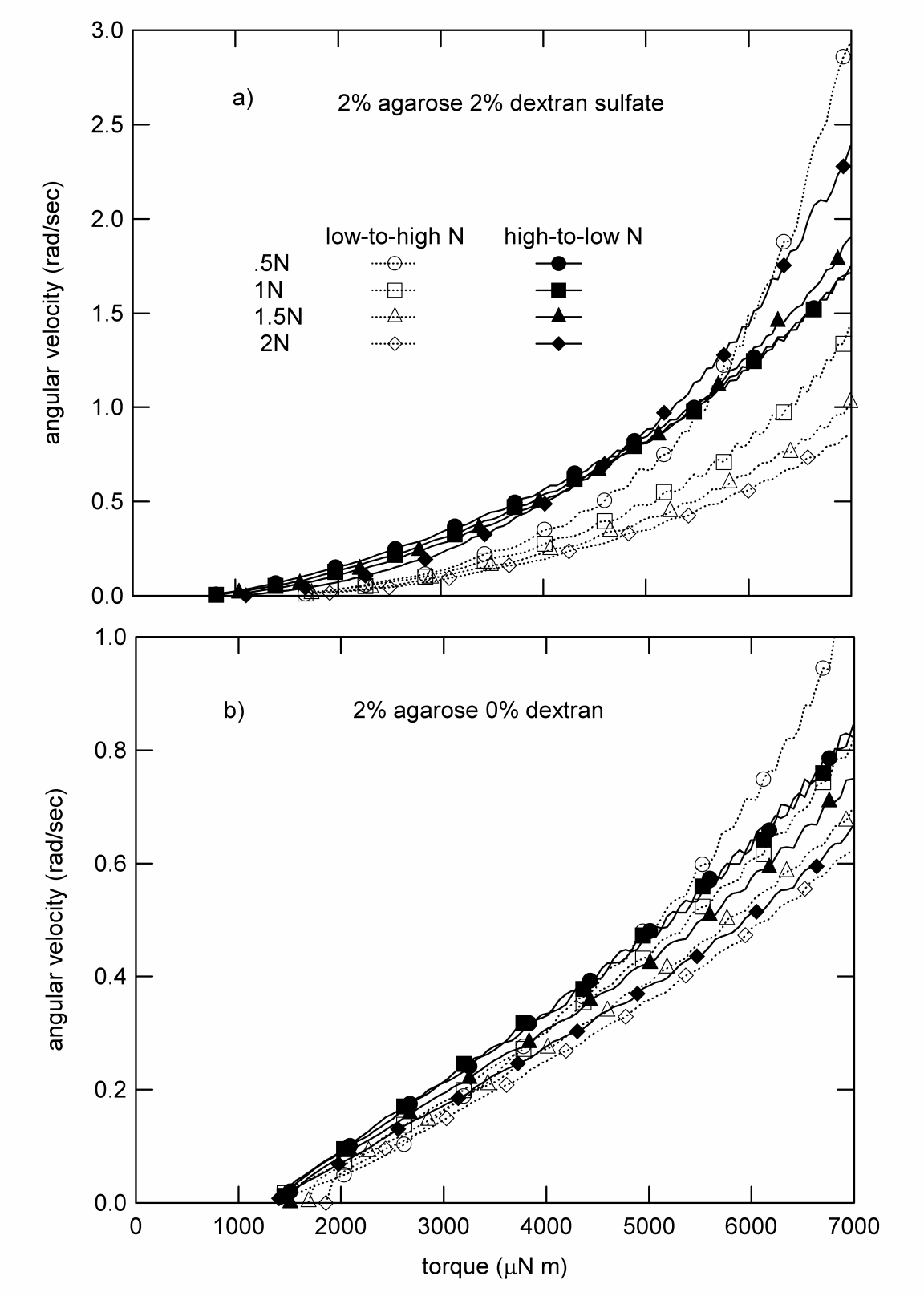
a)
2% agarose 2% dextran sulfate
low-to-high N
high-to-low N
.5N
1N
1.5N
2N
angular velocity (rad/sec)
3.0
2.5
2.0
1.5
1.0
0.5
0.0
b)
2% agarose 0% dextran
angular velocity (rad/sec)
1.0
0.8
0.6
0.4
0.2
0.0
0
1000
2000
3000
4000
5000
6000
7000
torque (μN m)

Figure 3.7 Comparison of two different protocols (high-to-low normal force versus low-to-high normal force) for measuring friction on hydrogel surfaces. Experiments were performed using In Air Protocol. a) Experiment performed on 2% agarose with 2% dextran sulfate. b) Experiment performed on 2% agarose gel.

