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TRIBOLOGICAL PROPERTIES OF GRADIENT-DENSITY HYDROGEL SURFACES

BY

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DISSERTATION

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ABSTRACT

Hydrogels are soft hydrated polymer networks that are widely used in research and industry due to their similarity to biological tissues. As one of the leading materials used for tissue surrogates or biological interfaces, hydrogels exhibit useful properties such as biocompatibility, high elasticity, and low friction. While there is a continuously expanding body of research investigating hydrogels, some tribological studies are seemingly contradictory, even showing vastly different frictional behavior for the same hydrogel composition. One explanation for this comes from the ‘mold effect’, first mentioned in 2001, whereby the mold material alters the polymerization process of the hydrogel, imparting different properties to the surface in contact with it. The ‘mold effect’ was not considered or studied in detail until recent work published in 2019, where researchers found that the effect drastically reduced the stiffness of hydrogels polymerized against polymer molds compared to glass-molded hydrogels. Several studies in subsequent years finally determined that the ‘mold effect’ is due to absorbed oxygen within the mold surface interfering with the polymerization, inducing a dilute gradient-density surface layer exhibiting altered properties. However, the precise structure of the gradient surface layer, its contact response, and its effect on lubrication have not yet been characterized. Such knowledge would prove useful for designs of composite hydrogels utilizing the gradient surface layer for its special frictional properties. In order to fully characterize the hydrogel gradient surface layer, we first developed a method to view contact area of a probe on a hydrogel substrate in real time using particle exclusion microscopy. We then utilized this technique during indentation, creep, and sliding experiments on a standard hydrogel composition. Indentation experiments confirmed the dilute gradient nature of the surface layer, showing that it follows an evolving contact response with depth. This contact response could be approximated through piecewise modeling starting with a polymer brush

contact model, then a Winkler foundation model, and finally the classic Hertzian contact model. Calculation of the contact area using these contact models verified that the indentation data was aligned with the piecewise model. This provided information regarding the polymer structure of the gradient layer: that it is composed of brush-like polymer segments swollen in water, where the polymer density and degree of crosslinking increase further into the depth. Creep experiments revealed that the gradient layer allows poroelastic relaxation even at pressures far below the reported osmotic pressure of the bulk crosslinked structure, which further supports the less-dense, ‘brushy’ nature of the gradient layer.

Sliding experiments showed enhanced lubrication and strong speed dependence on the friction, but no dependence on the contact area. The lack of transient friction behavior also demonstrated the quick rehydration of the gradient layer during the phases out of contact. Indentation, creep, and sliding experiments were also conducted on four other hydrogels of varying monomer and crosslinker percent in order to determine the effect of composition on the gradient layer. All compositions exhibited a poroelastic gradient layer that followed the evolving contact model previously formulated. Stiffer compositions had thinner gradient layers whose response under shear was less consistent with changes to load and speed. Finally, we found that changing the monomer-to-crosslinker ratio was more effective at changing the consistency of the shear response and the gradient layer thickness. These findings prove that the dilute structure of the gradient layer provides enhanced lubrication under sliding conditions by improving hydrodynamic lubrication and reducing polymer-probe interactions. This knowledge can potentially be used to create hydrogels with a stiff load-bearing bulk that retains optimal lubrication across a wide range of operating conditions.

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I am forever thankful to my dad for his love and support, both now and through every one of my years thus far. I made it this far because of you.

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CHAPTER 1

INTRODUCTION

1.1 Chemical Background

Hydrogels are a special case of polymer gels where the "pores" of the gel are occupied by water molecules. This is made possible due to the affinity of the polymer backbone to hydrogen bond with water, causing the network to trap a comparatively large amount of water compared to its own weight [1]. One of the most commonly used hydrogels is the polyacrylamide (pAam) chemically crosslinked hydrogel system, which, at an equilibrium state, can be comprised of up to 95% water by mass [2]. This is made possible by hydrogen bonding of the water molecules with the amine groups present along the acrylamide and bisacrylamide chains, which are crosslinked into a mesh network through free radical polymerization. The resulting mesh is often depicted in a 'fishing net' style, where the empty mesh spaces are the pores where water molecules can be held by the network. This pore size is related to the quality of the solvent and the amount of crosslinking that occurred during polymerization. The latter property is controlled by the ratio of monomer to crosslinker present during the initial reaction.

Hydrogels are capable of extreme strains before undergoing permanent deformation [3] or eventual rupture [4]. In most use cases, their behavior can be considered entirely linear elastic [5, 6]. Despite this, one of the largest challenges among hydrogels is their relatively low stiffness compared to other polymers. A typical 7.5% Aam polyacrylamide hydrogel has a modulus of 30 kPa, whereas a stiffer, but more brittle, hydrogel with 15% Aam will have a maximum modulus of 200 kPa [7]. More advanced hydrogels with variations such as bonding type (physical vs chemical bonding), composition, number of networks, composite fillers, charge, etc. are commonly created to improve mechanical or tribological

properties. For example, some of the commonly-used hydrogel compositions in research include polyvinyl alcohol hydrogels (PVA), polyacrylamide hydrogels, poly(2-hydroxyethyl methacrylate) (pHEMA), and many others [8, 9, 10]. Many researchers opt to improve stiffness and toughness of the hydrogel by using two interpenetrating networks, which can produce moduli of up to 1 MPa [11, 3, 12, 13]. Others have attempted to add second non-hydrogel elements to form a composite material with better mechanical characteristics [14, 15]. Some researchers have used charged hydrogels to improve lubrication in a sliding contact [16, 17, 18]. Alternatively, a heterogeneous structure with an entangled polyacrylamide network on top of a polyhydroxyethylmethacrylate (pHEMA) bulk has shown greatly reduced friction during sliding [19]. These studies are just a few examples of the many methods by which hydrogels can potentially achieve optimal mechanical properties.

1.2 Research and Industrial Use

Due to their biocompatibility and lubricity, hydrogels are one of the best materials for directly interfacing with or replacing tissues within the human body [20, 21, 22, 23]. Additionally, their biphasic composition resembles that of many biological tissues such as cartilage. Because of this, hydrogels are frequently researched and used in biomedical applications, such as scaffolding for tissue growth, and liners of medical devices [24, 25]. Many of these applications involve dynamic interfaces: for example, hydrogels have been heavily studied and used as low-friction contact lenses that interface directly with the eye [8, 26, 27, 28, 29, 30, 31]. As a result of this research, the contact lens market has fully transitioned from older "hard" lenses towards exclusive use of soft hydrogel lenses that offer a more comfortable experience with less friction and pressure on the eye. There has also been a significant body of work surrounding the use of a hydrogel system as artificial cartilage [32, 33, 34, 35, 36, 10, 37, 11]. However, cartilage is a complex heterogeneous material that has proven difficult to emulate with synthetic formulations. Cartilage exhibits a distinct composite-like heterogeneous struc-

ture that allows it to out-perform most hydrogels in lubricity and strength [38, 23, 11, 39]. Cartilage, and any surrogate, must be able to support impact and sustained loads of the weight of a human, while also maintaining sufficient lubrication between sliding joints without experiencing significant wear. This has been the largest issue for hydrogels as cartilage replacement thus far - no hydrogel formulation has been able to achieve the delicate balance of high stiffness and wear resistance while maintaining high lubricity.

1.3 Contact Mechanics of Soft Materials

At the simplest level, contact mechanics is the study of the interaction between two bodies where one elastic body acts on an elastic substrate with some force, producing a contact area between the two. The interaction between the bodies manifests as deformation, friction, and wear within the contact zone. The precise details of these contact phenomena were not actively studied until the first laws of friction were formed by Da Vinci and Amontons. The first analytic model for describing the contact profile between two generic bodies was not postulated until Hertz published his seminal work *On the Contact of Elastic Solids* in 1882 [40]. Since then, our understanding of contact mechanics and tribological phenomena has greatly expanded, with numerous elastic and hyperelastic contact models [41], wear models, and descriptions of the real contact area.

In both industry and research, indentation experiments are widely used to take advantage of these contact models, since these experiments can use contact models to determine material parameters such as the elastic modulus in a simple, nondestructive fashion. In these experiments, a rigid spherical or conical indenter of known material and stiffness is pushed into the substrate for some displacement, and the force response created by the contact is acquired. Depending on the indentation apparatus, the probe depth can be determined to construct a force-depth plot (see Figure 1). From this plot, a contact model can be fit to extract a Young's modulus, depth of first contact between the probe and substrate, contact

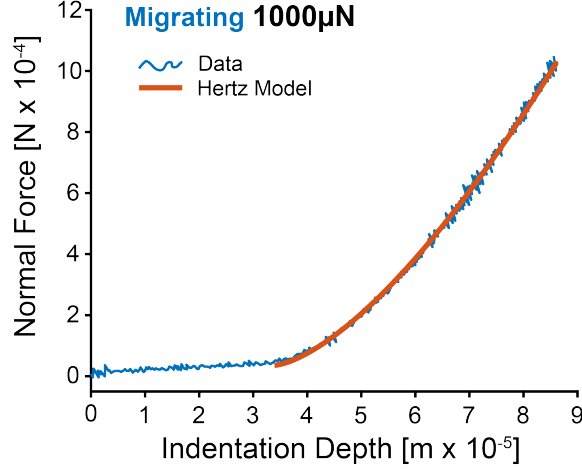


Figure 1: Example of an indentation experiment dataset, where force is measured as a function of the probe depth into the substrate.

area, contact pressure, and other useful parameters. Since a single indentation experiment is able to capture a relatively large amount of information, it is often considered the mandatory first step of any contact mechanics or tribological study. In the following subsections, we describe a few well-known contact models that we will make use of in this body of work to assess indentation experimental data.

Indentations into soft polymer materials requires an extra element of care due to the rate-dependent response of polymer chains. If an indentation rate is too slow, relaxation of the polymer network can occur during the initial indentation and be obscured from the indentation data. Indentation rates that are fast are preferable, but can create impulses in the experimental setup. Indentation of soft materials generally

1.3.1 Hertzian contact model

In the field of contact mechanics, there are a number of established analytic contact models that are widely used due to their accurate depiction of common contact geometries. The most well-known of these is the Hertz contact model, first published in 1882 [40]. This model relies on a number of assumptions including: substrate surface is an infinitely large half-space, strains are small and elastic, and the surfaces are frictionless, continuous, and

non-conforming. Because of this, it is mainly used for ideal contact setups that clearly satisfy these assumptions, such as hard homogeneous solids.

Equation 1.1 is the Hertzian model for an elastic sphere indenting into a flat elastic substrate, where F is the applied force, R is the sphere radius, d is the probe displacement, and d_o is the probe displacement at first contact with the substrate. E^* is known as the reduced modulus, or composite modulus, as it is composed of the elastic moduli E of both the sphere and the substrate and their Poisson ratios ν (see Equation 1.2). The value of ν is highly dependent on the material: a typical carbon steel has a value of $\nu = 0.3$, while hydrogels are generally considered near-incompressible with $\nu = 0.5$ as long as poroelastic squeeze-out is not occurring [42, 43]. The radius of the contact area projection a is equal to $a = \sqrt{Rd}$.

$$F = \frac{4}{3}E^*R^{\frac{1}{2}}(d - d_o)^{\frac{3}{2}} \quad (1.1)$$

$$\frac{1}{E^*} = \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \quad (1.2)$$

Despite the underlying assumptions of the Hertzian contact model, many researchers have attempted to apply it to softer polymer materials.

1.3.2 Winkler foundation model

The Winkler foundation contact model is a simple elastic contact model well suited for thin substrates, as it describes a confined strain distribution that only develops within the immediate contact area (see Equation 1.3). The Winkler model describes contact as a "bed of springs" where each 'spring' resists deformation in the normal direction, but exhibits no influence on its neighbors as it compresses. It is often used when the thickness of the substrate is much smaller than the contact diameter, which is related to the probe radius and penetration as $2a = 2\sqrt{2Rd}$. Since the substrate is relatively thin, there is less thickness for

which the strain can be distributed away from the contact zone. This model is particularly useful for describing contact mechanics in a soft layer placed on top of a stiffer rigid layer, as is seen in natural tissues and some composite systems.

$$F = \pi E^* \frac{R}{t} (d - d_o)^2 \quad (1.3)$$

1.3.3 Polymer brush contact models

Polymer brushes consist of an arrangement of dangling polymer chains grafted to a solid substrate. These brushes are of interest in scientific communities due to their unique response under contact and their similarity to structures found in nature. It has been found that brushes using hydrophilic polymers such as acrylamide have been shown to greatly improve lubrication under sliding conditions [44, 19]. An important analytic model of polymer brush contact was proposed by Fredrickson et al, who derived the expected force response of a polymer brush being indented by a spherical AFM probe using polymer physics principles (Equation 1.4) [45]. In this equation for deep indentation into the polymer brush, F is the force response, G is an effective shear modulus based on the monomer length, volume, and grafting density, R is the probe radius, H is the brush height, and d is the probe displacement. This model has been experimentally verified in later independent studies [46].

$$F = \frac{192}{\pi^2} G \frac{R^2}{H^3} (d - d_o)^3 \quad (1.4)$$

This expression implies that there is a very strong force response for a given probe penetration ($F \propto d^3$), even greater than that of aforementioned contact models. However, follow-up work on Fredrickson's model produced a different expression for the case when the penetration into the brush was small (Equation 1.5) [47]. Their derivation collapsed to what is essentially the Hertzian contact model of a rigid probe indenting into an elastic half-space with a modulus determined by the brush stiffness G (section 1.3.1).

$$F = \frac{16}{3}GR^{\frac{1}{2}}(d - d_o)^{\frac{3}{2}} \quad (1.5)$$

Both models of equations 1.4 and 1.5 are equal when the penetration depth is roughly $d \approx H^2/R$. In a ramping indentation test, it is then possible to calculate the approximate brush height H from the probe depth at which both models intersect.

1.4 Time-dependent Behavior of Hydrogels

Modern technology has increasingly made use of soft polymeric materials for medical and engineering applications. However, the contact behavior of polymers, and especially soft polymers, is also dependent on time due to the rate-dependent response of polymer chains. This requires a full contact characterization of a soft polymer to also monitor behavior across a period of time, such as with a creep experiment or relaxation experiment. Creep experiments are load-controlled experiments where a known load is affixed or applied to a sample over a long time duration while the deformation or displacement is recorded. From the displacement versus time data, the dependence of the rate of deformation on the magnitude of the load can be determined. However, this typically requires numerous experiments, since each creep experiment only provides information about the response over time at a single applied load. Relaxation experiments are similar to creep experiments, but are instead displacement-controlled such that the indenter is driven into a set depth while the relaxation of the force over time is monitored; the contact area is assumed to be constant throughout the experiment. Thus, one relaxation experiment provides the time-dependent force response for a single applied displacement. Both experiment types can be utilized in a probe-and-substrate contact setup, and both are useful for characterization of soft polymers.

1.4.1 Viscoelasticity

Viscoelasticity is a phenomenon of materials that exhibit both elastic and viscous properties. In an elastic material, a force induces a deformation, while a viscous material produces a rate-dependent resistance to the deformation. Together, the material then exhibits a rate-dependent elastic response over time. The widespread introduction of rubbers in the 20th century prompted the first detailed studies of rubber viscoelasticity by Schallamach, Barquins, and others [48, 49, 50, 51]. These findings showed that soft polymers exhibit viscoelasticity due to polymer chain rearrangement under load, which manifests as hysteresis between loading and unloading. The time associated with this rearrangement is dependent on the shear modulus and viscosity of the material and is independent of any length scale. In particularly soft materials such as biological tissues or hydrogels, this reorganization of polymer segments over time can alter the contact response based on the rate of loading as well as the time period of loading. As such, knowing the effect of viscoelasticity on the contact response is critical for a complete understanding of these materials.

1.4.2 Poroelasticity

Section 1.1 described how a typical hydrogel holds a large quantity of water within its mesh or "pores" due to hydrogen bonding; these bonds have an energy keeping the water attached to the hydrogel network. Under deformation, the pressure applied to the network acts upon these water molecules. With sufficient pressure, the water can be freed from the network causing the polymer structure to collapse and rearrange itself - this pressure is the osmotic pressure of the network. During such "squeeze-out" events, the polymer density is continuously changing, resulting in a time-dependent behavior similar to viscoelasticity. Poroelasticity is a rate-dependent and time-dependent effect, as it relies on movement of water throughout the porous medium and time-dependent chain relaxation [43]. This provides a second mechanism whereby a hydrogel can alter its contact response over time, which

makes it an important aspect to consider.

1.5 In-situ Contact Imaging

Contact imaging has long been a challenge in the field of tribology. The first to attempt imaging of the contact between soft solids was Schallamach, who discovered the phenomenon of waves of detachment through experiments using rubbers sliding against a transparent glass surface [48]. Such contrast-based techniques are still used to image dry elastomer contacts: one report utilized digital image correlation to produce a stress field from light reflected through a transparent polydimethylsiloxane (PDMS) substrate indented by a rigid probe [52]. Another study used a similar technique using variations in light reflections to determine the contact boundaries was used to image PDMS during sliding [53].

For hydrogels, which are ideally kept in a hydrated state and therefore require constant water immersion, imaging of the contact has been difficult. Capturing the physical network structure in a clear image is challenging, since hydrogels are naturally solvated in water. Rapid freeze-drying is one technique that has been attempted in order to visually measure the pore size of a chemically crosslinked hydrogel [54, 55]. Optical tomography techniques have been demonstrated for macroscale sliding hydrogel setups atop glass substrates, which were able to view 3D volumes of the contact in real time [56]. However, tomography techniques tend to require large setups, are comparatively low resolution, and require transparent probes and substrates. More recent attempts at imaging hydrogel contacts have used laser confocal imaging to view 3D volumes of a hydrogel contact with beads or dyes embedded in the hydrogel during polymerization. However, these volumetric techniques have proven difficult to apply due to the slow speed at which a confocal image stack can be acquired. For example, a representative volume through a hydrogel contact can take anywhere from 80 to 180 seconds to complete, at which point the hydrogel may have experienced significant deformation under load, or drastic changes in the contact profile if sliding. One group

of researchers used a "dynamic contact approximation" to extrapolate their confocal image stacks to a sliding hydrogel contact [57]. Particle exclusion microscopy (PEM) has been used on pAam hydrogels in order to determine their contact areas in quasi-static indentation over many hours [58]. This technique utilized a microscope view of the bottom of the contact, where violet particles in solution were excluded from the contact to create a contrast.

1.6 Hydrogel Lubrication

Lubrication between solid materials is typically described using the Stribeck curve (figure 2). The Stribeck curve is a well-established model describing the friction within various lubrication regimes and its relationship with sliding speed and normal pressure. The curve is often plotted against a parameter known as the Sommerfeld number, related to the viscosity of the lubricating fluid times the sliding speed divided by the normal pressure $\eta v/P$. The lubrication regimes, from low to high Sommerfeld number, include boundary lubrication, mixed lubrication, elasto-hydrodynamic lubrication, and finally hydrodynamic lubrication. Boundary lubrication consists of high friction resulting from extensive contact between the two solid surfaces. As the Sommerfeld number increases, the solid-solid contact decreases as a fluid boundary film forms, which results in decreasing friction with sliding speed. The lowest possible friction is obtained under elasto-hydrodynamic lubrication (EHL), where the minimum fluid film for full separation of the solid surfaces is achieved, often through extreme pressurization of the fluid and/or elastic deformation of the solid surfaces. At higher Sommerfeld numbers, the thickness of the lubricating film increases, causing friction to increase from viscous shear within the film. While the Stribeck curve is well-proven for most solid materials, it is less suited for materials capable of complicated time-dependent behavior such as poroelastic squeeze-out or viscoelastic friction. Additionally, polymer chain interactions such as chain adsorption reduce the applicability of the Stribeck model of lubrication.

Hydrogels, which exhibit high lubricity and structural similarity to tribological biomateri-

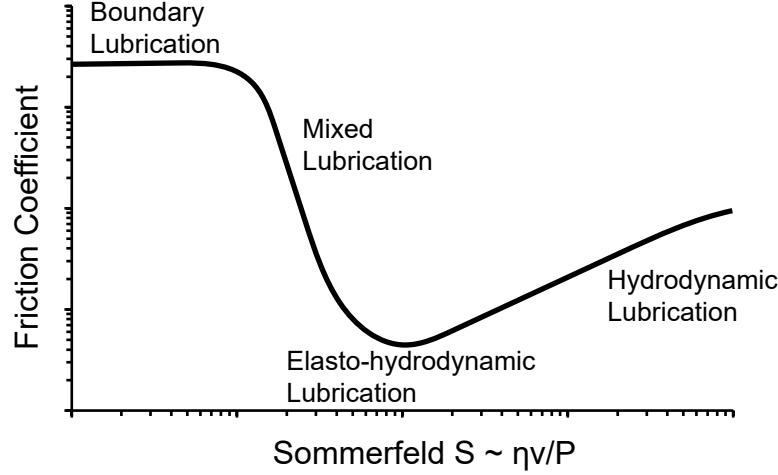


Figure 2: Example plot of the Stribeck curve, with classic lubrication regimes labeled. The Stribeck curve can be plotted as friction coefficient versus the Sommerfeld parameter, or as a shear stress versus a modified parameter $\eta v/N$.

als such as articular cartilage, have seen a significant amount of funded research to discover and optimize their sliding properties. One of the first notable lubrication models specifically for hydrogels was put forth by Gong in 1998. Gong’s investigation into hydrogels under sliding conditions against a hard probe resulted in the proposal of an analytic polymer physics-based ”repulsion-adsorption model” [59]. In this model, dangling polymer chains at the surface interact with a probe either during low sliding speeds or for a probe with high surface energy, adsorbing to the probe surface. These chains are then elastically stretched as the probe moves, until the chains de-adhere from reaching their maximum elongation. If instead, the probe has low surface energy or is moving rapidly, the dangling chains are unable to adsorb to the probe, and a fluid layer in-between the probe and substrate creates a hydrodynamic interface. The competition of the adsorption and repulsion behavior forms a lubrication curve where low speeds are dominated by elastic friction and high speeds are dominated by hydrodynamic lubrication [60]. The model was later refined by Kim et al by using a structural parameter similar to complex fluid flocculation [61]. In this model, hydrogel lubrication can additionally be described by dangling chain aggregation and shear de-coherence similar to how flocs in complex fluids break down under applied shear.

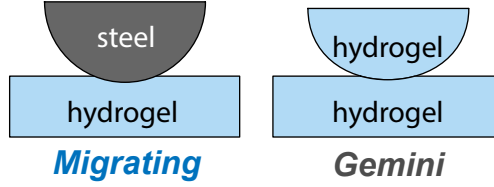


Figure 3: The most commonly studied contact configurations: soft-substrate i.e. migrating contact, and self-mated i.e. Gemini contact.

Gong’s repulsion-adsorption model serves as a solid starting point to qualitatively describe hydrogel lubrication where the hydrogel polymer chains are liable to adhere to the probe. However, there are reports that the model lacks quantitative support in real hydrogel contacts [62]. This is likely due to the propensity for the polymer chains to experience either high adhesion to the probe or limited to no adhesion at all. In cases where adhesion to the probe is significant, polymer interactions and their associated relaxation times contribute to the frictional behavior. For example, sliding of an AFM probe against pAam hydrogels of various compositions at various loads and speeds revealed a critical sliding velocity where the frictional behavior transitioned from high stick-slip behavior to lubricated hydrodynamic behavior [63]. But in contacts dominated by the predicted ‘repulsion’ portion of the model, the lubrication behavior is better predicted by a Stribeck curve [64, 65].

Self-mated contact, also termed ‘Gemini’ contact, has been extensively studied due to the extreme lubricity of a self-mated hydrogel interface, which is capable of friction coefficients as low as 10^{-3} [9, 19, 66]. These contacts are also closer in form to those seen in the body. Studies of self-mated sliding of hydrogels molded in a polystyrene mold show deviation from both Stribeck lubrication and Gong’s lubrication curve. In this special interface, friction appeared to reach a minimum speed-independent value below a critical sliding speed [67]. They proposed a two-regime model to describe their findings, where the speed-independent friction occurred due to ‘polymer fluctuation lubrication’, where thermal fluctuation of the dangling polymer chains at the interface were the primary driver of the overall friction. Beyond a critical sliding speed, the friction is instead controlled by polymer relaxation and

Gemini Hydrogel Surfaces

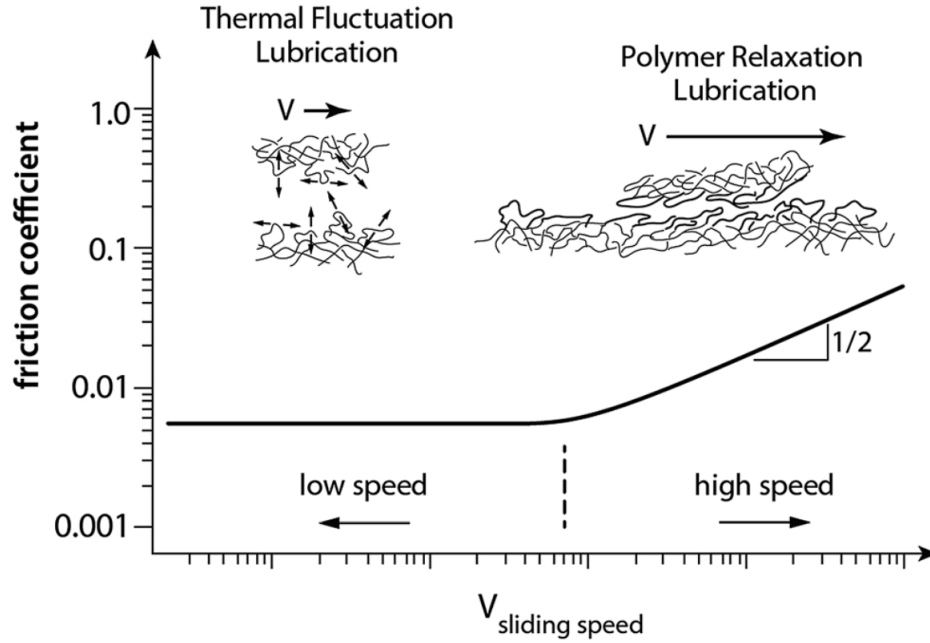


Figure 4: Graph and schematic delineating polymer fluctuation lubrication versus polymer relaxation lubrication. Reprinted with permission from the Royal Society of Chemistry [67].

chain interaction [68]. It should be noted that this latter proposition runs counter to Gong's proposed lubrication model, which may be due to the mold process of their gels.

1.7 Gradient-layered Hydrogels

Previous work with hydrogels showed very disparate, and occasionally contradictory, results. Li et al found that polyacrylamide gels experienced higher friction for larger monomer concentrations and decreased friction as the degree of crosslinking increased [69]. A study using an alginate/polyacrylamide IPN gel found higher friction for a larger crosslinker concentration at sliding speeds below 50 mm/s [70]. However, work with PVA gels found higher friction for more densely crosslinked gels [10]. Pan et al found that PVA hydrogels had lower friction with higher loads [14], while future studies by Pan et al found that reinforced PVA

hydrogels exhibited higher friction with higher normal loads [15]. Even when using polyacrylamide hydrogels of very similar composition, vastly different frictional and lubrication behavior was observed by different researchers [63, 71]. One potential explanation for these contrasting results is the 'mold effect', whereby the mold material alters the polymerization process of the hydrogel, imparting different properties to it.

The first mention of the potential affect of the mold material on the resulting mechanical or tribological behavior of a hydrogel was brought up by Kii and Gong in 2001, who believed it to be due to the hydrophobicity of the mold surface [72, 73]. But it wasn't until recently that the so-called 'mold effect' of chemically-crosslinked hydrogels was actively investigated. Meier et al showed that the choice of mold material impacts the stiffness of the first few microns of the hydrogel, with certain mold materials, particularly polymers, producing weaker force responses per indentation depth [74]. Based on these findings, Meier predicted that the surface energy of the mold material influenced the degree of crosslinking at the hydrogel. Characterization of hydrogels using neutron reflectometry and infrared spectroscopy revealed that the choice of mold material does influence the degree of crosslinking of the gel closest to the mold surface to create a 'brushy' surface layer on the order of 10-20 μ m thick [75]. Gombert found this layer to exhibit a gradient where the polymer concentration and degree of crosslinking decrease from the bulk to a much lower value at the outermost surface. Further investigations by both Meier and Gombert showed that the choice of mold material also affects the friction coefficient during sliding [55]. Finally, very recent work by Simic found that the 'mold effect' is due to the available oxygen at the surface during polymerization, with latent oxygen within polymer materials inducing the dilute soft surface layer [76]. He conclusively determined this to be true by comparing against surface energy variations and constructing an apparatus to control the available oxygen at the polymerizing solution surface.

As mentioned above, a significant amount of previous research on polyacrylamide hydrogels has utilized samples molded against polystyrene without accounting for the mold effect. By

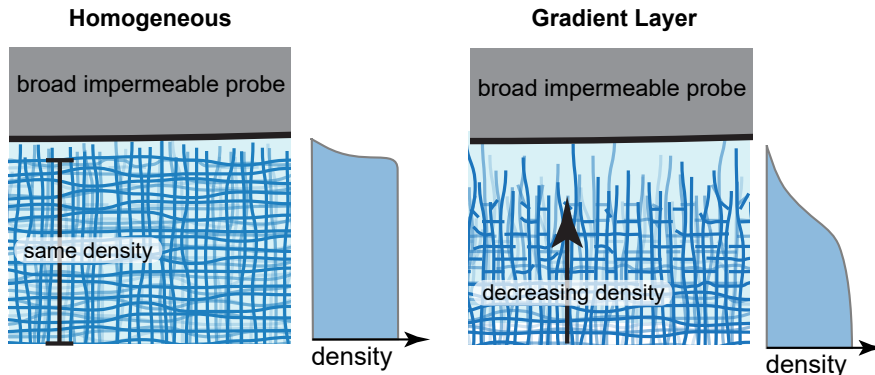


Figure 5: Illustration of the predicted polymer structures of a 'neat' hydrogel molded against glass, which produces a negligible gradient layer, and a 'brushy' hydrogel molded against a polymer such as polystyrene, which produces a significant gradient layer.

performing studies concentrated on the effect of the gradient layer and variations in its thickness, seemingly contradictory results can be resolved by attributing discrepancies to the gradient surface layer. Additionally, hydrogels possessing these gradient layers have been shown to exhibit ultra-lubricity [77], which makes intentional inclusion of such a layer appealing for many hydrogel applications.

1.8 Research Overview

Past research has attempted to use the mesh size of a hydrogel as a standard measure from which properties can be predicted [71]. This poses a problem if the crosslinks are not uniformly distributed, which may occur if the amount of crosslinker is comparatively high or if the total polymer percent is also very high. Some researchers even suggest that bisacrylamide clusters form the majority of the hydrogel structure, questioning the predicted "fishing net" structure possessing distributed crosslinks [55]. Heterogeneous crosslink distribution also occurs in gradient-layered hydrogels, which means that a mesh size descriptor of a gradient-layered hydrogel would have to be able to also predict the "mesh size" at the outermost surface of the gel as well as the depth at which the heterogeneity persists.

Low-shear layers at the surface of a polymer has been shown to control friction [19], and

is likely to also be true for polymeric hydrogels possessing this gradient layer. However, the characteristics of this surface layer have not been characterized in depth, likely due to the complexity of a material that gradually approaches complete fluid-like behavior at its boundary. More information regarding the surface layer’s structure and tribological response is necessary in order to design of better tissue surrogates. Such knowledge would provide the means to engineer composite hydrogel structures with favorable frictional and mechanical properties through selection of mold material, composition, and operating conditions.

In this body of work, we conducted a thorough contact mechanics characterization of Polyacrylamide (pAam) hydrogels possessing a significant less-dense gradient layer imparted by a Polystyrene (PS) mold material. We have investigated the nature of this gradient layer and its relationship with the amount of monomer and crosslinker present, as well as its effect on important tribological aspects that influence the ideal use cases of these hydrogels. For example, we have measured the contact-perceived depth of the gradient layer to be on the order of tens of microns, and inversely related to the monomer-to-crosslinker ratio and the total polymer concentration. The thickness of the gradient layer is primarily responsible for the resulting lubrication behavior of the sliding hydrogel interface, with larger gradient layers experiencing a shear stress state that is more consistent across sliding speed and normal load variations. Furthermore, the intentional inclusion of the gradient layer on a gel with a much stiffer bulk composition allows highly lubricated sliding even in very stiff hydrogel compositions.

CHAPTER 2

PARTICLE EXCLUSION MICROSCOPY

2.1 Motivation

One difficult aspect of determining the contact mechanics of complex materials is accurately predicting the contact area. More often than not, indentation experiments are used to obtain a force response per probe depth, which is then fit to an expected contact model that is ‘good enough’. The contact area is then calculated using analytic relationships provided by that model. This is especially problematic as the majority of existing contact models are developed around homogeneous hard materials such as metals, and become less accurate the softer or more heterogeneous a material becomes. Additionally, in sections 1.1 and 1.7, we described how hydrogel structures can be varied through processes such as the addition of extra networks, composite structures, or layered structures, which further impact the accuracy of these models. As such, we required a technique to observe the contact area of these hydrogels, in-situ if possible, whereby we could confirm or deny whether hydrogels followed well-known contact models such as the Hertzian or Winkler models introduced in section 1.3. Alignment with these contact models in both the contact area and force-depth response would reveal the physical nature of the polymer structure generating the response. Additionally, the structure of the gradient layer, and its response under load, will likely affect lubrication in moving contacts.

In addition, measurement of the contact area for these gradient-layered hydrogels is helpful for understanding their relaxation through viscoelastic and poroelastic processes. The time scale of viscoelastic relaxation is determined by the shear viscosity and shear modulus of the hydrogel, both of which are material properties [78]. In contrast, the rate of poroelastic relaxation is known to depend on the magnitude of the applied pressure, which is a function

of the contact area. We note that the contact area controls the volume of material from which water must vacate, showing that poroelastic relaxation has a length scale dependence [79]. Thus, the force/pressure drop over time for a number of fixed probe penetration depths can be used to determine the extent of each composition’s poroelasticity. Alternatively, by using a creep experiment with fixed normal load, the contact area and its rate of expansion across a range of pressures can be used to determine poroelasticity. We expect the degree of poroelasticity to differ based on polymer percent and relative amount of crosslinker. Studies on pAam hydrogels created from glass molds have predicted that the contact area stays constant for a given indentation depth [80, 79]. However, hydrogels molded against glass surfaces exhibit gradient layers on the order of $0.5\mu\text{m}$ or less, which is not perceivable in microscale experiments [74, 75]. Thus, the ability to visualize the contact during creep or relaxation experiments will help elucidate the effect of a significant gradient layer on stress relaxation (see appendix A.2.2). For a gradient layer of significant thickness and compliance compared to the bulk polymer, we expect contact areas to be underpredicted compared to predictions obtained from standard contact models (e.g. Hertzian).

2.2 Materials and Hydrogel Preparation

In section 1.7, we discussed the advent of the ‘mold effect’: a softer ‘brushy’ gradient surface layer imparted by the presence of free oxygen during polymerization. We also covered how intentional inclusion of such a layer may be favorable once it has been characterized in depth. For this reason, we chose to intentionally induce a gradient layer on all hydrogels used in this work.

Polyacrylamide (pAam) hydrogels were created using stock solutions of acrylamide (Aam) monomer, methylenebisacrylamide (BisAam) crosslinker, tetramethylethylenediamine (TEMED), and ammonium persulfate (APS). These solutions were combined to create a pre-polymerized solution that was quickly poured into cylindrical polystyrene molds of diameter 35mm and

height 4mm, then covered with a polystyrene surface in contact with the solution. After allowing the gels to cure in the mold for 45 minutes, the gels were cut down to a 25mm diameter and placed in a DI water bath for three to five days prior to testing.

Previous work on chemically-crosslinked hydrogels have found that variations in either the monomer percent or the ratio of monomer to crosslinker have significant effects on the contact and lubrication responses [81, 71, 66, 62, 63, 82, 83, 60, 84]. For this reason, we conducted experiments on up to five different hydrogel compositions in order to perceive the effects of both metrics. These hydrogels were created by altering the amount of Aam monomer and BisAam crosslinker stock solution used during the polymerization. The five compositions and their corresponding wt/wt percent of each constituent is shown in Table 1. Of these five compositions, three spanned variations in the monomer-to-crosslinker ratio, termed ' R ', while keeping a constant monomer percent of $M = 7.5\%$ (compositions 1, 3, 5). Three compositions also spanned different monomer percents ' M ' while retaining a constant monomer-to-crosslinker ratio of $R = 25$ (compositions 2-4). Compositions 1-4 were transparent, while composition 5 was translucent. This translucence, which colored the hydrogel milky-white, did not visibly impact the accuracy of the contact area measurements. However, further decreases to R would prevent measurement of the contact area using microscopy techniques. Compositions 1 and 2 had the greatest degree of swelling, while compositions 3-5 exhibited insignificant swelling. Composition 1 was expected to be primarily viscoelastic based on previous studies [85]. For experiments in chapters 3 and 4, we exclusively used composition 3 hydrogels, which have been extensively studied in the past [9, 86, 77].

The indenting probe material consisted of either a 4mm diameter steel spherical ball bearing, or a 4mm diameter hydrogel hemisphere. The rigid steel bearing was covered with a single coating of matte black acrylic paint, which eliminated any light reflection that would reduce image quality. Both probe types were attached to 10mm long threaded aluminum rods. To create hydrogel probes, we poured the pre-polymerized solution into a custom-made mold of Delrin and poly-olefin plastic parts. After 30 minutes, the probe was removed

Comp #	M/C Ratio R	Monomer % M	Crosslinker % C	Water %
1	250	7.5	0.03	92.2
2	25	5	0.2	94.5
3	25	7.5	0.3	91.9
4	25	15	0.6	84.1
5	15	7.5	0.5	91.7

Table 1: Polyacrylamide hydrogel compositions listed by number and wt/wt percentage of constituents. Compositions 1,3,5 span variations in the monomer-to-crosslinker ratio R , while compositions 2-4 have varying monomer percent M but a fixed ratio R . All compositions used 0.15% wt/wt TEMED and APS.

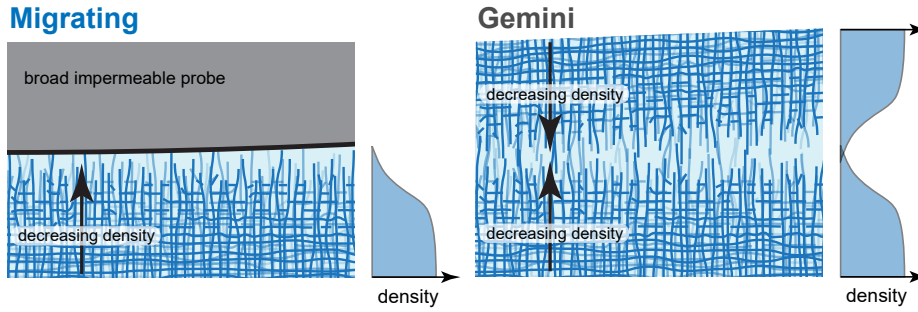


Figure 6: Illustration of the two contact types used for all experiments in this work: migrating and Gemini contact. By molding against polystyrene (PS), these hydrogels develop the gradient density surface layer.

from the mold and allowed to equilibrate in DI water for three to five days. Probe size was constrained to 4mm diameter based on the size of the hydrogel probe mold.

2.3 Experimental Process

2.3.1 Tribometer setup

All experiments used an experimental setup consisting of a microtribometer mounted atop an inverted confocal fluorescence microscope (see Figure 7). Two contact types were tested: a rigid spherical probe indenting into a flat hydrogel surface (‘soft-substrate’ or ‘migrating’ during sliding), and a hydrogel hemispherical probe indenting into a flat hydrogel slab (‘Gemini’ contact [9]). The indenting force was applied through precise vertical movement

of a four-bar cantilever flexure mounted to a $500\mu\text{m}$ piezoelectric stage. The flexure had known normal and lateral stiffness values of 49 and $51\ \mu\text{N}/\mu\text{m}$, respectively. The probe, attached to the aluminum rod, was attached to the end of the flexure. Also attached to the end of the flexure was a target box coated in a thin layer of silver. Capacitive sensors were then placed $25\mu\text{m}$ from the top and side surface of the target box. These sensors acquired voltages between +10V and -10V whose magnitude changed based on the distance from the conductive target box. The maximum distance at these voltage limits corresponded to 0 and $50\mu\text{m}$ for a conversion of $5\mu\text{m}$ per volt. As the target box on the flexure moved due to normal and frictional forces, the distance between the target box and the capacitive sensor(s) would change. Converting the voltage to a distance and multiplying by the cantilever stiffness produced a force value for either the normal or frictional force. Voltage data was acquired at a rate of 1000Hz and then averaged every ten points, producing raw data output at 100Hz. This microtribometer also included a horizontally-reciprocating piezoelectric-driven stage with stroke length $1500\mu\text{m}$, which was used for sliding experiments to move the substrate relative to the flexure.

Control of the vertical and lateral stages was performed using a custom program created in Matlab. For initial loading of the contact, a ramp rate of $25\mu\text{m}/\text{s}$ was chosen to apply quasi-static loading [87]. This speed was also compatible with our rate of image acquisition during each experiment, allowing sufficient data points (10+) to measure areas during indentation. While it is known that the rate of indentation changes the stiffness response of hydrogels [88, 89], we performed preliminary experiments showing that the perceived thickness of the gradient layer was relatively consistent with ramp rate ($\pm 20\%$).

2.3.2 Area measurement technique

In order to view contact area projections using the microtribometer setup described above, we required a technique that made use of our confocal microscope. Previous contact imaging

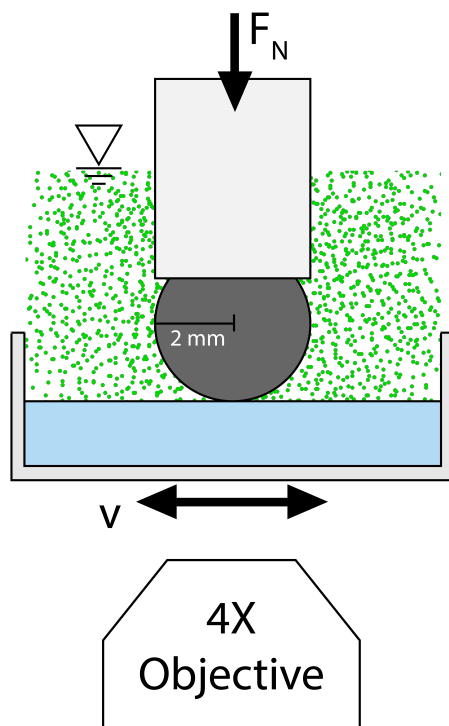


Figure 7: Particle exclusion setup used with the microtribometer mounted atop an inverted confocal microscope. The water bath consisted of a dilute solution with $1\mu\text{m}$ green fluorescent particles.

techniques on hydrogels have attempted confocal stack imaging [57] as well as 2D contact area projection through particle exclusion microscopy (PEM) [58], the details of which have been covered in section 1.5. We employed a method based loosely off the latter technique to measure contact areas throughout this work, which instead used $1\mu\text{m}$ microfluorescent particles in solution as the excluded particles.

One drop of a 1% solids solution of the $1\mu\text{m}$ green fluorescent particles (Thermofisher Scientific) was put into 15mL of de-ionized water and thoroughly mixed. This solution was then poured on top of the hydrogel substrate. Concentration of the fluorescent beads was roughly 0.0003% wt/wt, which was low enough to avoid impacting friction measurements through physical ploughing of particles. When attempting experiments with much larger bead concentrations, we found a large portion of the beads adhering to the probe. Additionally, the beads stuck to the probe reduced the clarity of the contact boundary, since the contact area was no longer defined by an exclusion of fluorescent particles. This led us to stick with the aforementioned particle concentration.

Light of wavelength 470nm was directed through the primary dichroic mirror through a 4X objective (NA 0.13) up towards the bottom of the sample to induce light emission in the particles and observe their movement via the confocal microscope. As the indenting probe approached the counterface, the fluorescent beads cleared the emerging contact due to fluid pressure, forming a distinct region devoid of particles that corresponded to the nominal contact area (see Figure 8). Video of this contact area projection was captured for each experiment at 15 fps using the confocal microscope and its accompanying program (Nikon Analysis). Still images were extracted at regular intervals from the videos to perform contact area analyses. The interval and total number of images analyzed was dependent on the experiment type. Image sizes were 512x512 pixels, corresponding to real dimensions of 2.05x2.05 mm. Contact areas were measured using ImageJ for image processing, point selection, convex hull fitting, and pixel area measurement. Image processing used a combination of contrast enhancement, image stack averaging, and background subtraction to

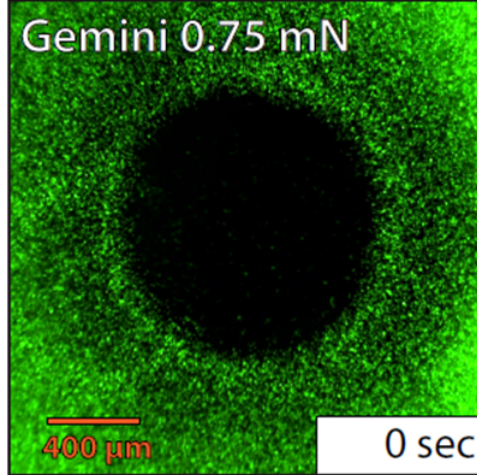


Figure 8: Example of an image obtained using the particle exclusion technique. The circular region devoid of particles corresponds to the contact area. Experiment was a creep test conducted in a Gemini contact setup with a normal load of $750\mu\text{N}$.

more clearly determine the contact boundaries (see Figure 9). We utilized ImageJ’s z-stack intensity averaging to create an average background image using the average pixel intensity across a collection of frames from the video. This image could then be subtracted from individual frames of the video to produce a higher contrast between the excluded area and the fluorescent particles. Contrast was enhanced as needed to mark the contact boundary. Standard deviation of the contact areas was determined by taking a representative image for a particular experiment and repeating the image processing and area calculation ten times. Average contact pressures were calculated by dividing the prescribed force by the nominal contact area. Standard deviation of pressure was calculated using error propagation and the uncertainties of the force and area.

2.4 In-situ Contact Measurement Assessment

In previous work utilizing PEM, contact areas were captured once every 50 seconds, and utilized violet-tinted particles and multiple light sources to produce the contrast between the particles and the excluded area [58]. In this body of work, we have instead used a single

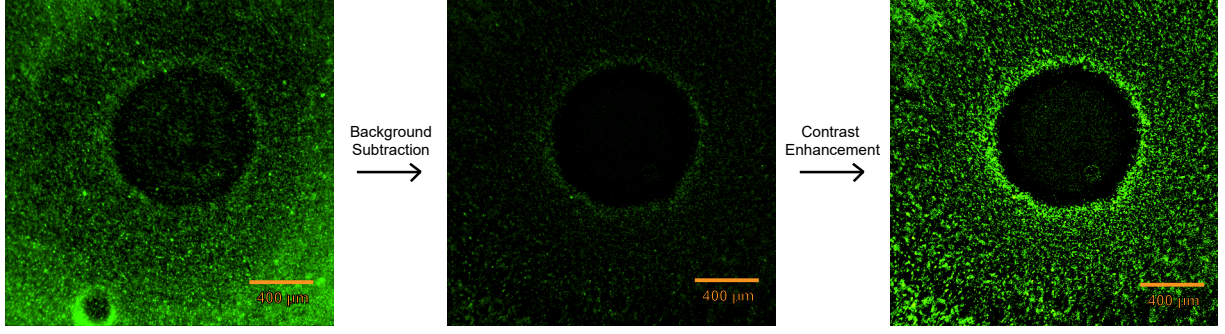


Figure 9: (Left) Example of a raw frame from a creep experiment. (Center) The same frame after subtracting a representative background from image stack averaging. (Right) Image after contrast enhancement in order to improve the contact boundary.

470nm light source emitted through a dichroic that causes excitation and light emission of green fluorescent particles in the water bath. This simplified surface detection and contact boundary detection, since the fluorescence intensity is related to the focus plane, allowing boundaries to be defined by particles at similar intensity levels. As we chose to use wide-field imaging, we retained the ability to detect particles with sufficient resolution $\pm 50\mu\text{m}$ from the focal plane along the z-direction. This allowed accurate detection of the contact boundary even for migrating contact setups with large penetration depths. This was made possible by using contrast enhancement, focus adjustment, and visual particle tracking. For detecting the point of first contact, fluorescent particles at the imminent point of first contact experience pressurization that causes them to "shoot out" into lower pressure regions of the solution. These particles move faster than any other particles displaced by the probe, since the pressure on the particles/fluid immediately underneath the bottom of the indenter is larger than any applied to particles pushed out later by the radius of an indenting probe. This leaves behind a region devoid of particles that continuously expands as the probe moves deeper into the hydrogel. The displacement of the beads manifests as a halo surrounding the area due to the temporarily increased bead concentration immediately surrounding the indenter.