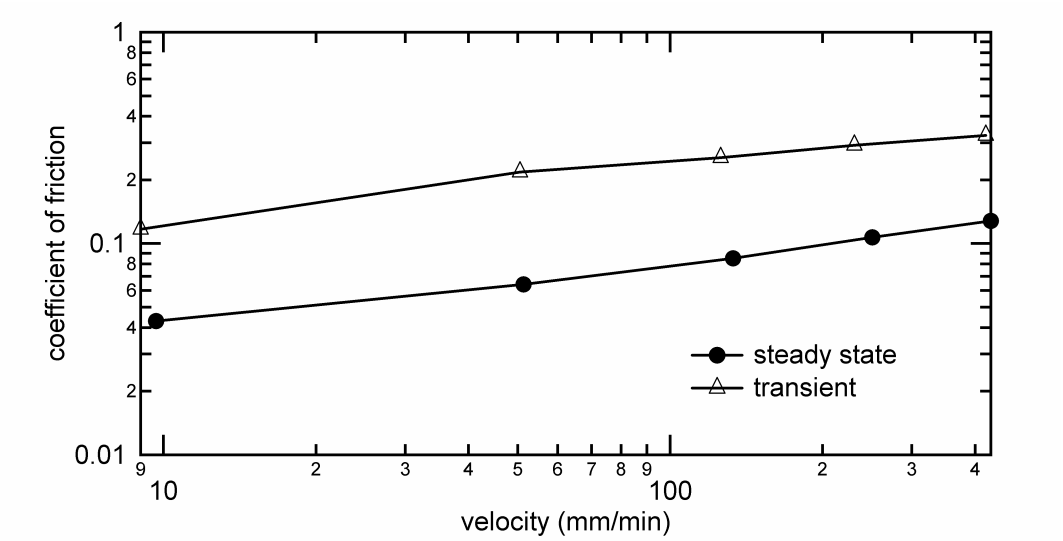

Figure 3.8 Coefficient of friction based on the steady state data in figure 3.5a plotted against linear velocity (of the outside edge of the contact area) for 2% agarose hydrogel. Coefficient of friction defined:

$$\mu = \frac{4T}{3NR}$$

where T is the torque applied by the rheometer, N is the applied normal force, and R is the radius of the hydrogel pad.[18] Also, results from a transient experiment (also performed with Protocol 1 against a 2wt% agarose gel, Figure 5.4) were used to calculate coefficients of friction at the same linear velocities as those measured in the steady state experiments.