The impact of the probe displacing water must also be accounted for. As the probe approaches the sample, it displaces water both in the region between the probe and substrate,

but also within the volume occupied by the probe. The latter causes both a buoyancy force and an osmotic pressure gradient towards the probe, which can cause beads to adhere to the probe if the probe material is also charged or hydrophilic. For the particle exclusion technique to work without disrupting the system, the fluid squeeze-out needs to be greater than any driving forces prompting beads to stick to the probe. The osmotic pressure results from the concentration differential caused by the indenter displacing solution. The magnitude of this differential can be controlled by choosing an appropriate bead concentration that minimizes the osmotic pressure while retaining a high enough concentration to preserve contact boundary clarity. For our experiments, we chose a concentration on the order of 0.0003%, which was low enough to discourage bead adhesion. This concentration also made their impact as a third-body of a sliding interface negligible, since we observed a negligible degree of first-pass run in (see Section 4.3).

In sliding experiments, z-stack image averaging allowed for more versatile techniques to determine the contact boundary even for fast sliding speeds. By taking an average pixel intensity across a set of frames covering unidirectional movement, a resulting "flow map" image is produced. This image is the average bead intensity over the time period covered by the stack of image frames, which means that a single bead can show up in multiple positions on the resultant image, plotting its flow trajectory (see Figure 10). This made the beads moving around the contact patch much more apparent compared to operations on a single frame, even with proper background subtraction, since the trailing edge of the contact frequently did not produce an immediately apparent particle boundary at higher sliding speeds. Whether or not the trailing edge of contact formed a distinct particle boundary was dependent on the density of the hydrogel surface and its compaction. In higher density hydrogels undergoing large compression, the polymer density is locally increased, which can cause locally increased osmotic pressure that manifests as suction of particles towards the collapsed structure.

A key aspect of this technique is that the microfluorescent particles must retain enough

mobility to move along with the solution displaced by the indenter. The mobility of the particles is primarily related to the surface energy of the probe, surface energy of the hydrogel substrate, and the size of the particles. As discussed in section 2.2, the rigid probe was covered with an acrylic paint that is hydrophobic, which helped reduce bead adhesion to the probe in migrating contact experiments. However, we noticed that certain hydrogel compositions were more likely to trap beads under the probe instead of permitting them to flow away from the contact. In particular, compositions 4 and 5 were more likely to retain fluorescent particles on the hydrogel surface(s). As such, it can be inferred that the surface energy of pAam hydrogels is higher for larger polymer percents M and lower monomer-to-crosslinker ratios R . The effect of the gradient layer on the relative degree of bead adhesion is discussed in the appendix (see appendix A.1.2). Finally, particle size influences the amount of beads sticking to the probe/substrate in all situations due to the ratio of surface area to volume: smaller particles with a higher surface area to volume ratio are less able to resist attraction to the probe/substrate due to their lower mass. This behavior was experimentally verified in preliminary experiments using $0.5\mu\text{m}$ fluorescent beads, where we observed non-negligible levels of bead adhesion when using hydrogels of compositions 2-5. As such, we chose to use $1\mu\text{m}$ fluorescent particles for all experiments to reduce the potential effects on contact pressure and friction that could arise from particle adhesion.

2.5 Conclusions

Utilizing microfluorescent particles, we were able to demonstrate an effective method to measure in-situ contact areas developed between a probe and substrate. This technique was viable for both migrating and Gemini contact setups in both stationary or moving experiments. In order to obtain clear contact profiles from all experiments, we used image processing involving frame stack averaging, background subtraction, and contrast enhancement. In addition, we chose a particle concentration that balanced low particle adhesion

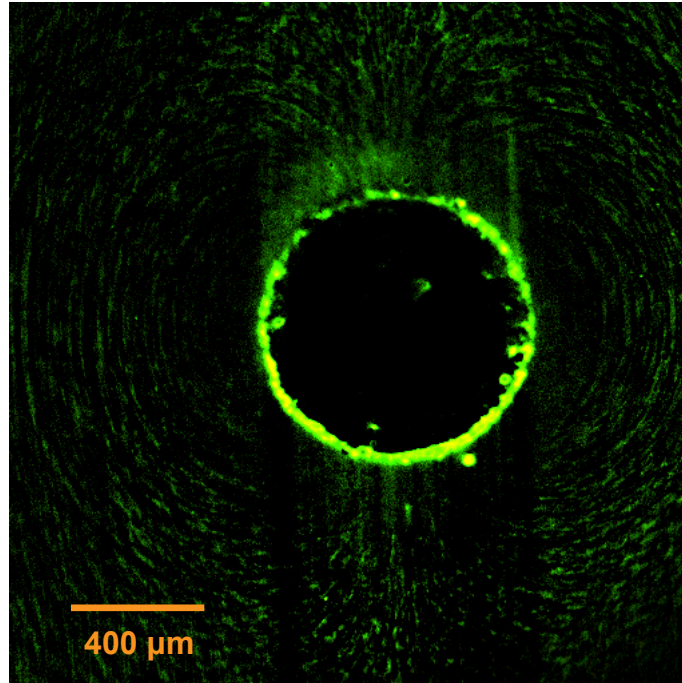


Figure 10: Example image obtained using z-stack intensity averaging in ImageJ. When averaging frames covering a time period of unidirectional sliding, a single particle can be displayed in multiple positions after the z-stack processing, resulting in a "flow map" showing its path in that time period. Experiment was conducted in a sliding migrating contact setup at $1000\mu\text{N}$ normal load and $100\mu\text{m/s}$ sliding speed.

with high clarity of the particle-formed contact boundary.

There are still ways in which this PEM method could be improved. For example, we covered how behavior of particles rapidly evacuating the first contact location could be used to mark the point of first contact. The use of detailed particle tracking through the microscope analysis program could be used to more precisely detect the point of first contact by tracking these fast-moving particles' positions. Particle tracking could also help keep track of the expanding contact boundary using the particle positions, reducing the contact area measurement error.

CHAPTER 3

MECHANICS OF GRADIENT-LAYERED HYDROGELS

3.1 Motivation

In section 2.1, we discussed how measuring the in-situ contact area would provide vital information allowing us to validate existing contact models and relaxation modes for our gradient-layered hydrogels. This is a vital step, since we hypothesized that the lower density and degree of crosslinking reported from previous studies would affect the resulting contact area and stress distribution [74]. As such, we performed probe-based contact experiments utilizing the in-situ contact area measurement method to gain a better understanding of the gradient layer response under load.

The first type of mechanical test enhanced by knowing the real area of contact is indentation. Indentation is an extremely common technique to determine bulk and surface properties of a material as it can be carried out with a simple probe-on-substrate technique. As discussed in section 1.3, these tests involve a relatively rigid probe pushing into the sample substrate, where the force and displacement are recorded throughout. Comparison against different contact models then allows useful parameters such as elastic modulus, hardness, contact area etc. to be determined. But in cases where a contact model inadequately fits, or only partially applies, measures of contact area and other parameters can be inaccurate, leading to incorrect conclusions about the behavior of the contact. By using our PEM technique to determine the contact area independently of contact model fitting, we gain a better understanding of which contact models, if any, are better suited to describe the behavior of a graded hydrogel surface. Contact models that are valid for even a portion of the indentation will indicate the possible polymer structure producing the response.

The second type of common mechanical test we utilize our PEM technique for is the creep

experiment. Section 1.4 described how this experiment can be conducted using a probe-on-substrate setup by using a comparatively rigid probe actively maintaining a prescribed load on a soft substrate. We made use of this experimental setup to reveal the time-dependent response of these hydrogels, especially how the pressure of the contact is redistributed over time within both the softer gradient layer and the bulk. Having direct measurements of the contact area over time provides us values of a^2 that are independent of any contact model, making determinations of poroelastic versus viscoelastic behavior more accurate. Previous studies of pAam osmotic pressure suggests that we must exceed a contact pressure of 11 kPa before any poroelastic squeeze-out can occur in a 'neat' crosslinked network [86, 90], but this type of relaxation may occur sooner due to the dilute nature of the gradient layer at the surface.

In this chapter, we conducted indentation and creep experiments of varying normal loads on a standard hydrogel with a significant gradient layer: a composition 3 hydrogel (see table 1) molded against polystyrene. By utilizing our microfluorescent PEM method during these experiments, we gained a detailed understanding of the gradient layer contact mechanics and relaxation behavior. We verified the lesser density and degree of crosslinking within the gradient layer described by Meier et al [74]. Of great importance was the finding that the contact mechanics of the gradient layer follows an evolving contact model, which begins with fluid film contact, transitions to brush-like and spring-like contact, and finally exhibits mechanics similar to a well-crosslinked bulk after sufficient probe depth. Furthermore, the gradient layer's dilute nature allowed poroelastic relaxation to occur at pressures far below the known osmotic pressure of these hydrogels. This detailed information regarding the structure and response of the gradient layer is important for designs involving hydrogel contact.

3.2 Indentation Methods

3.2.1 Experimental methods

Short-duration, displacement-controlled indentation was performed using the tribometer described in section 2.3.1. Indent and pull-off speed was set to $25\mu\text{m/s}$; dwell time was kept to zero. Indentations were performed reaching peak loads of 500, 750, or $1000\mu\text{N}$. Normal force and stage displacement were acquired at a rate of 100Hz. Experiments were performed on areas of the gel at least 4 mm away from each other, with ten minutes in between indentations to allow the gel to fully re-equilibrate. Each experiment was repeated three times at different locations on the hydrogel.

Contact area videos were acquired using the procedures described in section 2.3.2. The contact area videos were anchored together with the indentation data by matching the time of maximum indent depth to the time of maximum contact area. Video snapshots were extracted at 0.3-0.5 second intervals and analyzed for contact area. The time of first contact in each video was marked for each experiment by using the characteristic bead movement described in section 2.4. Nominal contact pressures were calculated as $P = F_N/A$ using the tribometer-obtained normal force F_N at the time corresponding to the particular contact area A .

3.2.2 Indentation analysis method

As described in section 1.3, indentation analysis typically involves curve-fitting of a contact model to determine both the reduced modulus and the initial point of contact. For example, in the Hertzian contact model (Equation 1.1), the force response is dependent on the probe geometry and the reduced modulus E^* (Equation 1.2) as well as the probe depth at first contact d_o , which are solved for simultaneously. However, traditional indentation analysis techniques pose a challenge when initial contact does not provoke a strong force

response. In very dilute or graded materials, the point of first contact is confounded by a weak force magnitude and poor fitting to established contact models, both of which apply to our hydrogels. Because of this, we instead analyzed indentation experiment data using a force-derivative method developed by Garcia et al [91]. By using this analysis method, the force-depth power relationship of the raw data is emphasized, allowing more accurate fitting of portions of the data to a given contact model. Once the appropriate contact model is determined, a reduced modulus can be calculated independent of the depth of first contact.

$$\frac{dF}{du} = K_G F^n \quad (3.1)$$

In the first step of the method, the derivative of the force with respect to indentation depth $\frac{dF}{du}$ is calculated for the data using forward differencing. We then utilize equation 3.1, which represents contact as a function of the force. In Equation 3.1, $K_G = PK^{1/P}$ and $n = (P - 1)/P$. K is a coefficient containing the constants associated with the force-displacement relationship of a particular contact model. K can include terms such as the reduced modulus, indenter radius, etc. For example, in the Hertzian model, $K = \frac{4}{3}E^*R^{0.5}$. P is the exponent relationship between the force and displacement for the contact model. For example, Hertzian contact has $P = 3/2$ and $n = 1/3$. The reduced modulus is found from fitting a contact model-based power-law to the data using least-squares error minimization to determine the value of K_G . This leaves the point of contact as the only unknown, which can be determined either using a single-parameter fit or, in our case, the video of each experiment. The point of first contact, $d_{contact}$ could be pinpointed by identifying the occurrence of unique bead behavior at the onset of contact, whereby the fluorescent beads at the center of the incoming contact would flow out of the zone at maximum velocity. The contact video could be anchored to the tribometer data by linking the maximum contact area of the video with the maximum vertical stage depth of the data. In a log-log plot of dF/du versus the force F , the magnitude of n affects the slope of a line on the plot, while the magnitude of K_G

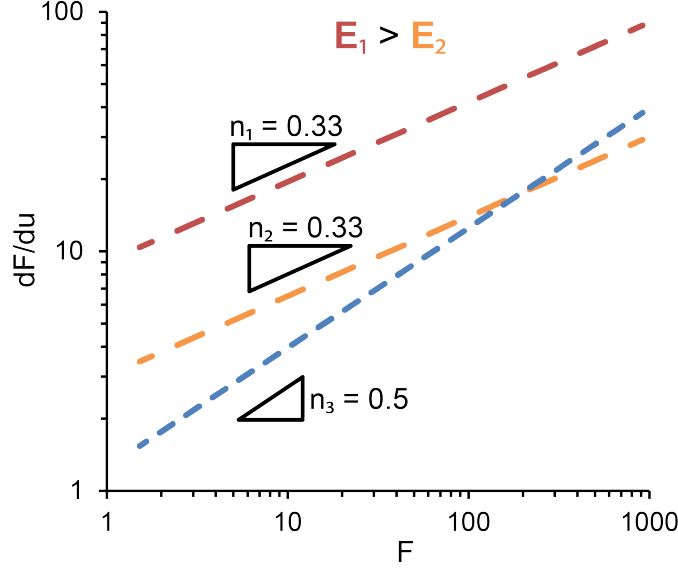


Figure 11: Example log-log plot using the Garcia method. In this plot, a power-law relation is represented as a straight line, where the slope represents the magnitude of n and the y-intercept is determined by the magnitude of the reduced modulus - higher moduli model lines are translated higher on the y-axis.

alters the vertical position of the line. For example, a coefficient of $n = 0.33$ represents a straight line on a log-log plot that corresponds to the Hertzian contact model (see Figure 11). A similar formulation can be made for the Winkler foundation contact model discussed in section 1.3 (equation 1.3). In the Winkler model, we instead have $K = \pi E^* \frac{R}{t}$, $P = 2$ and $n = 0.5$. Thus, a Winkler model represents a straight line on a log-log plot of dF/du versus F with a slightly higher slope due to a higher n value.

By using this log-log plot format, we were able to determine how the data related to existing contact models. Raw data was averaged every ten points to condense it for use with the Garcia method, then plotted on log-log axes. For data points fitting to a Hertzian contact model, values of K_G , and therefore E^* , were determined by fitting latter points whose inclusion strengthened an $n=0.33$ fit. A similar method was used to fit earlier points that fit to an $n=0.5$ fit corresponding to the Winkler model.

3.3 Creep Methods

3.3.1 Experimental methods

Long-duration force-controlled experiments were conducted to view contact area expansion over time. A fixed normal load of 500, 750, or 1,000 μ N was applied by the probe onto the gel substrate for at least 600 seconds. This load was servo-ed in real time, allowing the tribometer vertical stage to adjust to maintain the prescribed load (signal error = $\pm 20\mu$ N).

Image frames from the microscope video output were taken at 30 second intervals up to 180 seconds and 60 second intervals thereafter, for a total of 14 area measurements. Based on the observed speed of contact expansion, this variable interval was deemed sufficient to capture the area change over time. Contact areas were measured using procedures outlined in section 2.3.2.

3.3.2 Time-dependent relaxation analysis method

Creep experiment contact areas were measured using the methods outlined in section 2.3.2. These data points were then fit to an exponential model to determine the time constant associated with the contact area expansion.

$$A = A_f + (A_o - A_f)e^{-t/\tau} \quad (3.2)$$

$$\tau_P \approx \frac{a^2}{D_{SS}} \quad (3.3)$$

In section 1.4, we introduced the two relaxation mechanisms of interest for soft polymer hydrogels: viscoelasticity and poroelasticity. Both mechanisms affect the contact response of the hydrogel, and determining the relative degree which either one occurs within the gradient layer will inform us of the probable structure of the layer. To understand which of

these mechanisms were occurring within the hydrogel contact, we utilized theory developed by Hu et al [79, 42], which can identify the primary relaxation mechanism based on the relationship of the obtained time constants with the applied load. In poroelastic theory, the time constants associated with the squeeze-out of water from the pores is dependent on the pore size, and therefore, a length scale of the contact. In particular, Hu obtained that the poroelastic relaxation time is related to the contact radius of an indenter pushed into a porous substrate. This is in contrast to viscoelasticity, where the relaxation time is only related to the shear modulus of the material and is wholly independent of any experiment length scale [78]. Therefore, a plot of the obtained time constants versus the contact length scale reveals the dominant mechanism and allows calculation of the diffusion coefficient based on the slope of a linear fit. If the slope is close to zero, then the relaxation is primarily viscoelastic; if there is a significant slope, then the relaxation is primarily poroelastic. A steady-state diffusion coefficient can be calculated from the inverse of the slope produced by the time constants plotted versus the initial contact radius [80]. We fit time constants to each experiment's data of contact area versus time using least-squares regression (Excel Solver).

3.4 Indentation Results

Previous indentations on pAam hydrogels showed that hydrogels molded against glass surfaces exhibited Hertzian contact mechanics [92, 79, 77, 66]. This establishes a baseline whereby a uniformly crosslinked hydrogel shows a Hertzian contact response. Using this knowledge, we expected the latter portions of each indentation to fit well to a Hertzian contact model. When assessing the indentation data according to the Garcia method outlined in section 3.2.2, we found that the contact behavior does not exhibit behavior indicative of a single suitable contact model or single power-law fit. Immediately after the point of first contact, we observed the greatest variability in the data and any potential n exponent

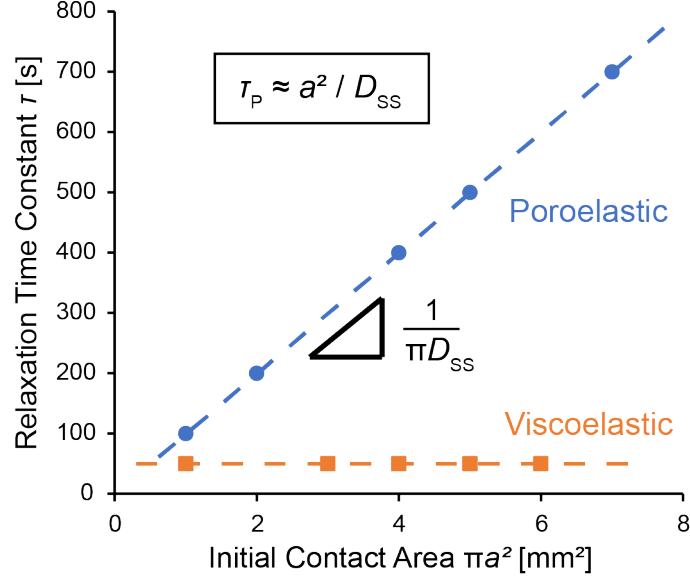


Figure 12: Example plot of exponential time constants versus contact area. When the time constant of relaxation correlates with the contact pressure, and therefore contact area, this indicates poroelastic relaxation. Alternatively, if the time constant is unchanged by varying pressure/area, the relaxation is viscoelastic.

fit, with values ranging from 0.3 to 0.8. We predict that this region of variability is due to squeeze-out of the water held by the loose polymer segments, which causes a ramping-up force response due to pressurization of the released water while it escapes the contact. After this initial variability, we could fit a portion of the contact to the Fredrickson high-penetration brush model (section 1.3.3, equation 1.4), which had $n = 0.67$ (Figure 15). This alludes to the lower polymer density and lower degree of crosslinking within the gradient layer, which would be composed of loosely-crosslinked acrylamide backbone chains extended outward toward the good solvent bath. The resulting structure would resemble a polymer brush of increasing density as the probe traveled further into the substrate. After this interval, the next portion of each indentation curve fit well to a Winkler contact model (see section 1.3, equation 1.3), suggesting that the compression of the outermost brush segments did not induce significant strain in the material adjacent to it [93]. Beyond the Winkler-fitting region, we were able to fit a Hertz contact model to the rest of the points, which implies that the compressed gradient-density surface layer had begun to emulate the response of the

well-crosslinked bulk.

The intersection between the Winkler-fitting region and the Hertz-fitting region occurs at a point we define as d_{match} . We can establish the contact-perceived thickness of the gradient layer as the probe indentation depth from the video-derived point of first contact $d_{contact}$ until the first point of the Hertzian-fitting region d_{match} - we term this distance as Δd . The magnitude of Δd can be considered the penetration depth after first contact before the Hertz contact model applies. Because it spans the substrate thickness before Hertz contact fits, it provides a rough estimate of the thickness of the gradient layer, which is how we will refer to this measure hereafter. This shows that the thickness of the gradient layer for our standard composition hydrogel is roughly $17.1\mu\text{m}$ thick (see table 2), which is within the proposed $10\text{-}20\mu\text{m}$ range estimated via neutron reflectometry [74, 75]. Of this thickness, approximately 80% of this distance comprises the brush-fitting and Winkler-fitting region, which indicates the degree of 'brushiness' as a function of the penetration depth: a higher percentage corresponds to the presence of loosely-crosslinked chains further into the depth. Gemini contact had a gradient layer thickness of $25.3\mu\text{m}$ - only 47% larger than the migrating case, and the portion of each indentation corresponding to a brush-fitting or Winkler-fitting region dropped to 67% for a Gemini contact configuration. The reason for this can be attributed to the interaction method between the two gradient layers. In a good solvent, it has been shown that acrylamide and bisacrylamide segments are unlikely to become entangled in a self-mated contact configuration, as they prefer instead to extend into the surrounding water [67, 71, 94, 95]. Williams, following up on Fredrickson's brush contact model, proposed that at low probe penetration depths, a rigid probe indenting into a polymer brush would experience a Hertzian force-depth relationship of $F \propto d^{\frac{3}{2}}$ based on the stiffness of the brush (equation 1.5) [47]. In a Gemini contact, these two combined findings would result in a larger portion of the indentation curve, including immediately after initial contact, to experience Hertz-like contact. In fact, it is possible to fit a rudimentary force-depth power-law of 1.5 to the first $2\text{-}5\mu\text{m}$ of the Gemini indentations, giving a brush modulus

Contact Setup	Elastic Modulus E [kPa]	Gradient Layer Thickness Δd [μm]	Winkler % of Δd
Migrating	33.8	17.1	79.5
Gemini	33.1	25.3	66.9

Table 2: Elastic moduli, gradient layer thickness Δd , and portion of the gradient layer thickness interval corresponding to a Winkler model, for each contact setup.

of 1.5 kPa. Gemini contact also produced a slightly lower elastic modulus (33.1 kPa) than migrating contact (33.8 kPa), which signifies faster onset of Hertzian contact.

It is important to note that the contact area observed throughout each indentation also deviated from a single contact model estimation. For example, using the probe displacement to predict a contact area using Hertzian contact mechanics would under-predict the actual contact area of these gradient-layered hydrogels by as much as 44% (see Figure 13). If we instead use a piece-wise analytic model, where we use a Winkler model for the probe displacement d spanning the gradient layer thickness Δd and a Hertzian contact model for values after that, we obtain a prediction of the contact radius that is much closer to that observed experimentally. We note that this fit is not perfect since we have assumed a Winkler contact model through the initial indentation regime where brush contact and fluid squeeze-out, not Winkler contact, is the prevalent behavior; deriving contact areas for these phenomena would improve the predicted contact area fit.

3.5 Creep Results

Creep experiments confirmed an increase in the contact area with time. The majority of contact area gain occurred within the first 100 seconds regardless of contact setup. Contact area growth from the initial contact area was highest for the lowest applied loads, with a 30% increase. Higher loads experienced less area growth relative to the initial area, only rising 20% over the full 600 second experiment. The average contact pressure in these experiments remained low, with initial pressures ranging from 0.8 to 1.8 kPa and decreasing over time.

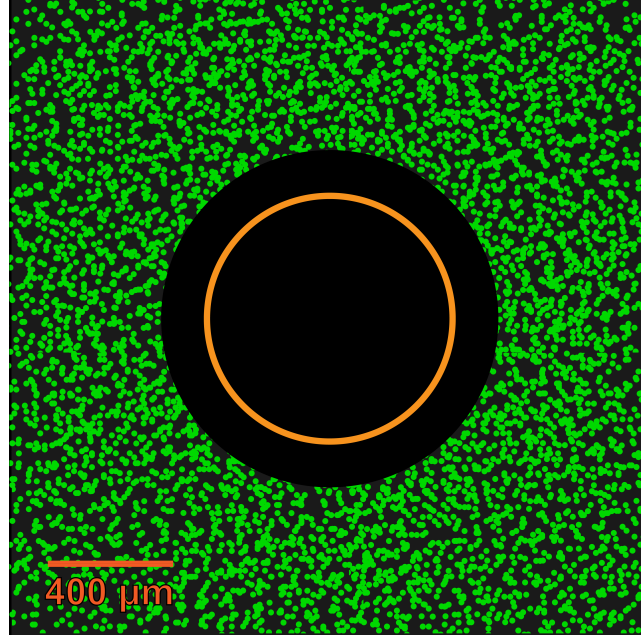


Figure 13: An illustration of a representative contact area projection observed using particle exclusion microscopy. The orange circle represents the expected contact area from a Hertzian contact model prediction, which under-predicts the actual contact area by as much as 44%.

When fitting the area growth curves to exponential functions and extracting time constants using the procedure from section 3.3.2, we were able to show that the time constants varied significantly with the initial contact radius, which is a function of the applied load / initial pressure (see Figure 18). The inverse of the slope created by the time constant trend with contact radius produced a steady-state diffusion coefficient for each contact setup [80]. For migrating contact, this was $12.4 \times 10^{-10} \text{ m}^2/\text{s}$, while Gemini contact had a coefficient value of $7.51 \times 10^{-10} \text{ m}^2/\text{s}$. Both of these values are close to reported coefficients in previous studies of pAam hydrogel poroelasticity, which had a diffusion constant of $5 \times 10^{-10} \text{ m}^2/\text{s}$ [79]. This, as well as the variation in time constant magnitude with initial contact radius, proves that poroelastic squeeze-out was the primary driver of the contact area expansion. This aligns with previous studies that have shown a low degree of viscoelastic relaxation versus poroelastic relaxation [84]. It should be noted that the maximum pressure of any single creep experiment on this composition was 1.8 kPa, while the osmotic pressure of a

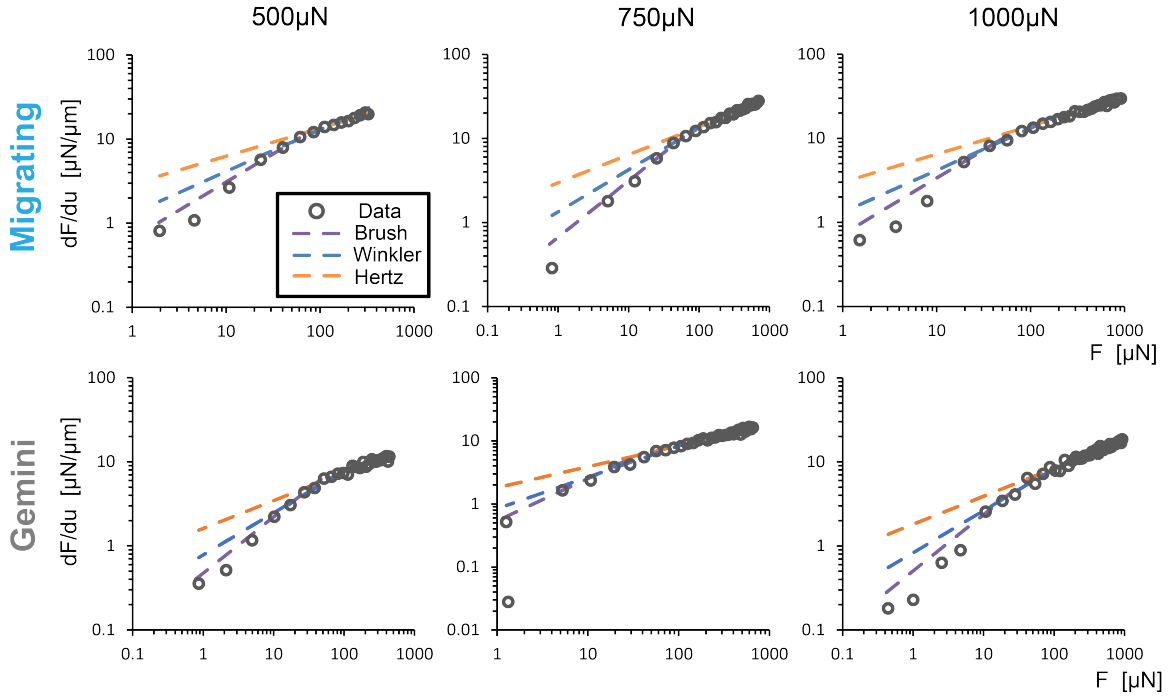


Figure 14: Indentations at all three maximum loads of $[500, 750, 1000] \mu\text{N}$ for migrating contact (top row) and Gemini contact (bottom row) setups. The dashed purple line corresponds to brush contact model. In dashed blue is the Winkler contact model, and in dashed orange is the Hertzian contact model.

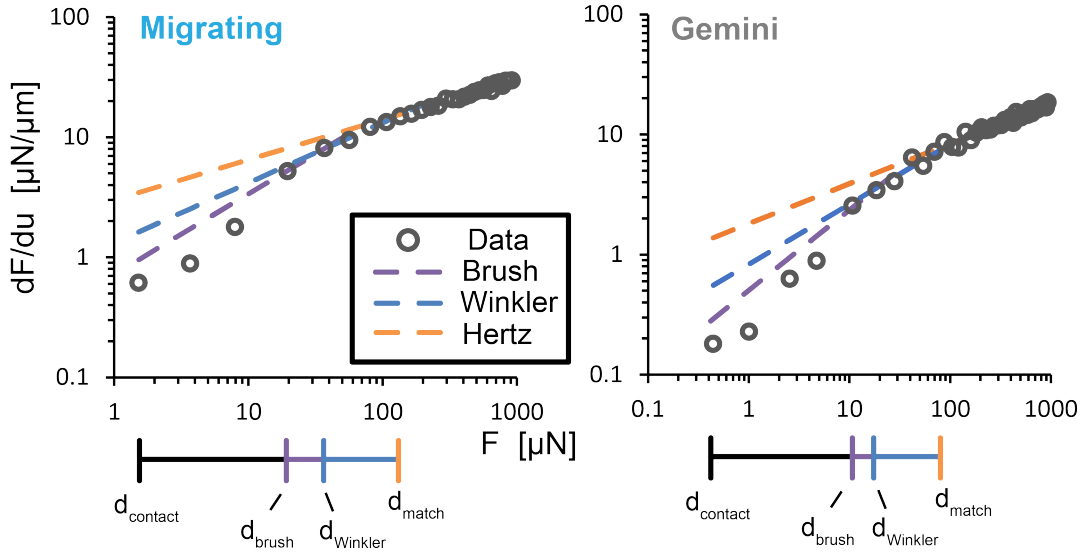


Figure 15: Indentations at peak loads of $1000\mu\text{N}$ for migrating contact and Gemini contact setups. The dashed purple line corresponds to brush contact model. In dashed blue is the Winkler contact model, and in dashed orange is the Hertzian contact model. The data corresponding to each model is marked on the bottom line, with demarcations for transitions between models. The distance spanned by the entire line, from d_{contact} to d_{match} , is equal to the gradient layer thickness Δd .

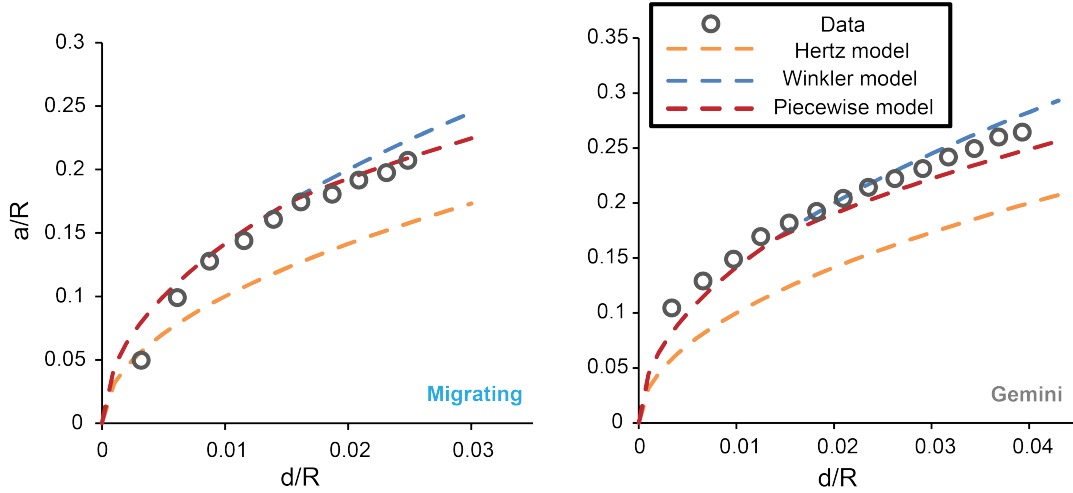


Figure 16: Compatibility plot of a/R vs d/R for both indentations of figure 15. In dashed blue is the predicted compatibility relationship solely using a Winkler model. In dashed orange is the predicted compatibility solely using a Hertzian contact model. The red dashed line is an analytic prediction using a Winkler model for the probe displacement spanning Δd , and a Hertzian model afterwards. This validates the need for multiple contact models to fully describe the contact.

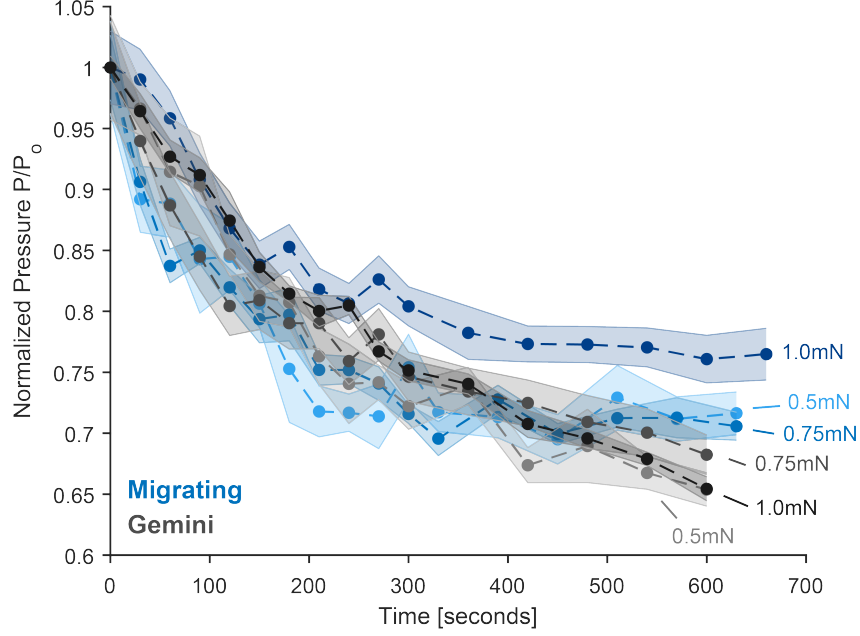


Figure 17: Pressure vs time for both migrating contact (blue) and Gemini contact (grey) setups. Pressure drops more substantially in lightly loaded contacts.

well-crosslinked hydrogel of the same composition has been reported to be 11 kPa [86, 90]. This discrepancy is explained by the dilute nature of the gradient layer, which is composed of dangling chains holding water that is easily displaced. As such, the gradient layer has a far lower osmotic pressure that allows poroelastic squeeze-out to occur even at pressures less than 10% of the reported osmotic pressure. The graded nature of the surface is expected to have varying osmotic pressure through its thickness, as the 'pore size' is inversely related to the degree of crosslinking [66], allowing poroelastic behavior to manifest within the gradient layer.

3.6 Conclusions

Through indentation experiments, we have demonstrated that Gombert and Meier's prediction of a gradient surface layer for these hydrogels molded against polystyrene is true [74, 75]. More than that, we show that this gradient layer alters the contact response such that it can only be described by using different contact models with increasing depth: initial

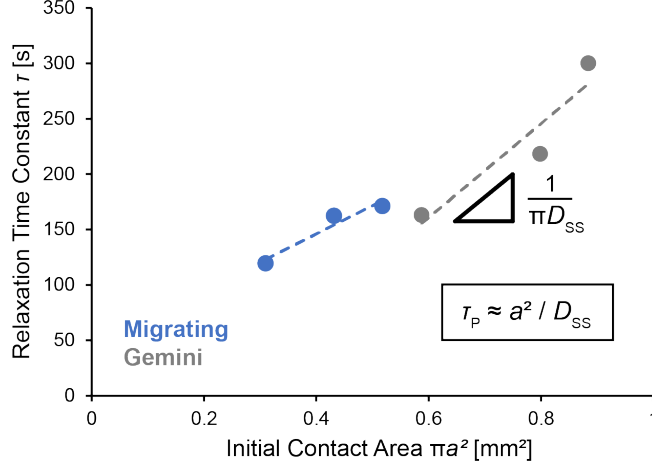


Figure 18: Time constants obtained from fitting exponential models (see Section 3.3.2) for both migrating and Gemini contact. In both contact setups, the associated time constant of relaxation differed based on the applied load. Steady-state diffusion coefficients were calculated from the inverse of the slope created by the varying time constants.

contact is controlled by fluid squeeze-out and pressurization, followed by brush-like contact, then Winkler contact, and finally Hertzian contact at sufficient indentation depths. The accuracy of these contact model fits reinforces the notion of an evolving polymer structure at the interface as the probe pushes into the substrate. The contact is first controlled by water squeeze-out from the sparse chains at the surface, followed by contact with those chains resembling deep polymer brush contact. Further compression of these polymer segments induces a "bed of springs" response, where the compressed chains do not yet interact with neighboring chains. Eventually, the chains are compressed to the point that their response emulates that of the well-crosslinked bulk. While Hertzian contact mechanics has an upper limit on viability based on substrate thickness and probe size, these findings establish a lower limit on the applicability of Hertzian contact for hydrogels possessing a significant graded surface layer. Consideration of brush-type and Winkler-type contact must additionally be accounted for in order to accurately predict the contact behavior of the interface. However, it should be noted that we were unable to decisively determine appropriate contact models for all portions of the gradient layer thickness Δd . In the work by Williams, it is expected that the low-penetration and high-penetration brush models should intersect at a transi-

tion point [47]. Our data shows no obvious transition, with power-law fits in the region between $d_{contact}$ and d_{brush} that exceed $F d^3$. While we propose the reason behind this large force-depth relationship to be caused by fluid pressurization, we lack the data to conclude this. Future work could potentially solve this question by using faster acquisition or quicker imaging techniques.

Creep experiments showed that the dilute nature of the gradient layer allows it to poroelastically exude water under pressures as low as 7% of the osmotic pressure of the bulk. As the osmotic pressure is inversely proportional to the mesh size, this provides further evidence supporting the graded nature of the surface layer, with a gradually increasing "pore" size towards the edge of the hydrogel. The advent of poroelastic-dominated relaxation within the gradient layer may be surprising considering the higher degree of viscoelasticity observed in comparatively dilute hydrogels [57]. But compared to their uniform hydrogels, the strain applied to our graded hydrogels is not well-distributed, as the more compliant surface layer will preferentially stretch to accommodate the pressure within itself compared to the bulk structure. When this compression is combined with the time-dependent relaxation of applied pressure through the network, the locally increased pressure can lead to water exudation from the gradient layer. Use of embedded particles in a hydrogel to monitor the strain within the gradient layer under load could be used to prove this conclusively. However, one would require a very efficient equipment setup to scan confocal volumes at a rate faster than the rate of relaxation.

CHAPTER 4

LUBRICATION OF GRADIENT-LAYERED HYDROGELS

4.1 Motivation

Section 1.2 discussed how hydrogels are used for research and industrial purposes involving dynamic contact conditions such as sliding. A significant portion of this research is focused on interfacing with biological tissues with minimal frictional shear [8, 26, 27, 28, 29, 31, 32, 33, 34, 35, 36, 10, 37]. As such, the ability to tune a hydrogel system to achieve the greatest possible lubricity is a necessary step towards the design of better-performing hydrogel interfaces. While chapter 3 uncovered the structure of the gradient layer and its evolving contact response under stationary conditions, we now look at how those aspects affect lubrication for a contact in motion. In this chapter, we apply similar techniques to observe contact area and friction throughout sliding experiments at various speeds. The dependence of friction on contact area will reveal more information on how the gradient layer affects energy dissipation in the contact over a prolonged period of time.

As we discovered in section 3.4, the gradient layer is comprised of a polymer structure that evolves with depth, consisting of dangling polymer chains at the outermost extent of the surface and gradually increasing polymer and crosslinking density towards the bulk. This structure retains water that is easily squeezed out under an applied pressure, allowing poroelastic relaxation to occur at pressures as low as 7% of the bulk osmotic pressure (section 3.5) [86]. Due to the comparatively dilute nature of the gradient layer, we hypothesize that the higher concentration of water within the contact zone will decrease polymer chain interactions and lower friction. This may be the reason why ultra-lubricity has only been observed thus far in hydrogels polymerized in polystyrene molds [2, 66].

In this chapter, we utilized our PEM method while monitoring friction to observe how the

gradient layer performed under sustained sliding. These independent measurements revealed that both the pressure and friction in the contact are consistent over time except in extreme Gemini cases involving persistent low-speed contact. Furthermore, we found that, unlike many soft material contacts, friction was not correlated with the contact area. Instead, friction was highly dependent on the sliding speed, showing that the water lubrication at the interface is a more prominent contributor to shear than the interaction of the polymer chains. These findings are an important step for designing hydrogels for optimal lubricity in contact conditions such as contact lenses or cartilage surrogates.

4.2 Methods

Sliding experiments were conducted on composition 3 hydrogels (Table 1) using the same microtribometer and confocal microscope setup described in section 2.3.1. The reciprocating stage was translated at sliding speeds of $[10, 30, 100] \mu\text{m/s}$ for 600 seconds, which corresponded to $[2, 6, 20]$ sliding cycles, respectively. These speeds were chosen to stay within the low-friction "fluctuation lubrication" observed in Gemini experiments by Pitenis/Uruena [2, 66]. Instantaneous friction coefficient was calculated by dividing the frictional force readout by the normal force readout. This created a 'friction loop' for each reciprocating cycle (see Figure 19). A cycle-average friction coefficient was calculated using 70% of the friction 'loop' data, measured from the center of the stroke length. This covered all free-sliding portions of the cycle while excluding measurements involving substrate shear deformation instead of sliding between the probe and gel substrate. Contact area acquisition and measurements were conducted using techniques from section 2.3.2. In particular, we made heavy use of the "flow map" technique, averaging across portions of a stroke length, to construct average contact profiles over an interval of time. This interval corresponded to 15-75 seconds of sliding: for example, at a sliding speed of $10\mu\text{m/s}$, stroke lengths were cut in half and averaged over each half. But faster speeds used the entire stroke length for averaging.

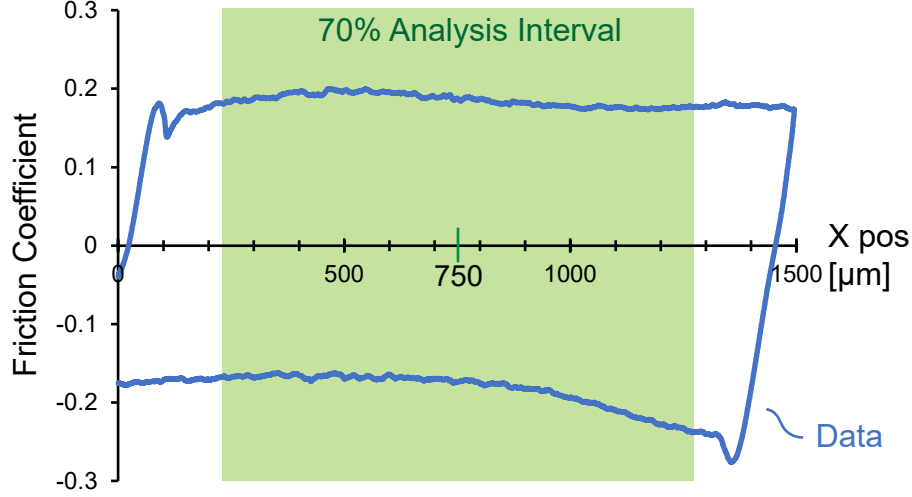


Figure 19: Example of a friction 'loop' obtained from data of friction coefficient vs horizontal stage position in a sliding experiment. The green shaded region corresponds to the analysis region, measured from the half-stroke length of $750\mu\text{m}$.

Pressure was calculated for each of these contact area measurements by dividing the average force of each stroke length interval by the measured area. For experiments conducted at $10\mu\text{m/s}$, friction coefficient was calculated over each of these intervals instead of using the aforementioned cycle averages.

Sliding experiments were conducted on portions of the hydrogel substrate at least 2mm from each other. The hydrogel substrate was allowed to equilibrate over ten minutes in-between experiments. For migrating contact experiments, the probe was gently cleaned with DI water in between experiments. For Gemini contact, the hydrogel probe was cleaned with DI water and submerged for ten minutes in-between each experiment.

4.3 Results

Using the aforementioned PEM technique, we observed asymmetric contact areas during each of the sliding experiments. During the first reciprocating cycle, contact areas were least symmetric with a truncated trailing-edge contact border of higher radius of curvature (Figure 20). The symmetry of the contact area increased rapidly with both the number of cycles and

sliding speed. At speeds of 30 and 100 $\mu\text{m/s}$, contact asymmetry was visually apparent only within the first reciprocating cycle, suggesting that the asymmetry is related to contact aging or 'run-in'. Similar contact asymmetry has been shown to occur in dilute pAam compositions of $M = 3.75\%$ and $R = 25$ [57]. McGhee suggested that the asymmetry observed in the dilute hydrogel was a result of increased viscoelasticity in a high water content hydrogel. Similar contact asymmetry has been observed in PDMS sliding [53] and cartilage sliding tests [96] and was found to occur due to a compressive buildup at the leading edge and a resulting tensile zone at the trailing edge. Observing this contact asymmetry phenomenon in our composition 3 gels of 7.5% monomer concentration further supports the presence and dilute nature of the gradient layer. However, we observed a lack of consistently asymmetric contact areas at higher speeds where it should be more pronounced [97, 39]. Additionally, results from section 3.5, where the gradient layer dominated the area expansion, suggest that the gradient layer does not behave in a viscoelastic-dominated fashion.

The creep of the contact areas under an indenting probe was demonstrated in section 3.5, where increasing contact area corresponded to decreasing contact pressure because the load was held constant. The contact area evolution in sliding conditions did not follow the creep behavior - relaxation in the contact was suppressed by any degree of sliding. For both migrating and Gemini contact, the contact area remained constant over time for each experiment, manifesting as consistent contact pressure over time ($\pm 4\%$) (Figure 21). This allowed us to calculate a single average contact pressure for each experiment. The magnitude of this average contact pressure increased as the sliding speed increased due to shrinkage of the contact area. However, these average contact pressures were a few percent smaller than the initial creep contact pressures (see table 3). In migrating contact, the steady-state contact area was nearly the same across the three tested speeds, which implies that contact area and contact pressure are either insensitive or independent of the sliding speed. This was not true for Gemini contact, which exhibited greater speed dependence on the contact pressure.

Sliding friction was highly dependent on speed and contact configuration. Slower sliding speeds experienced comparatively larger contact areas and larger friction coefficients (Figure 22). For an order of magnitude decrease in the sliding speed, the contact area increased by 15% at most, but the friction increased by as much as 400%. It was therefore clear for both contact configurations that sliding speed was the critical predictor of the friction. Friction in the migrating contact setup quickly reached steady state within a single reciprocating cycle. Higher friction during the first pass may occur from the hard probe orienting dangling polymer chains into less interactive positions. For Gemini contact, friction coefficient at $30\mu\text{m/s}$ and $100\mu\text{m/s}$ sliding speeds experienced stable friction coefficients after the first full cycle. Friction increased over time for the $10\mu\text{m/s}$ sliding speed, doubling in magnitude over the course of each experiment. This transient behavior was exclusive to the slowest sliding speed. In Gemini experiments, water exuded by both the probe and contacting substrate is allowed to move in all directions instead of being forced into the lubricating fluid film against an impermeable probe. This may reduce hydrodynamic lubrication and increase probe-substrate interactions, increasing friction. A direct comparison of friction between the two configurations shows that, for a given load and sliding speed, the Gemini configuration experienced higher friction (Figure 23). This suggests a larger interaction between the polymer surfaces in Gemini contact, which Gong’s adsorption-repulsion model predicts higher friction for [59, 73].