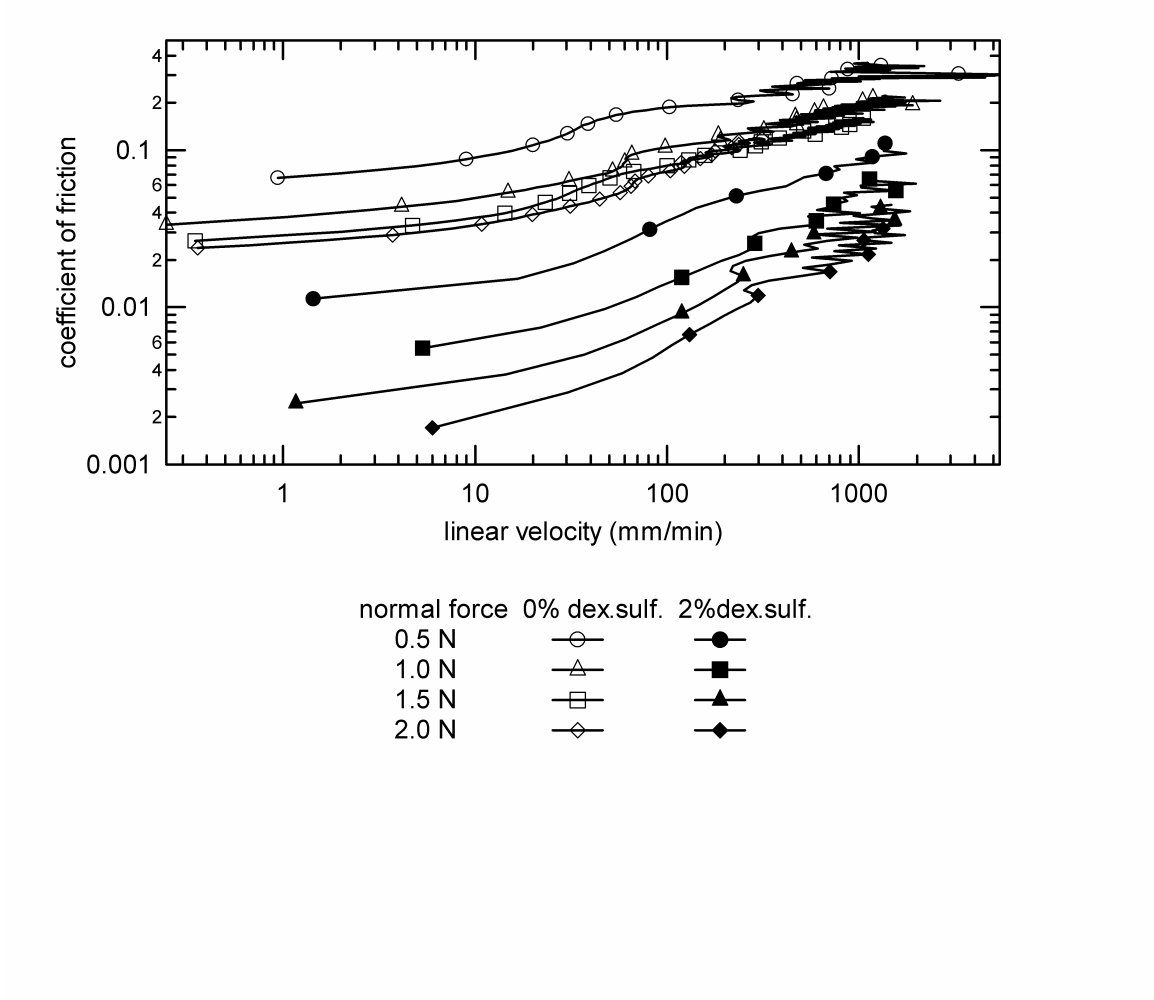

Figure 3.9 Transient experiments plotted as the coefficient of friction versus linear velocity. Data was taken using Protocol 1 against clean glass. Data is shown in Figure 5.4.

3.7 References

1. Kim, S. H.; Opdahl, A.; Marmo, C.; Somorjai, G. A., AFM and SFG studies of pHEMA-based hydrogel contact lens surfaces in saline solution: adhesion, friction, and the presence of non-crosslinked polymer chains at the surface. *Biomaterials* **2002,** 23, (7), 1657-1666.

2. Kim, S. H.; Marmo, C.; Somorjai, G. A., Friction studies of hydrogel contact lenses using AFM: non-crosslinked polymers of low friction at the surface. *Biomaterials* **2001,** 22, (24), 3285-3294.

3. Graiver, D.; Durall, R. L.; Okada, T., Surface-Morphology and Friction Coefficient of Various Types of Foley Catheter. *Biomaterials* **1993,** 14, (6), 465-469.

4. Roberts, A. D.; Brackley, C. A., Friction of Surgeons Gloves. *Journal of Physics D-Applied Physics* **1992,** 25, (1A), A28-A32.