For the other sliding experiments, the consistency of the friction coefficient over time suggests that the contact patch is able to either retain water or quickly rehydrate itself through some mechanism(s). In section 3.5, we showed how poroelastic relaxation occurs within the gradient layer. Despite this, we saw no indication of poroelastic dwell-induced friction for almost all of the experiments (except $10\mu\text{m/s}$ Gemini). Gemini contact experiments conducted at 6 kPa with ‘brushy’ 10% pAam by Simic et al led them to conclude that rapid rehydration occurs during the period of time that the substrate is out of contact [98]. Their sliding speeds were as high as 15mm/s across a 10mm stroke length, implying that the rehy-

dration process must take place within fractions of a second even at their large pressures and sliding speeds. Experiments by Gombert et al with ‘brushy’ 7.5% pAam gels found friction to be speed-independent for speeds up to 10.5 mm/s [75]. They posit the presence of a resilient water layer held by the dangling chains at the less-crosslinked surface, and suggest that this rapidly rehydrating layer is primarily responsible for the tribological properties of the hydrogel. In our sliding experiments, the stroke length was $1500\mu\text{m}$, while contact radii were at least $600\mu\text{m}$. A sliding speed of $100\mu\text{m/s}$ would give the center of the substrate track 3 seconds to rehydrate in time for the next pass. This brief period of time out of contact appears sufficient to recapture the exuded water back into the dangling polymer segments forming the ‘brushy’ layer, restoring its lubricity. The resulting non-transient friction behavior for the faster sliding speeds supports this notion of sufficient rehydration of the less-dense surface layer occurring on the order of seconds. Such behavior may be possible due to the preference for dangling pAam segments within the layer to swell in a good solvent instead of piling up against each other.

The transient friction for the Gemini $10\mu\text{m/s}$ experiments may be due to sustained drainage of water from both the hydrogel substrate and hydrogel probe. Reale et al found that water squeeze-out from a hydrogel substrate by a rigid probe will increase startup friction due to osmotic suction arising from dehydration [99]. Similar dehydration-induced adhesion has also been observed in indentation experiments conducted by Lai et al [81]. Rotational sliding of a hydrogel ring on a hydrogel disk has also shown transient friction even in a self-mated ‘brushy’ contact setup [100]. In the Gemini $10\mu\text{m/s}$ experiment, a typical contact diameter during sliding was $1,250\mu\text{m}$. Because the stroke length was only $1500\mu\text{m}$, the central portions of the track are in contact for as much as 125 seconds of each 150 second stroke length. This likely led to extensive dehydration that could not be fully reversed in the 25 second out-of-contact interval. However, we must also consider the dehydration of the hydrogel probe to explain the transient behavior. In Gemini contact, the hydrogel probe is always under pressure throughout each experiment. Due to the slow sliding speed and long

duration of contact, extensive poroelastic relaxation within the probe would cause higher friction from osmotic suction as Reale described. Relaxation in the probe may be the key differentiator causing the drastic friction increase in the Gemini contact but not the migrating case. Relaxation in both the probe and substrate may be required for transient friction behavior, since we did not see transient friction in the faster Gemini experiments conducted at 30 and 100 $\mu\text{m/s}$. This may be due to 'tribologically-induced rehydration', where the porous medium is able to recapture water without unloading the contact [96, 101, 102]. Alternatively, due to the Gemini nature of the contact, adequate hydration of the probe may be sustained via water from the squeeze-out-induced fluid film moving into the probe.

The exact mechanisms by which faster sliding speeds affect the polymer structure to reduce friction is not yet known, but recent studies on polyacrylamide shear mechanics provide some hints. The lower coefficients of friction for faster sliding speeds may be due to floc-like behavior of the less-dense hydrogel surface. Flocculation, which is clumping of polymer elements in a melt, tends to break down as the shear rate is increased. Such behavior has been well-fitted to hydrogels through rheological testing [103, 61]. Furthermore, work by Gombert et al suggests that the hydrogel network does not resemble that of a fishing net or lattice, but rather some highly-linked bisacrylamide clusters connected by a few bridging chains [55]. Taken together, this characterizes the less-dense hydrogel surface as a collection of bisacrylamide "flocs", which then 'de-floc' as the sliding speed is increased. However, additional in-depth experiments and imaging would be required to verify these explanations.

4.4 Conclusions

In this chapter, we confirmed the presence of the less-dense, less-crosslinked surface layer of our hydrogels, and showed how their high lubricity is primarily dependent on sliding speed. Unlike the creep experiments of chapter 3, contact pressure over time was consistent for all experiments, with any degree of sliding suppressing contact expansion. Migrating

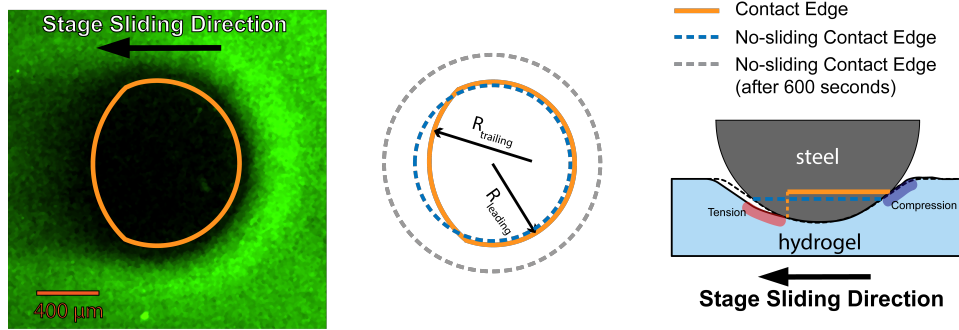


Figure 20: Asymmetric contact areas were observed in low sliding speed migrating contact experiments. This behavior is made possible due to the increased compliance and viscoelasticity of the less-dense gradient surface layer.

Contact Setup	Normal Load [μN]	Initial Creep Pressure [kPa]	Sliding Pressure $10\mu\text{m/s}$ [kPa]	Sliding Pressure $30\mu\text{m/s}$ [kPa]	Sliding Pressure $100\mu\text{m/s}$ [kPa]
Migrating	500	1.53	1.34 (-12%)	1.41 (-8%)	1.57 (+3%)
Migrating	750	1.74	1.62 (-7%)	1.59 (-9%)	1.65 (-5%)
Migrating	1000	1.83	1.80 (-2%)	1.88 (+3%)	1.92 (+5%)
Gemini	500	0.79	0.77 (-3%)	0.79 (+0%)	0.76 (-4%)
Gemini	750	0.94	0.81 (-14%)	0.87 (-7%)	0.94 (+0%)
Gemini	1000	1.15	0.93 (-19%)	0.99 (-14%)	1.04 (-10%)

Table 3: Contact areas of each sliding experiment could be consolidated to produce an average contact pressure across the entirety of each experiment. These pressures were generally smaller than the corresponding initial creep pressure, with their percent increase compared to the initial creep pressure shown in parentheses.

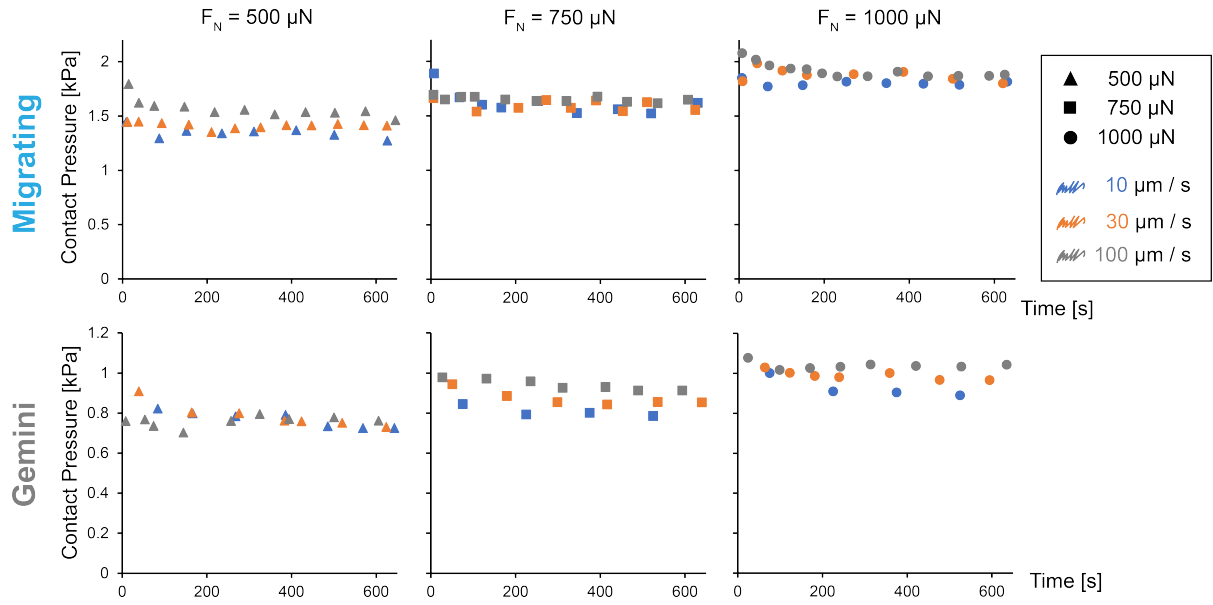


Figure 21: Sliding pressure versus time for applied normal loads of $[500,750,1000]\mu\text{N}$ at sliding speeds of $[10,30,100]\mu\text{m/s}$. Pressure is consistent over time for all experiments.

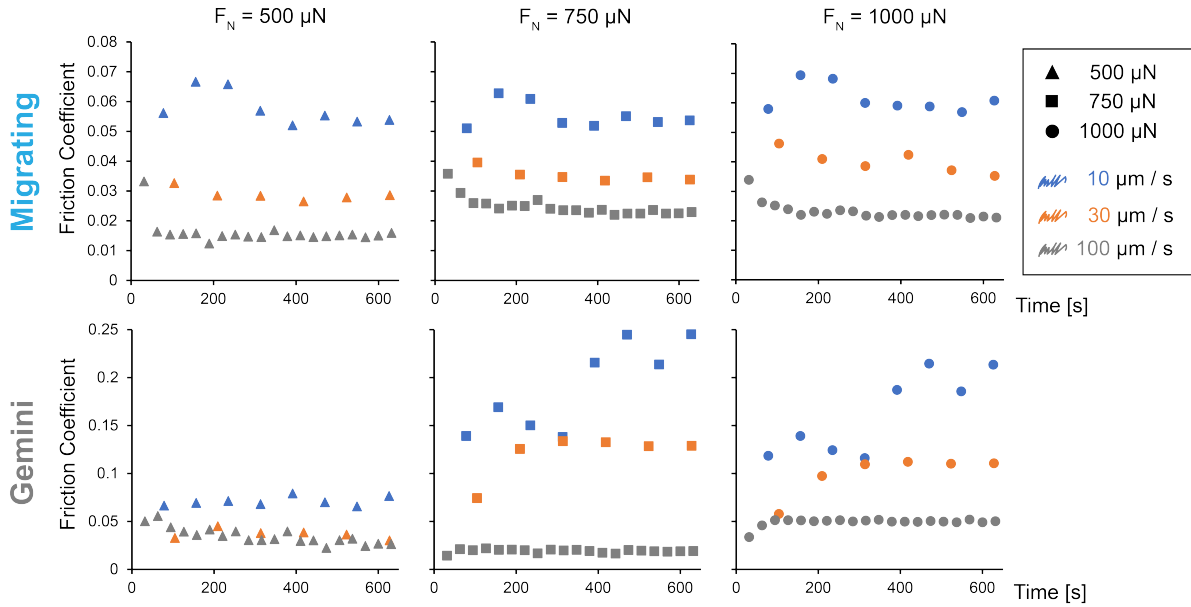


Figure 22: Friction coefficient versus time for applied normal loads of $[500,750,1000]\mu\text{N}$ at sliding speeds of $[10,30,100]\mu\text{m/s}$. Friction is consistent over time for all experiments except for Gemini experiments at the slowest sliding speed of $10\mu\text{m/s}$.

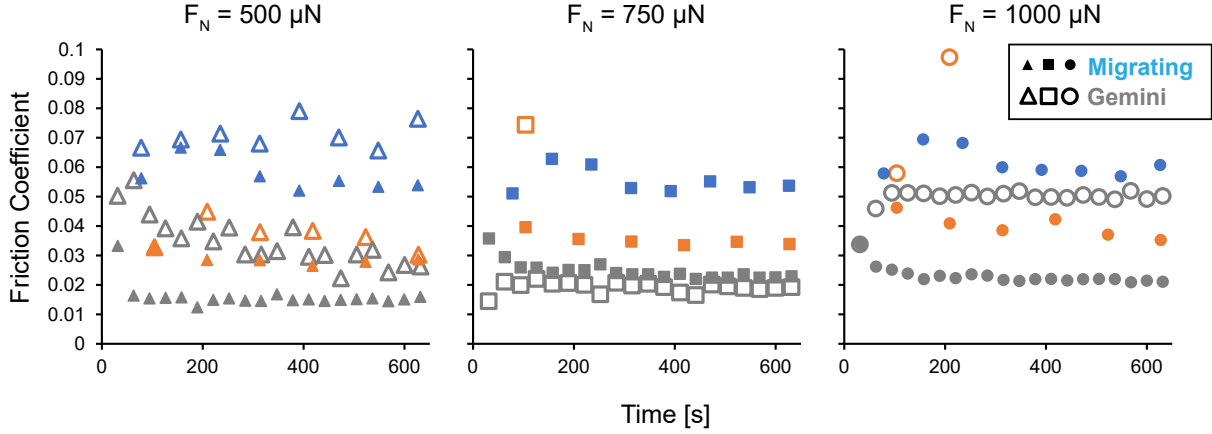


Figure 23: Friction coefficient versus time for an applied normal loads of $750 \mu\text{N}$ at sliding speeds of $[10, 30, 100] \mu\text{m/s}$. Both contact setups are shown, with migrating in blue and Gemini in black. For a given load and speed, friction was larger in Gemini contact setups.

contact saw near-identical contact areas, suggesting that **the contact area is insensitive or independent of the sliding speed**. Gemini contact saw a slight area decrease of up to -15% for faster sliding speeds. However, in both contact setups, we observed drastically larger friction coefficients for slower sliding speeds. A change in contact pressure due to a change in normal load resulted in similar friction, while a change in the sliding speed at a given load resulted in a 2-4x change in the friction. This shows that **the friction of these graded hydrogels is essentially independent of the contact area and contact pressure, but is dominated by the sliding speed**. Thus, optimal lubrication in the contact is heavily dependent on a fluid barrier film sufficiently separating the probe from the gradient layer polymer chains. We also demonstrated that the 'brushy' gradient layer, despite experiencing poroelastic water squeeze-out at low pressures, is capable of rapid rehydration when out of contact in order to maintain lubricious conditions over long periods of time. However, the exact timescale over which the contact is able to rehydrate is not yet known. Experiments involving fluorescent solution could elucidate the required out-of-contact time for a substrate to rehydrate to optimal conditions.

CHAPTER 5

COMPOSITIONAL EFFECTS ON GRADED HYDROGEL MECHANICS AND LUBRICATION

5.1 Motivation

Thus far, we have discovered that the graded hydrogel experiences an evolving contact model that suggests a 'brushy' structure of increasing density towards the bulk (section 3.4). It was also shown that this structure allows poroelastic relaxation at pressures far below the osmotic pressure of squeeze-out for the bulk (section 3.5), and this also improves lubricity by providing a readily-available fluid boundary layer for hydrodynamic lubrication of the contact (section 4.3). However, these findings have been specific to a single hydrogel composition (composition 3) of a specific gradient layer thickness. In many applications, a hydrogel of a larger or smaller elastic modulus may be desirable, which could impact the thickness of the gradient layer, its structure, and its lubricity. In section 1.1, we provided examples of other chemically-crosslinked hydrogel systems, novel hydrogel formulations including multiple interpenetrating networks, and hydrogels with charge variations. For these reasons, the ability to generalize the effects imparted by the gradient layer, for a gradient layer of arbitrary thickness atop a bulk network of arbitrary stiffness, would be ideal. To this end, we assess variations in monomer and crosslinker within the polyacrylamide system, which we know to have major effects on the resulting mechanical and tribological behavior of the system (section 2.2).

In this chapter, we utilized five pAam hydrogel compositions: three compositions spanning variations in the monomer percent M with a fixed monomer-to-crosslinker ratio R , and three compositions with different monomer-to-crosslinker ratios R but identical values of monomer percent M (see table 1). We conducted the same sets of experiments performed in chapters 3 and 4 on each composition, discovering that the gradient layer thickness is highly

dependent on each compositional metric: softer compositions generally had larger gradient layer thicknesses. This influenced the lubrication afforded by the gradient layer, with the larger gradient layers of the compliant compositions producing a highly lubricated state that was less dependent on the applied load or sliding speed. The variation in the gradient layer thickness and the behavior of the gradient layer thickness compared to the modulus of the bulk polymer has implications in the design of consistent lubricated hydrogel interfaces.

5.2 Methods

Five different hydrogel compositions were created using the procedures of section 2.2. These compositions spanned three different monomer percents M with a fixed monomer-to-crosslinker ratio of $R = 25$, and three different monomer-to-crosslinker ratios R for a fixed monomer percent of $M = 7.5\%$ (see section 2.2 and table 1).

5.2.1 Indentation & creep experiment methods

Indentation experiments were conducted on each composition at up to three maximum normal loads using the same techniques as in section 3.2. The magnitude of these loads depended on the composition (see table 4). These normal loads were chosen in order to capture areas that were large enough to reduce area measurement error, which increases with decreasing contact widths, but small enough to fit the $2 \times 2 \text{ mm}^2$ microscope viewport. Indentations were repeated at least three times. Analysis of the indentation data was performed using the Garcia method (section 3.2.2). Creep experiments were performed on each composition using the methods from section 3.3. Three normal loads were held for at least 600 seconds. The normal load magnitudes applied to each composition are the same normal loads listed in table 4. Time constants were determined using relaxation theory and exponential fitting as was done in chapter 3. Contact areas were measured throughout each indentation and creep experiment using the PEM technique.

Comp #	Min Load [μN]	Intermediate Load [μN]	Max Load [μN]
1 (R250)	100	300	500
2 (M5)	100	300	500
3 (M7.5,R25)	500	750	1000
4 (M15)	1000	2000	2500
5 (R15)	500	750	1000

Table 4: Composition number and the experimental loads tested for each composition. Indentation, creep and sliding experiments were conducted at each of the listed normal loads for each composition.

5.2.2 Sliding experiment methods

Sliding experiments were conducted on each of the hydrogel compositions at the normal loads listed in table 4. For each of the three normal loads, sliding speeds of $[10,30,100]\mu\text{m/s}$ were applied for 600 seconds, corresponding to $[2,6,20]$ reciprocating cycles. Contact area projections using our PEM technique were measured from videos of each experiment by using z-stack image averaging across stroke lengths; the process is described in section 2.4.

Results from experiments at the initial three speeds above, along with results shown in section 4.3, show that the contact pressure and friction coefficient are stable over time. This made it possible to calculate average values for the contact pressure and friction coefficient. Moving forward, average values of normal pressure and friction coefficient (averaged across all cycles) are reported for each sliding condition. This averaging allowed calculation of a characteristic contact shear stress σ , which is calculated as the product of the average friction coefficient and the average normal pressure P , using the definition of the friction coefficient (see Equations 5.1 and 5.2). Thus, each sliding experiment produced one contact shear stress value. In order to obtain stronger support for any potential trends, we conducted additional sliding experiments in a migrating contact setup for up to 180 seconds at sliding speeds of $[5,7,500,1000]\mu\text{m/s}$ at the three normal loads in table 4. This produced average friction and pressure values for three loads, each completed at sliding speeds of $[5,7,10,30,100,500,1000]\mu\text{m/s}$, which spans the entire low-friction "fluctuation lubrication"

scheme described by Pitenis et al and Urueña et al [64, 2, 66].

$$\mu = \frac{F_f}{F_n} = \frac{F_f}{A} / \frac{F_n}{A} = \frac{\sigma}{P} \quad (5.1)$$

$$\sigma = P\mu \quad (5.2)$$

The contact shear stress represents the overall shear stress state of the contact, which is a more comprehensive measure of the frictional response in soft materials that is less affected by surface inhomogeneities compared to normal pressure or friction coefficient alone. Some researchers already question the validity of exclusively relying on friction coefficient to represent shear in complex soft materials, since sliding interfaces involving these materials very often violate many of the initial assumptions that formed Amontons-Coulomb frictional laws [104, 105, 99, 63]. In order to consolidate the frictional stress behavior with respect to both sliding speed and normal load, we further define a parameter called the ‘pseudo-Sommerfeld’ parameter. This parameter is calculated as the experiment sliding speed divided by the prescribed normal load, v/F_n . We then graph each sliding experiment on a log-log plot of the contact shear stress σ versus the pseudo-Sommerfeld parameter. We utilize a log-log plot, as both the Stribeck curve (section 1.6, figure 2) and previous Gemini pAam experiments suggest power law responses to describe particular lubrication regimes [2, 66, 63].

5.3 Indentation & Creep Results

5.3.1 Indentation Results

Indentations at the maximum load conducted on each composition (table 4) are shown in figures 24 and 25, plotted using the Garcia method on log-log axes. We first calculated elastic moduli for each composition from the indentation data. This was done using the Garcia analysis method’s K coefficient (see section 3.2.2), which was found using a single-

parameter least-squares fitting of a Hertzian contact model to the high-displacement data. From experiments in chapter 3 and previous research on pAam hydrogels, it is known that a 'neat' fully-crosslinked hydrogel follows Hertzian contact [92, 79, 77, 66]. The resulting elastic moduli are listed in table 5. The total polymer concentration M had a larger affect on the elastic modulus compared to the crosslinker ratio R . In fact, the effect of increasing crosslinker concentration (decreasing R) appears to have diminishing returns: a 67% increase in the available crosslinker increased the modulus by only 19%, while a 90% reduction in crosslinker reduced the modulus by 92%. This suggests that crosslinking is potentially inhibited by self-linking of the bisacrylamide, which has been predicted to be the polymer structure for high concentrations of crosslinker [55].

After fitting the Hertzian regime of each indentation, we then determined regions of each indentation that corresponded to Winkler "bed-of-springs" contact (equation 1.3) or the high-penetration brush model (equation 1.4) proposed by Fredrickson [45]. In every experiment, we found portions of the indentation data that fit these models (figures 24,25), which means that changes to the composition cannot eliminate the 'brushy' layer of pAam hydrogels molded against polystyrene. This additionally shows that the progressive contact modeling of the gradient layer described in section 3.4 holds true for all compositions. Some portion of the indentation data of the stiffer compositions 3-5 (R25, M15, R15) had a higher slope as large as $n = 0.9$, which may be attributed to pressurization of water within the gradient layer that is unable to vacate the contact in time. The thickness of the gradient layer for each composition, measured as the probe depth spanned from the video derived point of first contact $d_{contact}$ and the start of the Hertz-fitting regime d_{match} , was different for each composition (table 5). For all compositions and setups, the thickness was between 10-40 μm , which is similar to the order of magnitude predicted by Simic et al [98]. For changing monomer percent M and constant ratio R (compositions 2-4), the gradient layer thickness was correlated with monomer percent M , with composition 2 having the largest gradient layer and composition 4 having the smallest. The portion of the gradient layer

corresponding to a brush or Winkler contact model was largest for composition 2 at 89%, and decreased to 67% for composition 4. Similar trends were obtained for a reduction in the monomer-to-crosslinker ratio R , where a gradient layer thickness of $43.7\mu\text{m}$ was found for composition 1 (R250) while composition 5 (R15) only had a layer thickness of $12.7\mu\text{m}$. The portion of the gradient layer that followed brush or Winkler contact modeling was 89% for composition 1 and 63% for composition 5. Thus, for all migrating contact experiments, the proportion of the Δd interval corresponding to a brush-fitting or Winkler-fitting region increased for larger gradient layer thicknesses. This also hints that both composition metrics M and R are influential on the resulting gradient layer structure.

However, the results from Gemini contact were not as predictable. While we saw larger gradient layer thicknesses perceived for compositions 3-5 compared to their migrating contact values, compositions 1 and 2 showed smaller gradient layer thicknesses. Gemini contact perceived gradient layers of $9.6\mu\text{m}$ and $4.9\mu\text{m}$ for compositions 1 and 2, respectively. The portion of each Δd thickness interval corresponding to a brush or Winkler model was 100% for both compositions; the initial brush response in composition 1 (R250) is stiffer than the bulk response (figure 25). In migrating contact, these two compositions showed thick gradient layers with a high percentage consisting of brushy behavior. This says that the response of the layer emulates that of a dilute polymer brush, with loose chains collapsing with little effect on the neighboring structure until they reach a compression that emulates the bulk response. But for Gemini contact, we see a major constriction and near-elimination of this non-Hertzian region for these two softer compositions, implying that the interaction between the identical low-density gradient layers is not dissimilar to a response from the bulk. In section 3.4, we noted that a larger portion of the contact response should resemble Hertzian contact for a number of reasons. First, widespread interaction or entanglement of surface chain segments between the probe and substrate are discouraged compared to chain collapse for energetic reasons [67, 71]. This makes the low-penetration brush contact model by Williams (equation 1.5), which is essentially Hertzian contact, a more accurate

Comp #	Elastic Modulus E (Migrating) [kPa]	Elastic Modulus E (Gemini) [kPa]	Gradient Layer Thickness Δd (Migrating) [μm]	Gradient Layer Thickness Δd (Gemini) [μm]
1 (R250)	2.42	2.84	43.7	9.6
2 (M5)	7.26	6.36	21.4	4.9
3 (M7.5,R25)	33.8	33.1	17.1	25.3
4 (M15)	169.7	153.1	13.4	17.1
5 (R15)	40.1	38.7	12.7	18.8

Table 5: Composition number and their corresponding elastic moduli determined from indentation experiments. The indentation-derived gradient layer thickness, Δd , is also listed for each contact setup.

descriptor at the onset of contact. Secondly, if the stiffness of the brush G (from equation 1.5) is close to the stiffness of the bulk polymer, then the Hertzian response at the onset of contact will blend with the Hertzian response of the bulk and constrict the apparent gradient layer thickness. Additionally, the high-penetration brush model and the Winkler model will have larger relative stiffnesses compared to the bulk stiffness, since their stiffness is related to the stiffness of the polymer chains making up the polymer 'brush' at the surface. In the case of composition 1, we do find that the brush stiffness is larger than the response generated by the bulk. This means that the captured water is primarily responsible for the rigidity of the hydrogel, which is lost when the water is exuded under pressure. Fitting low-penetration brush models to the stiffer three compositions gives a brush stiffness of 2.4 kPa for composition 3, 3.6 kPa for composition 4, and 3.8 kPa for composition 5. Despite the vast differences in bulk stiffness, the magnitude of the brush layer stiffness is similar across compositional changes. This would suggest that, while the gradient layer thicknesses of compositions 1 and 2 may be larger, the stiffness of the brush and the bulk are close enough that distinguishing them from each other is difficult.

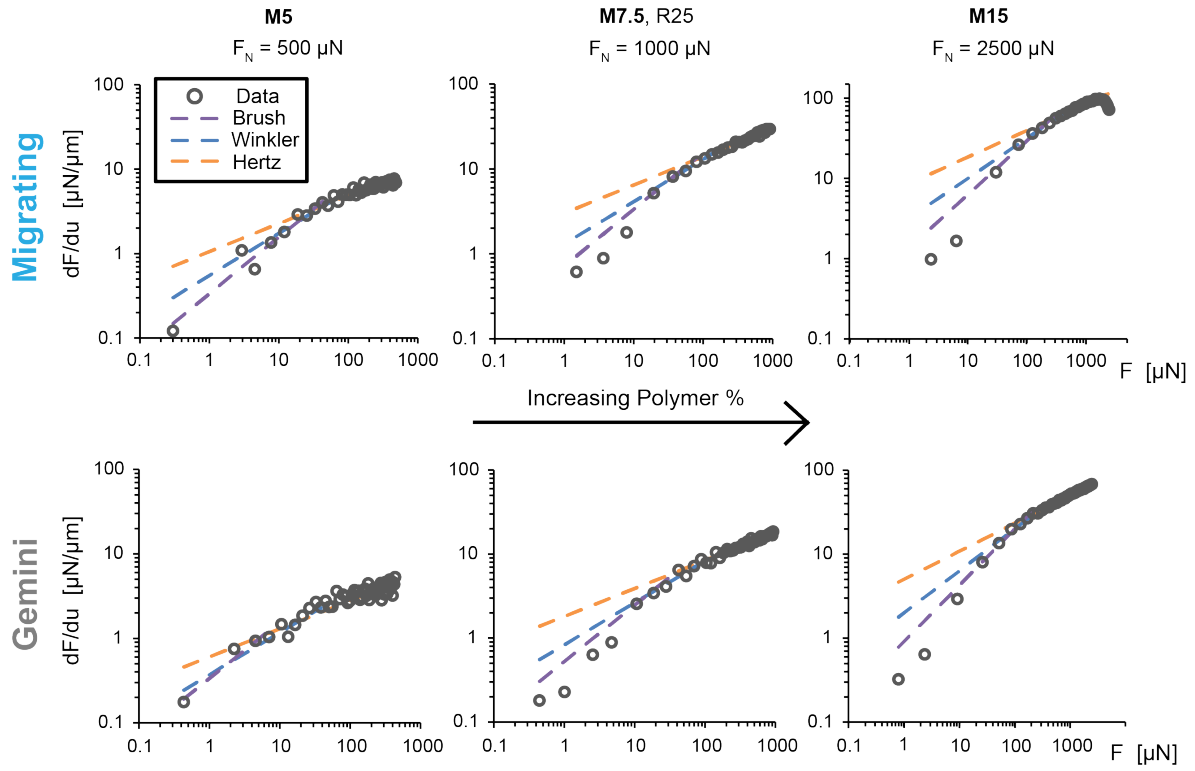


Figure 24: Max load indentations for the three compositions spanning varying total polymer percents (compositions 2-4) in a migrating contact setup. The brush model fit line is shown as a dashed purple line. The Winkler-fit line is marked in dashed blue, while the Hertz fit line is dashed orange.

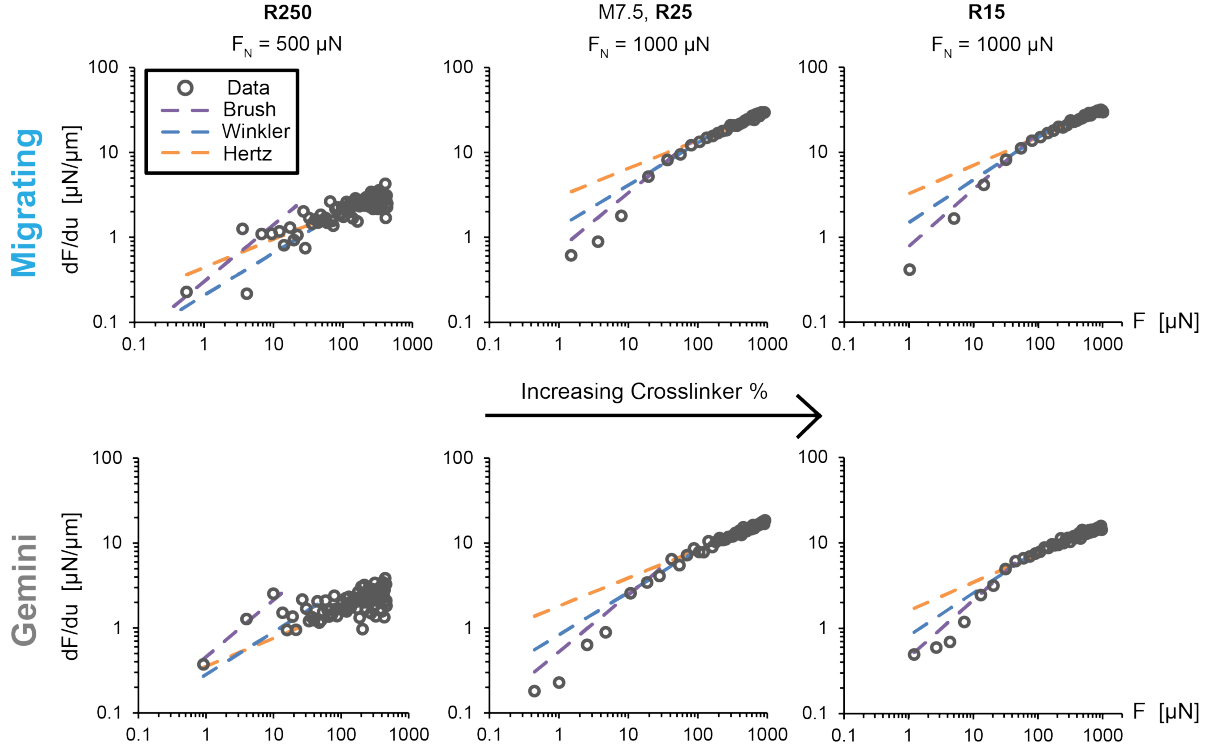


Figure 25: Max load indentations for the three compositions spanning varying monomer-to-crosslinker ratios (compositions 1,3,5) in a migrating contact setup.

5.3.2 Creep Results

Contact area expansion over time occurred for all five compositions under all loads and contact configurations. Area expansion was most rapid within the first 200 seconds, similar to the behavior previously found for composition 3 creep (section 3.5). In general, smaller loads experienced greater area growth by percentage compared to larger loads. Area expansion was larger in Gemini contact compared to the hard-probe setup. The softer two compositions (1,2) relaxed to a greater degree than the other compositions when under low loads, but saw the greatest discrepancy between low-load and high-load relaxation. Particularly in self-mated contact, we postulate that the initial probe deformation reduced the capacity for the contact to relax over time.

Single time constants were fit to the area expansion over time data (see section 3.3), from which we found that the time constants correlated with the initial contact area. This further

supports that poroelastic squeeze-out was the primary driver of the area expansion, since the time associated with contact relaxation was dependent on a length parameter (contact radius a) [79]. This was true even under exceedingly low contact pressures far below that of the osmotic pressure of the bulk [86], supporting the less-dense, less-crosslinked nature of the gradient layer. The only exception to this behavior was composition 1, which we had initially predicted to show viscoelastic-dominant behavior [85]. Composition 1, with a crosslinker ratio of $R=250$, showed consistent time constants with varying normal load / contact radius, indicative of viscoelastic-dominant relaxation behavior. This means that, while poroelastic squeeze-out was likely to also be occurring, it was not as significant of a contributor to the area expansion as the viscoelastic stress relaxation throughout the gel. Diffusion coefficients were calculated using the slope produced by the time constants. These coefficients give a measure of the relative mobility of the water within the gel, and particularly within the gradient layer. In general, the steady-state diffusion coefficient decreased for stiffer compositions i.e. for larger M and smaller R . This aligns with the results from indentation, which showed thinner gradient layers for stiffer compositions, which reduces the amount of water that can be exuded under pressures below the osmotic pressure of the bulk crosslinked structure. In composition 3, we see values 50-100% larger than those found in previous work on glass-molded pAam gels of identical chemical composition ($5 * 10^{-10} \text{ m}^2/\text{s}$) [79]; this further supports the theory of increased water mobility within the gradient layer.

5.4 Sliding Results

5.4.1 Sliding Pressure

Many of the observations noted in section 4.3 for the pressure evolution during sliding of composition 3 were also applicable to the other four compositions. Sliding experiments on compositions 2-5, regardless of contact configuration, showed little to no area expansion

Comp #	Area Expansion (min load) (Migrating) %	Area Expansion (max load) (Migrating) %	Area Expansion (min load) (Gemini) %	Area Expansion (max load) (Gemini) %
1	69.2	44.3	68.3	17.6
2	80.2	22.2	103.1	51.1
3	45.3	38.3	71.0	51.3
4	54.5	68.1	39.6	47.4
5	51.8	44.3	68.2	50.9

Table 6: Contact area expansion compared to the initial contact, for both contact configurations and for the minimum and maximum loads. Minimum loads experienced larger contact growth % compared to maximum loads.

Comp #	D_{SS} (Migrating) [10^{-10} m^2/s]	D_{SS} (Gemini) [10^{-10} m^2/s]
1	N/A	82.3
2	10.4	20.0
3	12.4	7.51
4	3.16	10.1
5	6.70	6.62

Table 7: Diffusion coefficients obtained from exponential fitting of the area relaxation of each experiment, for both contact setups. Composition 1 experienced a far greater degree of viscoelasticity compared to the other four compositions.

over the duration of each 600 second experiment (see appendix A.3 for plots). We observed asymmetric contact profiles within the first sliding cycle, particularly for the slower sliding speeds of the compliant compositions (1,2) (see Figure 20). Composition 1, with a crosslinker ratio of $R=250$, was the only composition to experience contact growth over time while sliding. Contact area rose 18% over 600 seconds when sliding at $10\mu\text{m/s}$. These hydrogels produced such large contact areas at the maximum normal load that the central portion of the stroke length was always in contact. Sustained contact leading to relaxation may be the reason that area expansion was seen even while sliding.

Because the contact pressure over the majority of experiments was consistent with time, we calculated average contact pressures for each experiment. There was a general trend across all migrating contact experiments where faster sliding speeds produced a marginally lower contact area, and therefore higher average contact pressure (figures 26 and 27). This increase was load-dependent, with larger loads showing less contact area shrinkage with increasing sliding speed. The average contact pressure was essentially constant with speed beyond a sliding speed of $10\mu\text{m/s}$ for most experiments. Gemini experiments were less consistent, with pressure generally increasing or staying constant with sliding speed based on the normal load (figures 28 and 29). Higher loads experienced increased average contact pressure with speed due to reduced relaxation producing smaller contact areas.

5.4.2 Friction

The friction experienced in each contact was highly dependent on the normal load and sliding speed, with changes in composition affecting the strength of these dependencies. Similar to the findings of section 4.3, we found that the friction coefficient of nearly all experiments reached a steady-state value within a single reciprocating sliding cycle. This allowed us to take the average friction coefficient of an entire experiment to better assess the effects of sliding speed and normal load on friction. Friction coefficients were generally

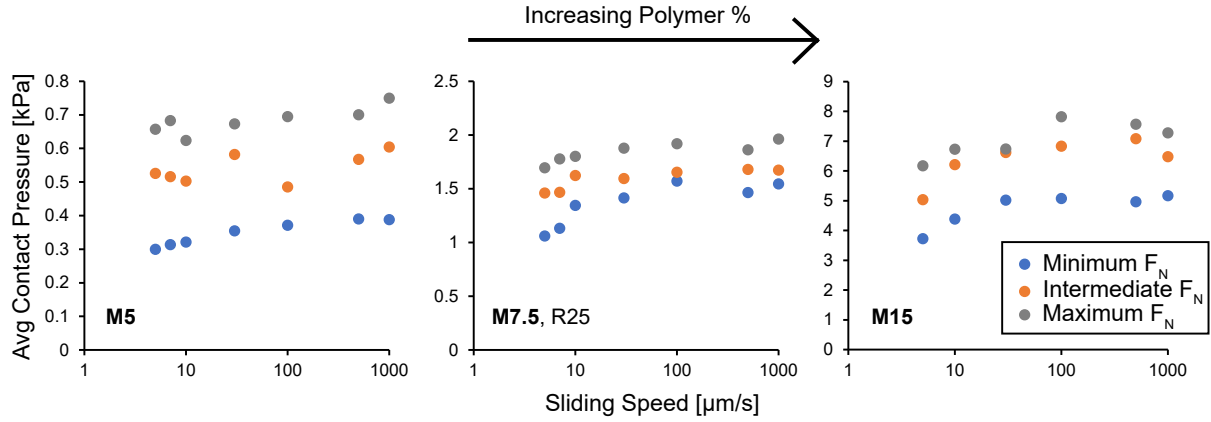


Figure 26: Average contact pressure versus the sliding speed for migrating contact setups. Shown here are compositions with varying monomer percent M (compositions 2-4). The average contact pressure is consistent above $10\mu\text{m/s}$ sliding speeds.

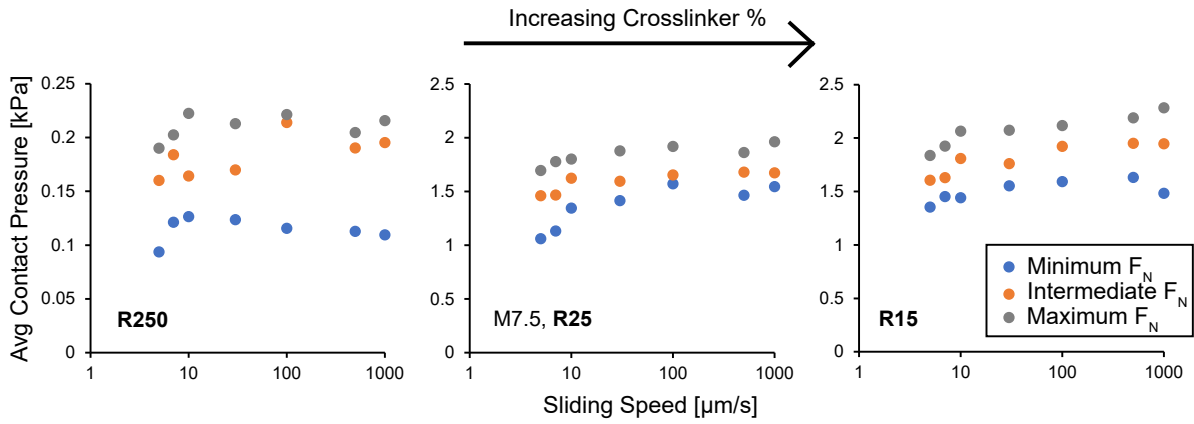


Figure 27: Average contact pressure versus the sliding speed for migrating contact setups. Shown here are compositions with varying monomer-to-crosslinker ratios R (compositions 1,3,5). The average contact pressure is consistent above $10\mu\text{m/s}$ sliding speeds.

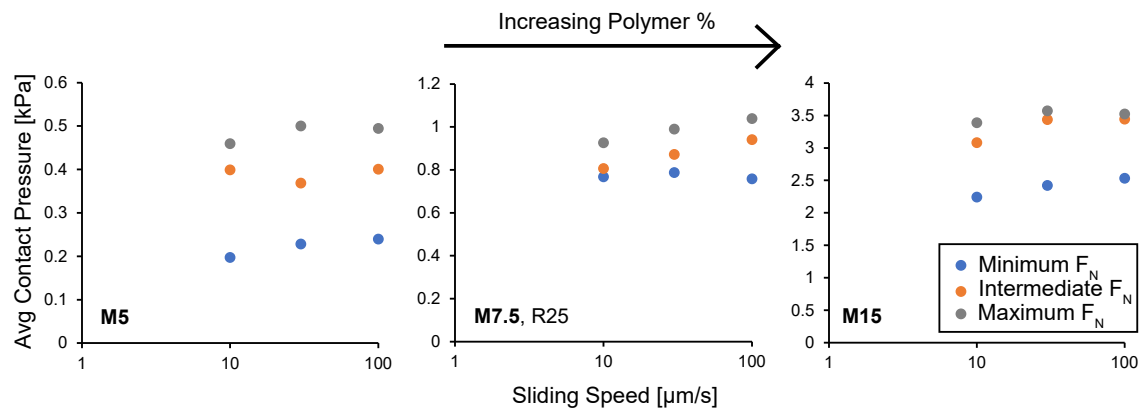


Figure 28: Average contact pressure versus the sliding speed for Gemini contact experiments. Shown here are compositions with varying monomer percent M (compositions 2-4).

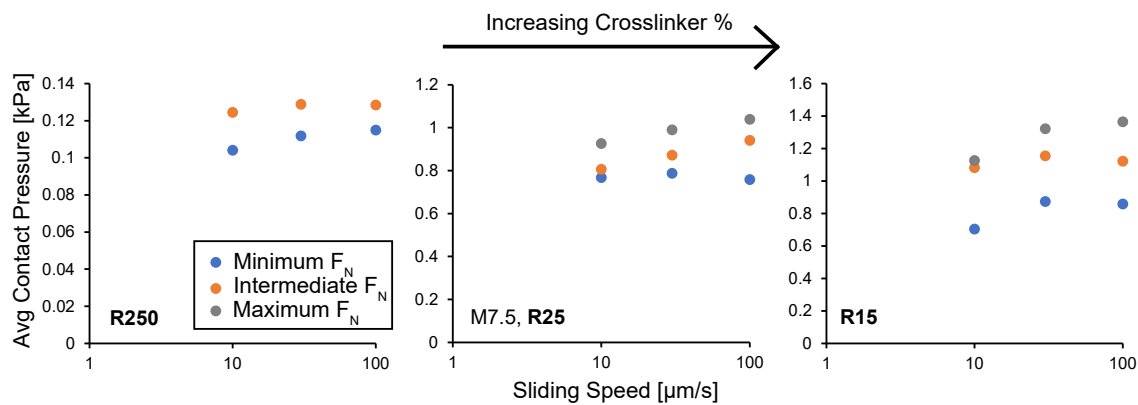


Figure 29: Average contact pressure versus the sliding speed for Gemini contact experiments. Shown here are compositions with varying monomer-to-crosslinker ratios R (compositions 1,3,5).

low, and much lower than friction values reported for 'neat' pAam hydrogels molded against glass [62, 63, 82, 100]. Shearing of polymer brush surfaces has been shown to produce very low friction coefficients [106, 107], further supporting the brush and Winkler-fit regions of the indentations.

For migrating contact, lower friction was observed for faster sliding speeds and higher normal loads (figures 30 and 31). The dependence on the friction coefficient with speed decreased for the more compliant compositions (compositions 1,2). For composition 1 (R250), there was no apparent speed dependence on the friction. For these two compositions, the normal load had a much larger influence on the friction. Counter-intuitively, it was the minimum normal force that produced the largest friction, with magnitudes two to three times higher than the friction under a higher normal force. However, composition 1 (R250) was previously found in section 5.3.2 to be viscoelastic-dominant and not poroelastic-dominant. In section 5.3.1, we also found that the brush response of the gradient layer is slightly stiffer than that of the bulk, which means that water is not readily exuded at any applied pressure. Combined with the minuscule pressure of only 0.11 kPa (from figure 27), the contact likely lacked a sufficient fluid film for hydrodynamic lubrication to occur. In compositions 2-5, which show negative frictional dependence with the speed, friction must be reduced through a reduction in polymer-probe interactions caused by faster speed or larger separation by the fluid film. In work by Kagata and Gong, they reinforced that polymer repulsion from the sliding indenter established a strong relationship between the friction and the sliding speed, which increased as the normal pressure increased [108]. However, for our experiments, we found the normal pressure to play a comparatively insignificant role in the overall friction – sliding speed was by far the dominant factor. Figures 30 and 31 show that larger loads in compositions 3-5 have little effect on the friction coefficient - only composition 2 sees improved lubrication through a higher load, suggesting that the larger load on this composition induced a more substantial hydrodynamic fluid film through water exudation from the gradient layer. For compositions 3-5, we once again propose that either floc-like behavior of the

gradient layer [61] and/or tribologically-induced rehydration [96, 101, 102] are responsible for the friction reduction with sliding speed. This also confirms that the friction mechanisms are controlled by the composition through control of the gradient layer thickness, structure, and crosslinking.

The consistency of the contact areas and friction coefficients over time suggests that water reuptake within the gradient layer is a rapid process (<1 second). Stable contact areas and friction coefficients persisted even at sliding speeds of up to $1000\mu\text{m/s}$, where each portion of the substrate was out of contact for as little as 0.6 seconds. The presence of the gradient layer appears to improve water mobility due to its low density, which is predicted by the larger diffusion coefficients for thicker gradient layers (section 5.3.2). Additionally, compositions 3-5 are highly poroelastic, which is a time-sensitive process. Limiting the time that any portion of the hydrogel substrate is under pressure will therefore reduce the amount of poroelastic relaxation that would lead to transient frictional behavior.

The only exceptions to the steady-state frictional behavior were Gemini experiments on compositions 3,4 conducted at slow sliding speeds, which showed increasing friction over time. Friction in composition 4 increased by 40% over experiments conducted at sliding speeds of $10\mu\text{m/s}$. As first suggested in section 4.3, this transient behavior is likely due to sustained dehydration of the hydrogel probe’s gradient layer. This causes increased polymer chain interaction between the probe and substrate, as well as osmotic suction within the probe that increases adhesion in the contact zone.