5. Kobayashi, M.; Oka, M., Characterization of a polyvinyl alcohol-hydrogel artificial articular cartilage prepared by injection molding. *Journal of Biomaterials Science-Polymer Edition* **2004,** 15, (6), 741-751.

6. Suciu, A. N.; Iwatsubo, T.; Matsuda, M.; Nishino, T., A study upon durability of the artificial knee joint with PVA hydrogel cartilage. *Jsme International Journal Series C-Mechanical Systems Machine Elements and Manufacturing* **2004,** 47, (1), 199-208.

7. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y., Double-network hydrogels with extremely high mechanical strength. *Advanced Materials* **2003,** 15, (14), 1155-+.

8. Kaneko, D.; Tada, T.; Kurokawa, T.; Gong, J. P.; Osada, Y., Mechanically strong hydrogels with ultra-low frictional coefficients. *Advanced Materials* **2005,** 17, (5), 535-+.

9. Na, Y. H.; Kurokawa, T.; Katsuyama, Y.; Tsukeshiba, H.; Gong, J. P.; Osada, Y.; Okabe, S.; Karino, T.; Shibayama, M., Structural characteristics of double network gels with extremely high mechanical strength. *Macromolecules* **2004,** 37, (14), 5370-5374.

10. Gong, J. P.; Higa, M.; Iwasaki, Y.; Katsuyama, Y.; Osada, Y., Friction of gels. *Journal of Physical Chemistry B* **1997,** 101, (28), 5487-5489.

11. Gong, J. P.; Iwasaki, Y.; Osada, Y.; Kurihara, K.; Hamai, Y., Friction of gels. 3. Friction on solid surfaces. *Journal of Physical Chemistry B* **1999,** 103, (29), 6001-6006.

12. Gong, J. P.; Iwasaki, Y.; Osada, Y., Friction of gels. 5. Negative load dependence of polysaccharide gels. *Journal of Physical Chemistry B* **2000,** 104, (15), 3423-3428.

13. Baumberger, T.; Caroli, C.; Ronsin, O., Self-healing slip pulses along a gel/glass interface. *Physical Review Letters* **2002,** 88, (7).

14. Baumberger, T.; Caroli, C.; Ronsin, O., Self-healing slip pulses and the friction of gelatin gels. *European Physical Journal E* **2003,** 11, (1), 85-93.

15. Nitta, T.; Haga, H.; Kawabata, K., Time dependent static friction force of agar gel-on-glass plate immersed in water. *Journal De Physique Iv* **2002,** 12, (PR9), 319-320.

16. Nitta, T.; Kato, H.; Haga, H.; Nemoto, K.; Kawabata, K., Static friction of agar gels: Formation of contact junctions at frictional interface. *Journal of the Physical Society of Japan* **2005,** 74, (11), 2875-2879.

17. Haraguchi, K.; Takada, T., Characteristic sliding frictional behavior on the surface of nanocomposite hydrogels consisting of organic-inorganic network structure. *Macromolecular Chemistry and Physics* **2005,** 206, (15), 1530-1540.

18. Gong, J. P.; Kagata, G.; Osada, Y., Friction of gels. 4. Friction on charged gels. *Journal of Physical Chemistry B* **1999,** 103, (29), 6007-6014.

19. Kagata, G.; Gong, J. P.; Osada, Y., Friction of gels. 6. Effects of sliding velocity and viscoelastic responses of the network. *Journal of Physical Chemistry B* **2002,** 106, (18), 4596-4601.

20. Kagata, G.; Gong, J. P.; Osada, Y., Friction of gels. 7. Observation of static friction between like-charged gels. *Journal of Physical Chemistry B* **2003,** 107, (37), 10221-10225.

21. Chang, D. P.; Dolbow, J. E.; Zauscher, S., Switchable friction of stimulus-responsive hydrogels. *Langmuir* **2007,** 23, (1), 250-257.

22. Bhushan, B., *Introduction to Tribology*. John Wiley & Sons, Inc.: New York, 2002.

23. Gong, J. P., Friction and lubrication of hydrogels - its richness and complexity. *Soft Matter* **2006,** 2, (7), 544-552.