The lowest coefficient of friction obtained from any of our Gemini contact experiments was 0.01, which agrees with work from Pitenis and Urueña on hydrogels molded against polystyrene [64, 71]. For Migrating contact experiments, the lowest obtained friction coefficient was 0.004 from an intermediate stiffness composition at the fastest sliding speed of $1000\mu\text{m/s}$, which suggests that the solid interface at fast enough speeds sees better lubrication than a comparable Gemini interface. Because water exuded from the gradient layer cannot diffuse into the probe as in Gemini contact, the extra confinement may increase the

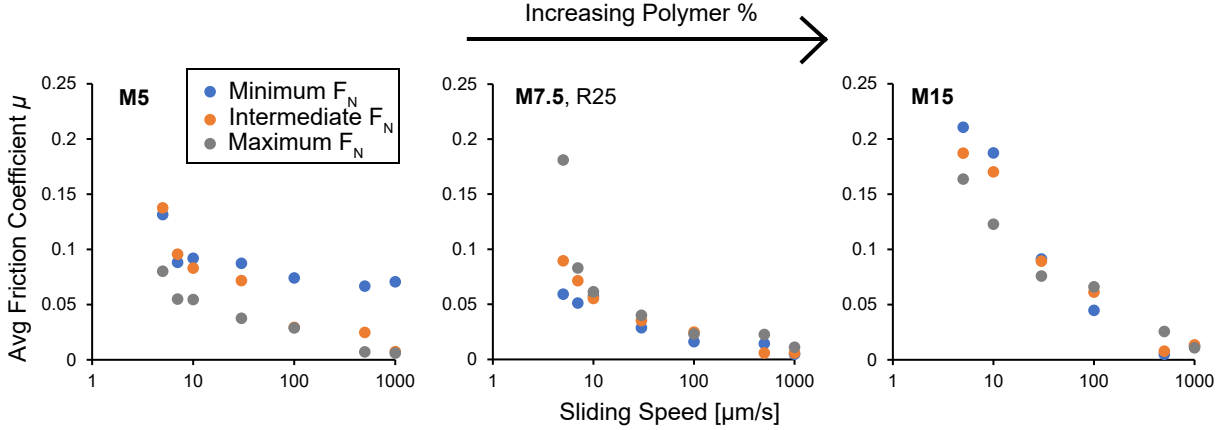


Figure 30: Average friction coefficient versus sliding speed for experiments in a migrating contact setup. Shown here are compositions with varying monomer percent M (compositions 2-4). Friction is highly dependent on sliding speed.

pressurization of the fluid film at the interface.

In a Gemini contact, polymer chains at the surface preferentially collapse under load instead of interpenetrating between the surfaces [94, 95]. This further supports the formation of a load-bearing fluid layer between the two hydrogel surfaces. In Gemini contact experiments using polystyrene-molded hydrogels, it was proposed that the lubrication of the interface is directly related to the mesh size (pore size) of the hydrogel, with larger mesh sizes causing lower friction coefficients [71]. Further work by Urueña showed that, in a Gemini contact, increasing normal load reduced the friction coefficient [66]. While the latter conclusion is true for our Gemini experiments on compositions 3 and 5 (figure 33), we see the lowest consistent friction values across sliding speed variations for composition 4 (M15). Investigation of the polymer structure across compositional changes by Gombert suggests that a hydrogel composition identical to composition 3 has the smallest average mesh size, while increasing monomer and crosslinker content reduces pore homogeneity, increasing the average mesh size [55]. While this could be one explanation for the trends we observed, we also note that Urueña determined the mesh size using hydrogels molded against quartz glass, which is expected to create a homogeneous ungraded hydrogel surface that is not representative of the gradient layer mesh sizing [74].

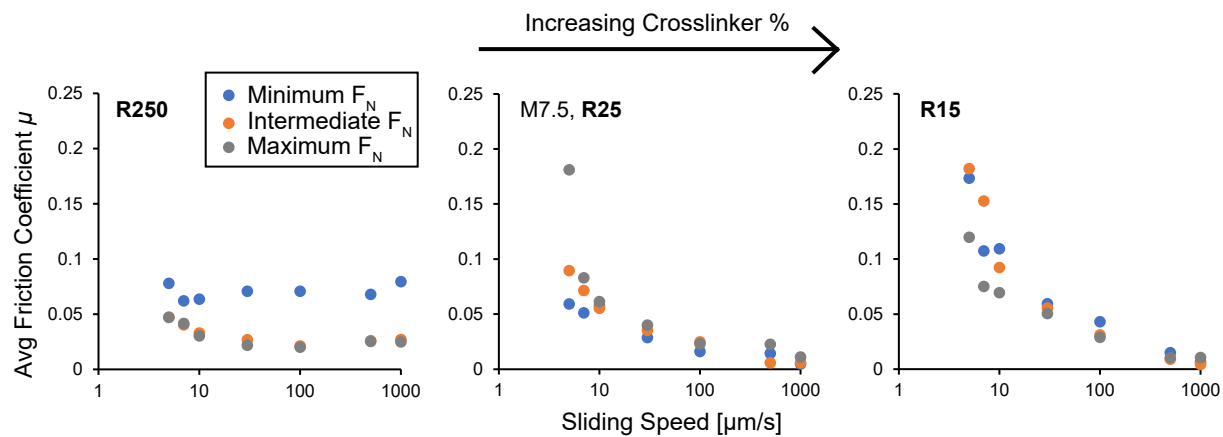


Figure 31: Average friction coefficient versus sliding speed for experiments in a migrating contact setup. Shown here are compositions with varying monomer-to-crosslinker ratios R (compositions 1,3,5). Friction is highly dependent on sliding speed.

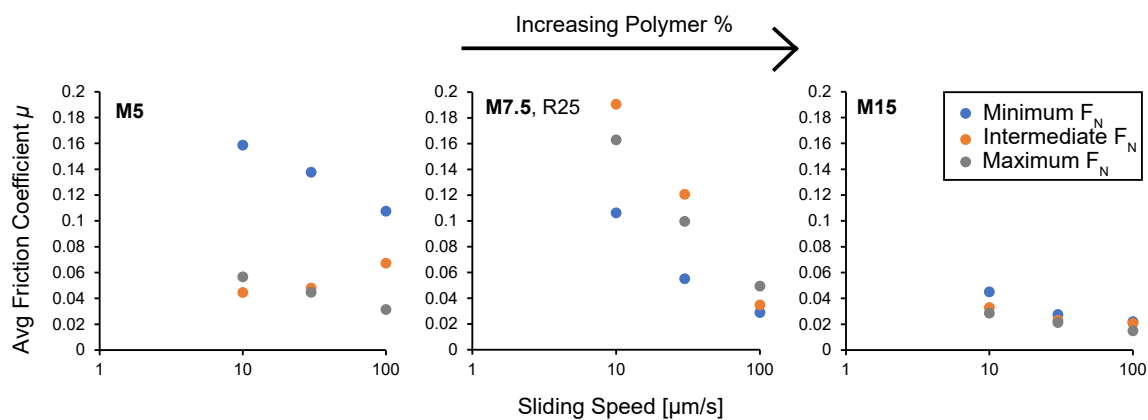


Figure 32: Average friction coefficient versus sliding speed for experiments in a Gemini contact setup. Shown here are compositions with varying monomer percent M (compositions 2-4). Friction is highly dependent on sliding speed.

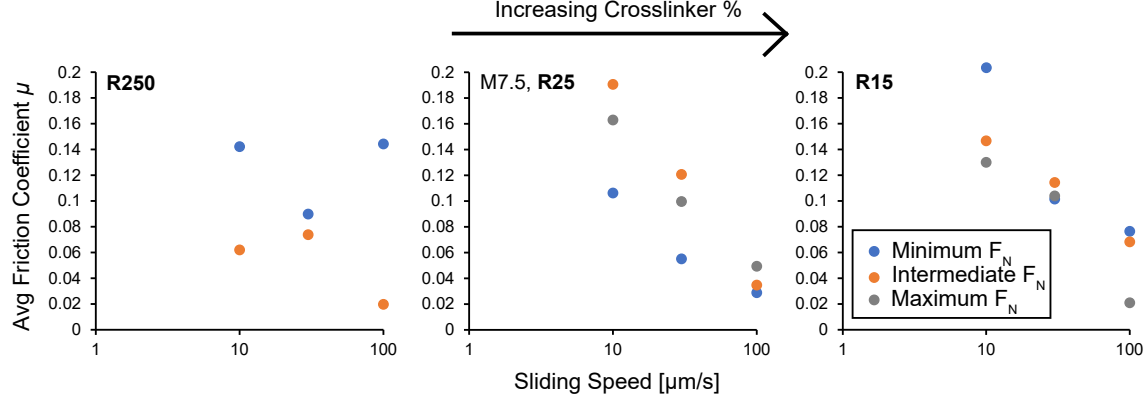


Figure 33: Average friction coefficient versus sliding speed for experiments in a Gemini contact setup. Shown here are compositions with varying monomer-to-crosslinker ratios R (compositions 1,3,5). Friction is highly dependent on sliding speed.

5.4.3 Contact Shear Stress

In section 5.2.2, we discussed how using a characteristic contact shear stress σ provides a better measure of the overall stress state in the contact (equation 5.2). When plotted versus the pseudo-Sommerfeld parameter, we obtain an inverse relationship between the contact shear stress state and the pseudo-Sommerfeld parameter for all compositions (figure 34), showing that the contact shear stress decreases as the sliding speed is increased and/or the normal load is decreased. This relationship can be fit to a power law from which we extract a power fit exponent for each composition (see Table 8). The power exponent magnitude represents the stability of the contact shear stress across variations in the sliding speed and normal load - smaller magnitudes are more stable. The magnitude of the power fit exponent was smaller for the more compliant compositions, which implies that the shear stress state is more consistent across load/speed for these compositions compared to the stiffer compositions (3-5). On the other hand, this also implies that there still exist faster sliding speeds / lower normal loads for which the shear stress state of the sliding contacts of compositions 3-5 can be further decreased. This suggests that the variable shear stress behavior exhibited by compositions 3-5 arises from a greater relative engagement of the bulk structure at lower pseudo-Sommerfeld numbers. Normalizing the shear stress by the

modulus of each composition makes this clear, showing that compositions 1-2 have already reached their lower limit on the shear stress state with respect to operating load / speed (figure 35). In section 5.3.1, we found that the stiffness of the initial brush response was the same order of magnitude across all compositions, with the compliant compositions having brush stiffness values close to their bulk modulus values. This explains both why these compositions are at higher normalized shear stress states and why these stresses are more consistent over speed/load changes: engaging a greater portion of the substrate depth does not significantly change the stress distribution since the gradient layer structure is relatively similar to the bulk. This is in contrast to the stiffer compositions, where higher sliding speeds and/or lower normal loads cause the stress to engage the gradient layer more substantially than the bulk.

Thicker gradient layers tended to stabilize the contact shear stress across load/speed. Comparing each composition's power exponent to the gradient layer thickness shows a trend between the contact shear stress stability (the power exponent magnitude) and the thickness of the gradient layer, with larger gradient layers experiencing a smaller magnitude power fit exponent (figure 36, left). This trend appears to be consistent for variations in either the crosslinker ratio R or the total polymer percent M . To compare the difference on the gradient layer behavior between M and R , we calculated the linear stiffness rate of change over the thickness of the gradient layer, $E/\Delta d$. This is more accurately calculated as $(E_{bulk} - E_{brush})/\Delta d$ where $E = E_{bulk}$, but as noted in section 5.3.1, the initial stiffness of the brush is between 2-4 kPa for all compositions, making the two calculations essentially the same. We then plotted the power exponent versus the stiffness rate of change of the gradient layer in figure 36 (right). From this, we find that increasing the monomer-to-crosslinker ratio R is more effective at increasing the shear stress stability while retaining a similar gradient layer stiffness profile. This manifests as a greater influence on the thickness of the gradient layer with less influence on the stiffness of the bulk. Conversely, we see that changing M can drastically change the stiffness profile of the gradient layer, but has a weaker effect on the

shear stress stability. By creating a large gradient layer through appropriate selection of R and M , it is therefore possible to create a stiff hydrogel that also has a consistent shear stress response across various operating loads and sliding speeds (see supplemental results A.4). This may provide one simple avenue to synthesize a stiff hydrogel that maintains consistent lubricity under a wide variety of loads and speeds.

There are many potential reasons why we observe the shear stress state to have a strong dependence on the speed. When the sliding speed increases, the polymer chains at the ‘brushy’ gradient layer do not have enough time to adhesively interact with the solid probe before the point of contact changes. This corresponds to a reduction in the ‘adsorption’ portion of Gong’s adsorption-repulsion model [59, 108]. For the stiffer compositions (3-5), the consistent negative power law relationship with the pseudo-Sommerfeld parameter suggests that the loose chains of the ‘brushy’ gradient layer, and their capacity for poroelastic relaxation, effectively extend the portion of the hydrogel lubrication curve between the local maximum and local minimum, where adsorption of the polymer chains cannot occur, but full hydrated lubrication is not yet occurring. In the more compliant compositions, we are likely already reaching full hydrated lubrication, which manifests as a near-zero power law relationship. Gong also suggests that, when sliding against a polymer brush, chains vastly larger than the nearest neighbor distance are detrimental to lubrication [73], tightening the velocity interval at which friction benefits and even increasing the friction compared to a crosslinked gel surface. This means that the length of dangling polymer segments produced by molding against polystyrene must be short enough to retain the friction benefits compared to the bulk. This may contribute to the smaller power exponent magnitudes of compositions 1 and 2, which would have comparatively longer chain segments at the surface. Modeling of friction between polymer brushes of varying degrees of crosslinking shows that larger degrees of crosslinking increase the friction coefficient, likely due to a lesser degree of latent water available at the sliding interface [73, 109]. This gives further support to the importance of available water for hydrodynamic lubrication at the interface.

Plotting the contact shear stress versus pseudo-Sommerfeld parameter for the Gemini experiments revealed a similar inverse relationship between the shear stress and the pseudo-Sommerfeld parameter (figure 37). However, the power-fit exponent magnitude was reduced for all compositions except composition 3. This is an indication that the self-mating of two gradient layers produces a shear response similar to having a thicker gradient layer in a hard-probe contact setup. This reduction in speed dependence aligns with previous migrating vs Gemini experiments performed by Dunn [9], and begins to resemble the nearly speed-independent lubrication regime described by Pitenis in their Gemini experiments [64, 77]. If we plot the shear stress power exponents obtained from Gemini contact against the gradient layer thickness measured from Gemini indentation, we observe an opposite trend as the migrating contact case: power exponent magnitude increases with increasing gradient layer thickness. Based on the results of sections 5.3.1 and 5.3.2, the smaller perceived gradient layer from compositions 1 and 2 result from elimination of the high-penetration brush contact regime and the comparable stiffness of the low-penetration brush response and the bulk response. Combined with the low contact pressures ($<0.5\text{kPa}$) made possible by the self-mated setup, we can attribute the lower perceived gradient layer thickness and low shear stress variability of these compositions to a lower degree of poroelastic squeeze-out within the gradient layer. The highest shear stress variability was seen in composition 3, which may have experienced greater poroelastic relaxation within both the probe and substrate causing higher dependence on the speed and load.

In work by Pitenis and Urueña, who tested Gemini contact at speeds ranging from 30 – 100,000 $\mu\text{m/s}$, the frictional response was consistent at its lowest value for sliding speeds less than 5000 $\mu\text{m/s}$, which is far greater than the fastest speed attempted by our experiments [64, 71, 66]. However, we observed frictional stress increases for speeds slower than 30 $\mu\text{m/s}$, which is slower than that tested by Pitenis and Urueña. This would suggest that the Stribeck model of lubrication is not incorrect, as they concluded, but that the boundary/mixed lubrication scheme does not begin until incredibly slow sliding speeds. This suggests two

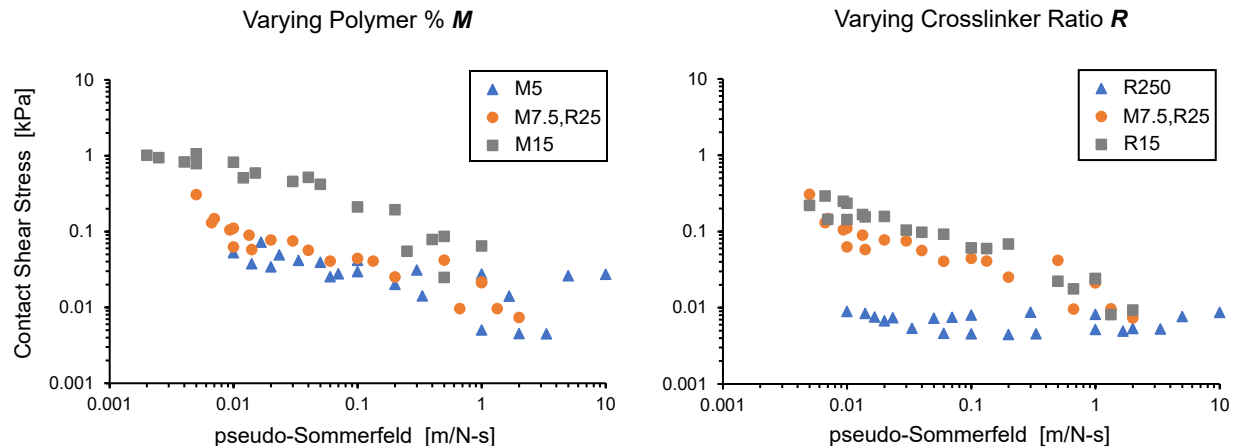


Figure 34: Shear stress versus the pseudo-Sommerfeld parameter (v/F_n) for a migrating contact setup, plotted on a log-log scale. Left shows data for variation in total polymer percent M . Right shows data for variation in monomer-to-crosslinker ratio R .

conclusions: 1. The elasto-hydrodynamic lubrication regime is effectively lengthened for hydrogels with gradient surface layers and 2. 'Mixed' lubrication of a hydrogel against a repulsive counterface resembles 'polymer fluctuation lubrication'. Particularly in the case of a Gemini hydrogel contact setup with gradient surface layers present, the ease of water exudation under load promotes the formation of a fluid boundary layer even for pressures far below the osmotic pressure of the bulk structure. Above near-stationary speeds, varying degrees of lubrication would occur based on the thickness of the gradient layer. This 'mixed' lubrication would correspond to the polymer fluctuation lubrication regime (figure 4), with increasing sliding speeds and decreasing contact loads promoting less chain interaction with the probe surface.

5.5 Conclusions

In this section, we conducted indentation, creep, and sliding experiments on five compositions spanning two design variables: changing monomer percent M with a fixed monomer-to-crosslinker ratio of $R = 25$, and changing the monomer-to-crosslinker ratio R with a fixed monomer content of $M = 7.5\%$.

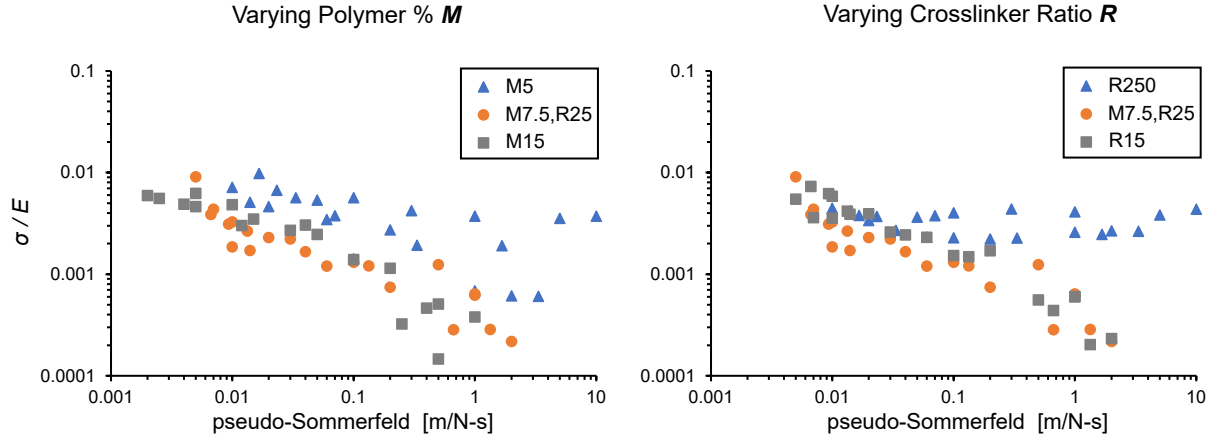


Figure 35: Contact shear stress σ normalized by the elastic modulus of each composition E , plotted against the pseudo-Sommerfeld parameter (v/F_n) for a migrating contact setup. Left shows data for variation in total polymer percent M . Right shows data for variation in monomer-to-crosslinker ratio R .

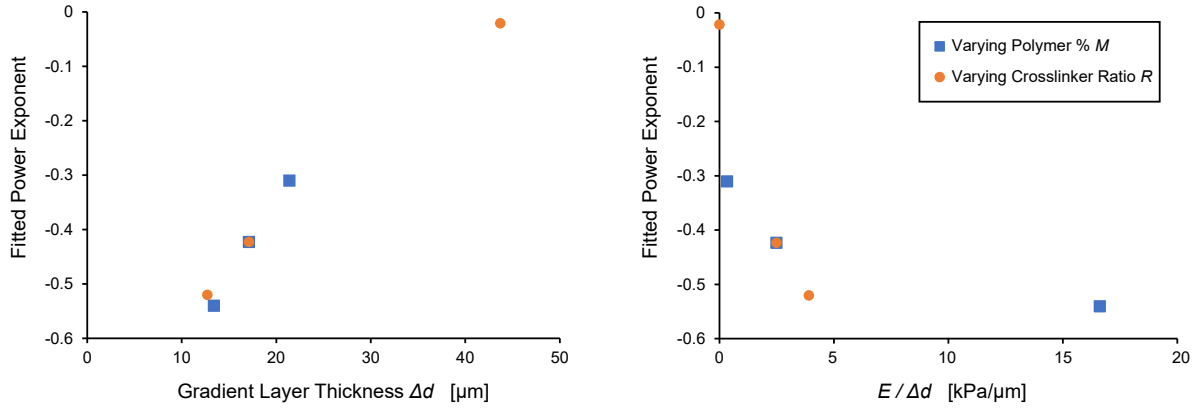


Figure 36: (Left) The power exponent obtained from a power-law fit of each composition's data from figure 34 is plotted versus the gradient layer thickness Δd measured via hard-probe indentation. The magnitude of the exponent is inversely related to the gradient layer thickness. (Right) The same power exponent plotted versus the stiffness change per gradient thickness, $E/\Delta d$. Changes to R have a significant effect on the shear stress stability with less stiffness change than M .

Comp #	Fitted Power Exponent	Gradient Layer Thickness Δd (Migrating) [μm]
1 (R250)	-0.02	43.7
2 (M5)	-0.31	21.4
3 (M7.5,R25)	-0.42	17.1
4 (M15)	-0.54	13.4
5 (R15)	-0.52	12.7

Table 8: Composition number and their indentation-derived gradient layer thickness, Δd . Also listed is the power exponent from a power-law fit on all the shear stress vs pseudo-Sommerfeld data from figure 34.

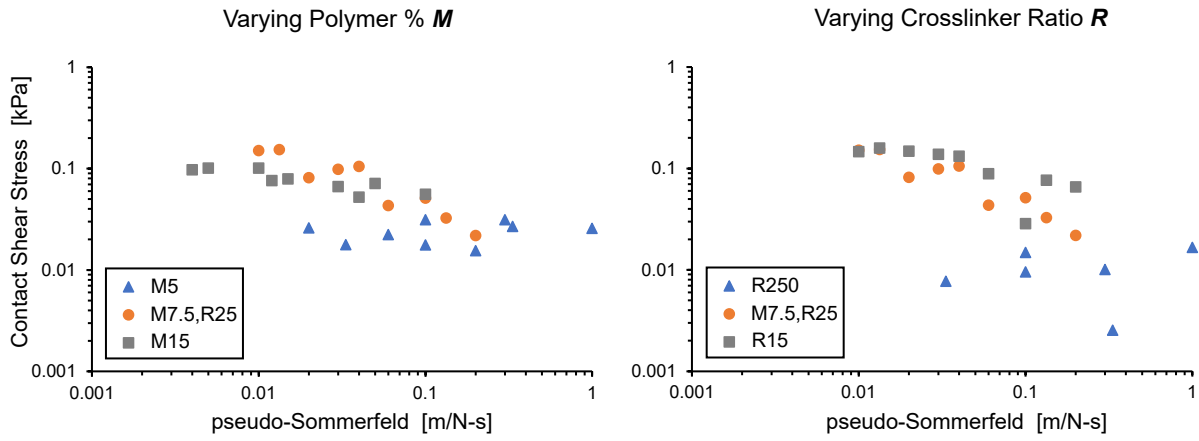


Figure 37: Shear stress versus the pseudo-Sommerfeld parameter (v/F_n) for a Gemini contact setup, plotted on a log-log scale. Left shows data for variation in total polymer percent M . Right shows data for variation in monomer-to-crosslinker ratio R .

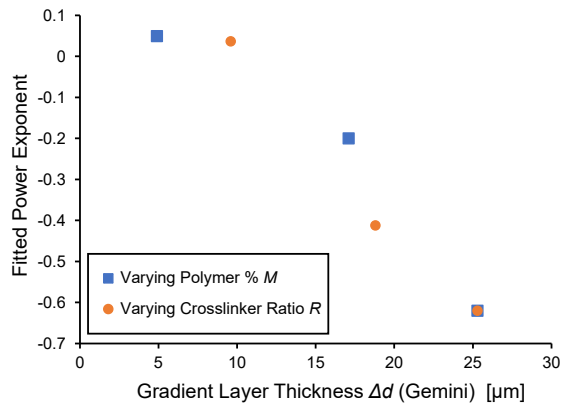


Figure 38: The power exponent obtained from a power-law fit of each composition's data from figure 37 is plotted versus the gradient layer thickness Δd measured via Gemini indentation. The magnitude of the exponent is correlated with the perceived gradient layer thickness.

Indentation experiments confirmed the presence of a 'brushy' gradient layer for all compositions, with the more compliant compositions (1,2) exhibiting the largest gradient layer thicknesses. The brush modulus G was on the order of 2-4 kPa for all compositions, which made it close in magnitude to the bulk stiffness of compositions 1 and 2. This also manifested as a comparatively smaller gradient layer thickness perceived via Gemini indentation. It is possible that the gradient layer thickness, as perceived through indentation, also gives a measure of the degree of poroelastic relaxation in the contact setup, with lower gradient layer thicknesses indicating less poroelastic relaxation under the given load due to smaller volumes of water being engaged.

Creep experiments showed that compositions 2-4 relaxed poroelastically under a sustained load over time. Composition 1 showed viscoelastic-dominant behavior based on our analysis of the time constants of relaxation. Poroelastic diffusion coefficients were found to be at least 50% larger than that found for glass-molded gels. These coefficients were larger for more compliant compositions, which indicates that the water mobility within the gradient layer is higher for more dilute layers.

Lubrication of these hydrogel compositions was greatly enhanced by the poroelastic behavior of the 'brushy' gradient layer. Contact pressures were independent of the sliding speed for migrating contact, and had a small positive dependence in Gemini contact. However, friction was highly dependent on sliding speed in both contact configurations and for all compositions except composition 1. We utilized the contact shear stress, calculated as $\sigma = \mu P$, and the pseudo-Sommerfeld parameter, calculated as v/F_N , to better understand each composition's shear response under varying loads and speeds. In migrating contact, the shear stress fit a negative power law for all compositions - the magnitude of the power law exponent could be considered the contact shear stress stability with load/speed. Compositions 1 and 2 showed good stability, suggesting that large gradient layers offer more shear stress stability. The contribution of the monomer-to-crosslinker ratio R was found to be more influential on the shear stress stability while having less effect on the elastic modulus within

the gradient layer; this manifested as a thicker gradient layer. Conversely, the monomer percent M had a greater effect on the stiffness of both the bulk hydrogel and the gradient layer stiffness profile, but was less influential on the shear stress stability. Variations in both parameters could induce a thick gradient layer on an otherwise stiff hydrogel for optimal tribological properties.

These findings show that a 'brushy' gradient layer on pAam hydrogels molded against polystyrene is inevitable. However, the presence of the gradient layer is highly desirable in tribological applications requiring ultra-low friction. The 'brushy' layer, which exhibits increasing polymer and crosslink density towards the bulk, greatly aids lubrication by providing extra water for poroelastically-driven hydrodynamic sliding.

CHAPTER 6

CONCLUDING REMARKS

6.1 Summary of Findings

While the hydrogel 'mold effect' may be a confounding factor in an already complicated field, it also serves a simple method to achieve incredible lubrication from a given hydrogel system. Throughout this work, we have used a novel PEM technique together with careful contact and sliding experiments to decipher the contact mechanics, structure, relaxation behavior, and shear response of the hydrogel gradient layer. Our results show that the 'mold effect' of chemically-crosslinked hydrogels can critically impact the resulting tribological properties and should be carefully considered during hydrogel polymerization.

Hard-probe indentation allowed us to perceive the less-dense gradient layer for the five different compositions; this allowed approximation of the thickness of the layer, Δd (section 5.3.1). Fitting different contact models to portions of the indentation curve showed an evolving contact response with depth that reveals the structure of the gradient layer. Immediately at the onset of contact, the contact behavior is predicted by low-penetration polymer brush physics, where the resistance to deformation comes from the stiffness of the brush G . Further penetration into the substrate causes exudation of water held by these chains, pressurizing the water within the contact zone until it flows away from the contact. Next, high-penetration polymer brush contact occurs as some of the dangling segments that have lost water begin to compress. Further compression of these chain segments produces a 'bed-of-springs' response until the chains are compressed to the point they emulate the bulk (Hertzian) response. This evolution of brush- and fluid-controlled behavior leading into Winkler contact and eventually Hertzian contact is able to predict the contact areas we observed with good accuracy, which validates the accuracy of the technique and the determination of

the evolving gradient layer structure with depth.

The less-dense nature of the gradient surface layer enabled poroelastic squeeze-out of water for pressures significantly lower than the reported osmotic pressure of the bulk network (section 5.3.2). This is made possible by the evolving "mesh size" within the gradient layer, which approaches infinity towards the open water bath. The one exception to this was a composition with extremely low amounts of crosslinker (composition 1), which was predicted to show comparatively viscoelastic-dominant behavior. Despite this, the gradient layer was able to rapidly rehydrate when out of contact from re-swelling of the loosely-linked chains.

Sliding experiments showed that hydrogels with gradient surface layers exhibited lubricious interfaces with friction coefficients as low as 0.005 (section 5.2.2). This was made possible due to the dilute structure of the gradient layer and the mobility of the held water, which could be exuded out and contribute to hydrodynamic lubrication under a wider range of pressures than would be predicted by bulk osmotic pressure estimates. While the friction was independent of the contact area, it heavily depended on the sliding speed. Hence, the ultra-lubricity achieved under the most ideal combination of load and sliding relied on a sufficiently thick hydrodynamic film to separate polymer-probe interactions. This film formation was favored in migrating contact setups, where the hydrophobic probe served as a barrier for water exudation, forcing it to contribute to the lubricating film for longer. It was more difficult to achieve ultra-lubricity ($\mu < 0.01$) in Gemini contacts due to the ability of the water to move into the dehydrated gradient layer of the probe. In fact, Simic et al recently showed that a 'neat' well-crosslinked hydrogel probe sliding against a 'brushy' graded hydrogel substrate produced a more lubricated interface than self-mated 'brushy' hydrogel sliding [100]. Thus, paradoxically, it is both the exudation and confinement of the water within the gradient layer that leads to the best lubrication within the contact.

Lubrication differences based on composition metrics M and R showed that each parameter has a different effect on the gradient layer and the shear response of the hydrogel. Compliant compositions (1,2) produced large gradient layers that had a consistent contact

shear stress σ with respect to normal load and sliding speed. Compositions 3-5 showed a greater dependence on speed/load which, when normalized against the modulus of the bulk, suggests that they have not yet reached the limit of lubrication efficiency, which would occur at faster speeds and lower normal loads. Despite the similar shear stress responses between many of the compositions, it is important to note that the gradient layers were notably dissimilar. While we found that the stiffness of the outermost "brush" portion of each hydrogel was between 2-4 kPa, the stiffness change over the thickness of the gradient layer $E/\Delta d$ was vastly different among the compositions. When compared with the shear stress stability (power fit exponent), we found that the monomer-to-crosslinker ratio R has a greater ability to influence the stability and thickness of the gradient layer with little impact on the modulus of the bulk hydrogel. Changing the monomer percent M has a smaller effect on the shear stress stability, but a much larger effect on the modulus of the hydrogel. It is therefore possible to make a hydrogel with a stiff bulk by increasing M but a large gradient layer by increasing R . This would ideally produce a hydrogel capable of sustaining heavy loads while maintaining consistent lubrication across various sliding conditions.

The additional elasticity provided by the hydrogel gradient layer promotes greater deformation of the hydrogel such that a Gemini contact experiences far greater flattening and improved lubrication across a wider range of normal loads and sliding speeds. Combined with the ability for poroelastic squeeze-out to occur at more pressures, the elasto-hydrodynamic regime of the classic Stribeck curve is essentially broadened in a Gemini contact with gradient-layered hydrogels.

All together, the picture of the physical nature of the sliding hydrogel contact has been clarified by this body of work. In these gradient-layered hydrogels, the top layer consists of loose polymer chains with brush-like formation, whose density increases moving into the hydrogel depth. Contact with this surface prompts water exudation that can be used to lubricate the contact. The dilute brushy nature of the gradient layer produces a significant lubricating fluid film even for miniscule pressures well below the osmotic pressure of the

bulk, which promotes ultra-low friction coefficients. The gradient layer greatly expands the operating conditions where hydrodynamic and elasto-hydrodynamic lubrication occurs, allowing a larger span of conditions where minimal friction can be obtained from a sliding hydrogel interface.

6.2 Future Considerations

While we were able to draw on polymer brush physics and brush contact models to help explain a portion of the indentation response, we have not approached this work from the perspective of polymer brush lubrication. Shearing of a polymer brush has been shown to produce low friction similar to what we observed for our gradient-layered hydrogels [106, 107]. However, a deeper review of the behavior of polymer brush friction may reveal unanswered questions from this body of work. For example, the fluid-controlled portion of each indentation is a prediction that has no contact model associated with it. Polymer brush physics, particularly studies involving fluid confinement and brush contact, could provide useful insights.

Direct imaging of the gradient surface layer could also be used in future work to provide confirmation of the gradient structure. Our evolving contact model for the gradient layer of the hydrogel suggests that its structure resembles that of a polymer brush in good solvent with increasing polymer and crosslinking concentration towards the bulk. However, the structure is also very dilute towards the outer extent of the hydrogel, which means that any imaging technique must be able to preserve the arrangement of the dangling polymer chains at the surface. One method in which this may be possible is freeze-drying, which is a method that has been previously applied to hydrogels to observe their bulk pore sizes [55]. These methods remove the water content that would interfere with imaging techniques such as scanning electron microscopy (SEM), but shrink the gel network in the process. Color changes were also observed by Gombert depending on the speed of the drying pro-

cess, which hinted that any form of drying altered the polymer structure. It is therefore unlikely that SEM via hydrogel freeze-drying would be a suitable method to directly view the delicate gradient layer structure. As potential in-situ imaging methods such as optical coherence tomography or fluorescence microscopy lack the resolution to distinguish the polymer structure, it is unlikely that the gradient layer can be directly imaged using current technology. Future advances in SEM technology may eventually allow the structure to be directly visualized.

Future work investigating more composition variations would also strengthen conclusions from this work and improve future hydrogel designs. Within this work, we characterized changes to both the monomer percent M and the monomer-to-crosslinker ratio R . Our results showed how the effect of M is different than R , allowing creation of a stiff-bulk hydrogel with a large gradient layer. We additionally demonstrated one example of this, with $M=20$ and $R=100$, in supplemental results (supplemental section A.4). However, within our main results, we only looked at three compositions spanning changes in each variable while the other parameter was fixed (e.g. $M5$, $M7.5$, $M15$ but all $R=25$). While this was necessary to determine the relative effect of M and R , we were not able to conduct extensive experimentation on compositions with variations of both parameters. Though we had time to conduct limited experiments on one special composition, proving that it is possible to create a stiff hydrogel with large gradient layer, we were not able to obtain as much data on its shear response with varying speed/load as we desired. Other compositions with smaller gradient layers from high M and low R values are also of interest, since we demonstrated in section 5.4.3 that stiff compositions with smaller gradient layers can potentially achieve better ratios of surface shear stress compared to their bulk stiffness. Experiments on such compositions across many magnitudes of the pseudo-Sommerfeld parameter would help characterize the viability of such compositions. With these additional compositions and experiments, the benefits of inducing a specific gradient layer thickness would be further strengthened. For example, an application with consistently high sliding speeds and low normal loads may be

well-suited to a smaller gradient layer, whereas applications with dynamic conditions may prefer a hydrogel with a large gradient layer but stiff bulk structure. This can simplify synthesis of hydrogels that would normally use a secondary grafted brush/network to meet their tribological needs.

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APPENDIX A

SUPPLEMENTAL FINDINGS

A.1 Contact Area Supplemental Information

A.1.1 Image processing

Below, we demonstrate an example where the contact area is not clearly visible until the frame is processed using techniques from chapter 2. While the area may be noticeable during the video, when the contact boundary is visually shifting, it is otherwise incredibly difficult to determine the boundary with minimal error from a still frame.

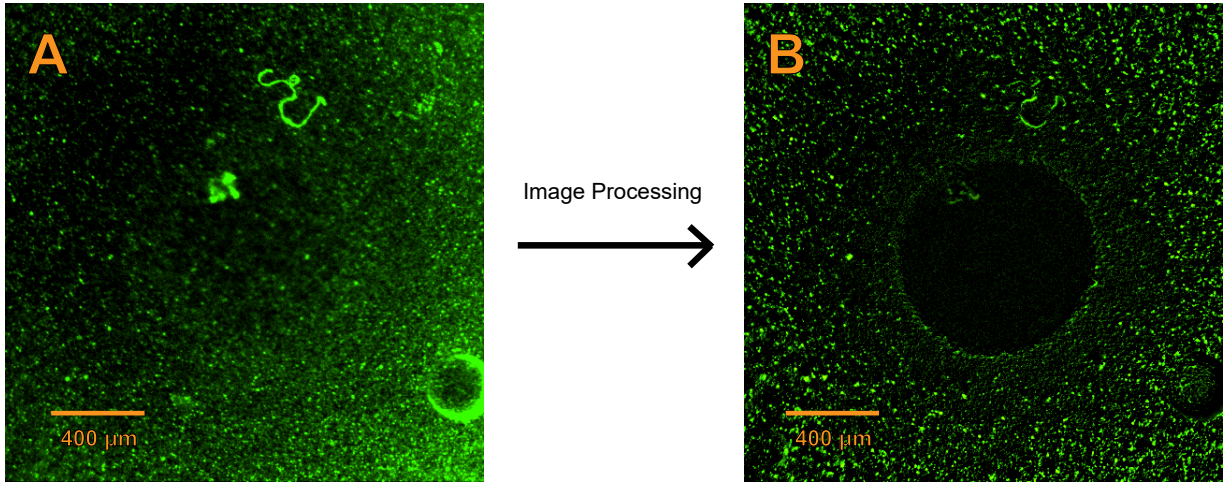


Figure 39: Before (A) and after (B) images of an isolated frame from a creep experiment. This illustrates an extreme example of how the processing technique allows better demarcation of the contact boundary.

A.1.2 Gradient layer bead adhesion

Microfluorescent particle adhesion to the substrate hydrogel was more commonly observed for compositions 4 and 5. In section 5.3.2, we discovered that the water mobility is related to the gradient layer thickness, of which these two compositions have the thinnest layers. These compositions are additionally the stiffest of the five compositions used. These properties result in three important effects: 1. There is less water within the gradient layer available to be exuded, 2. Of the water in the gradient layer, less of it can be exuded at a given pressure due to the higher stiffness increase per gradient layer thickness (linear approximation $E/\Delta d$), and finally 3. Water that is exuded has restricted mobility through the gradient layer compared to other compositions. The combination of these three effects means that beads will naturally rest on the surface of the hydrogel substrate due to electrostatic attraction and then stay there, as the fluid pressure from squeezed-out water will not be enough to remove the particle from the surface and return it to the water solution. Often, the only particles that clear the contact are those at the edge of the contacting probe, which corresponds to the top-most portion of the gradient layer where water mobility is highest. Despite these challenges, microfluorescent spheres that are caught in the contact experience a focus shift that appears during z-stack image averaging, allowing the contact to be obtained.

A.2 Relaxation Experiments

A.2.1 Relaxation experiment methods

To further understand the time-dependent relaxation of these hydrogels, we conducted displacement-controlled experiments and monitored both the force and contact area over time (see Methods section 2.3.2). These relaxation experiments were completed by holding the vertical stage displacement at a fixed position after indenting into the hydrogel substrate. We used a rigid steel probe indenting into a hydrogel substrate of one of the five compositions, holding a fixed vertical stage displacement between 50 and 200 μm for at least 600 seconds. The resulting force versus time data was fit to an exponential model outlined in section 3.3.2, which produced time constants associated with the force drop over time. The contact areas were measured at regular 100 second intervals and fit to an exponential model using the same procedure from section 3.3.2.

A.2.2 Relaxation Results

Relaxation experiments showed a drop in the force over time, which could be fit to an exponential to extract a time constant. However, the contact area also showed an increase over time, which was likewise fit to an exponential. This produced two time constants per experiment: a force-related time constant, and a contact area-related time constant. Plotting both of these time constants versus the original contact radius showed that the force relaxation was linked to poroelastic squeeze-out of the hydrogel pores, whereas the area increase over time resulted primarily from viscoelastic relaxation. The increased rate of contact area expansion in the first 150 seconds of the creep experiments could be attributed to this viscoelastic response, since the area expansion of the relaxation experiments reached steady state within this time frame.

A.3 Friction over Time for All Compositions

Here, we show friction coefficient versus time for the four compositions 1, 2, 4, 5 listed in section 2.2. Friction coefficient versus time for composition 3 is already shown in section 4.3.

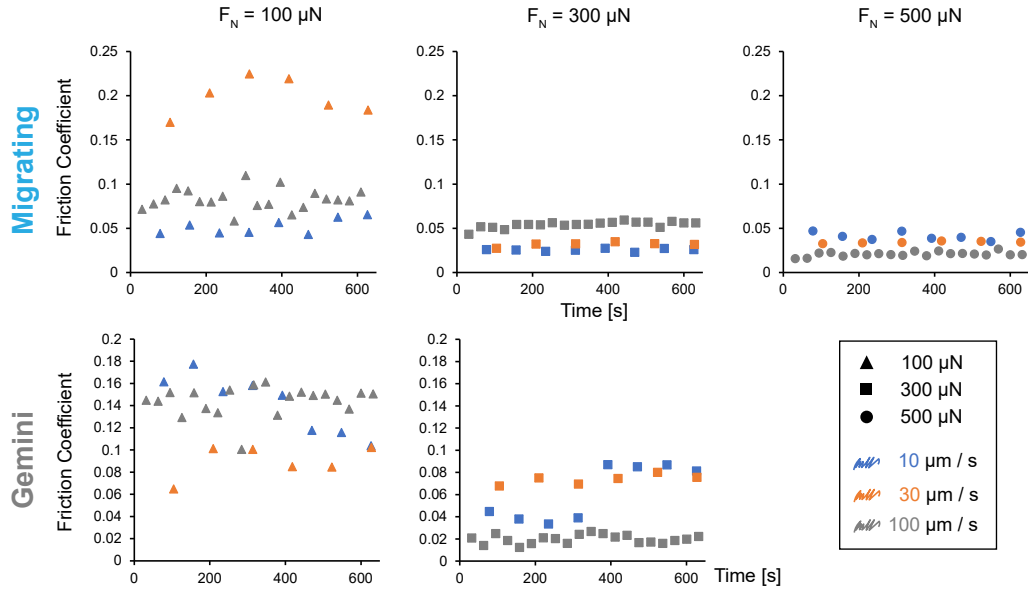


Figure 40: Composition 1 (R250). Friction coefficient versus time for applied normal loads of [500,750,1000] μN at sliding speeds of [10,30,100] $\mu\text{m/s}$.

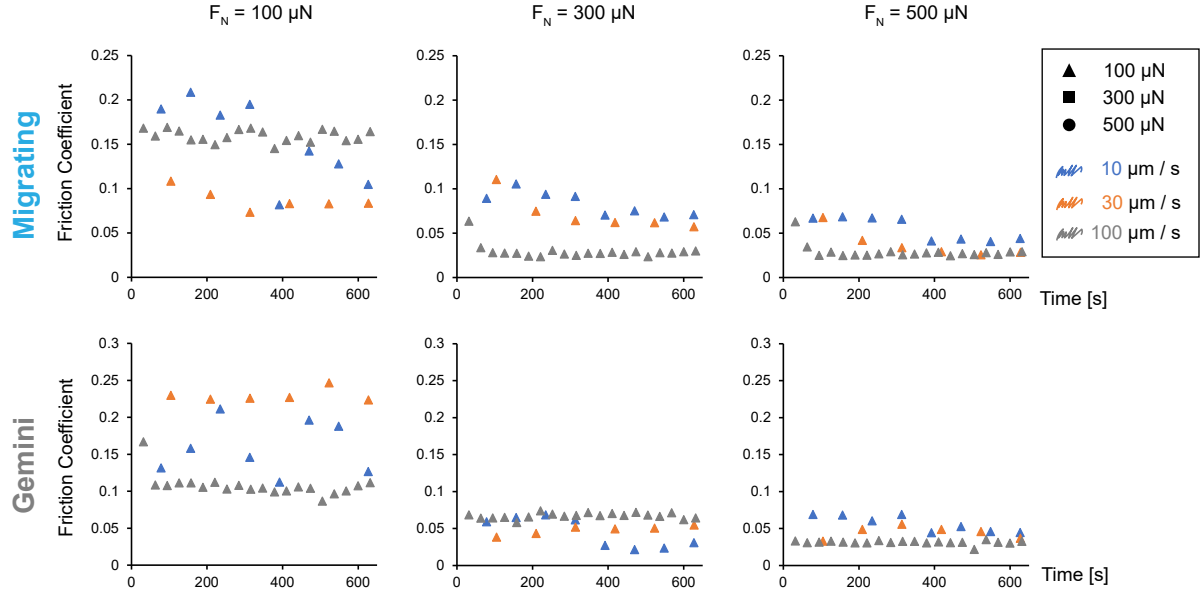


Figure 41: Composition 2 (M5). Friction coefficient versus time for applied normal loads of $[500,750,1000]\mu\text{N}$ at sliding speeds of $[10,30,100]\mu\text{m/s}$.

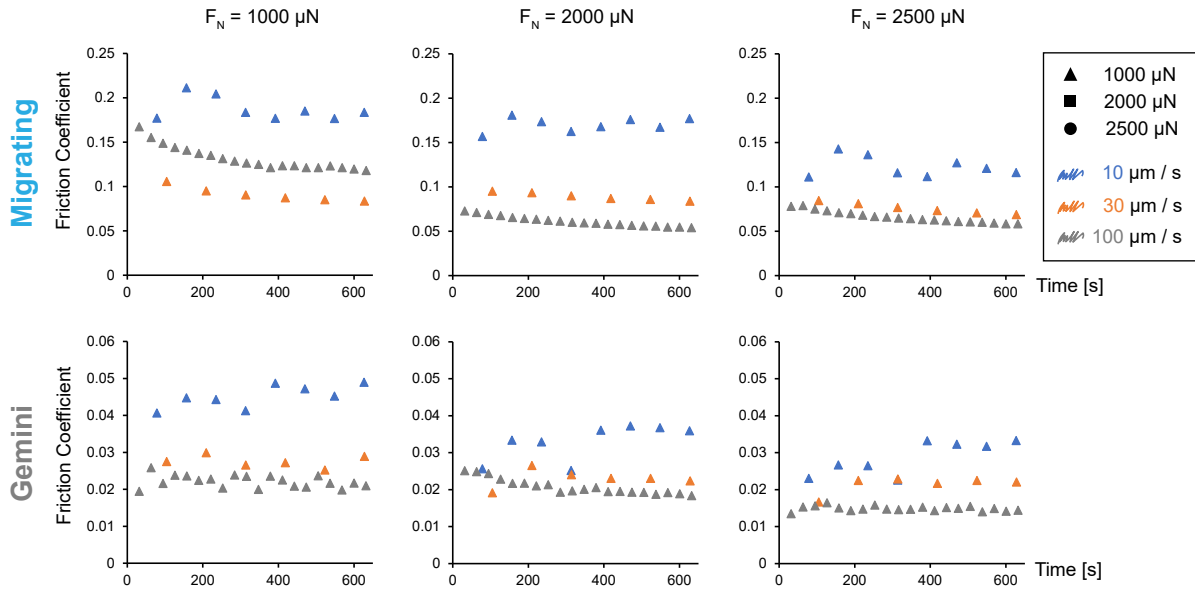


Figure 42: Composition 4 (M15). Friction coefficient versus time for applied normal loads of $[500,750,1000]\mu\text{N}$ at sliding speeds of $[10,30,100]\mu\text{m/s}$.

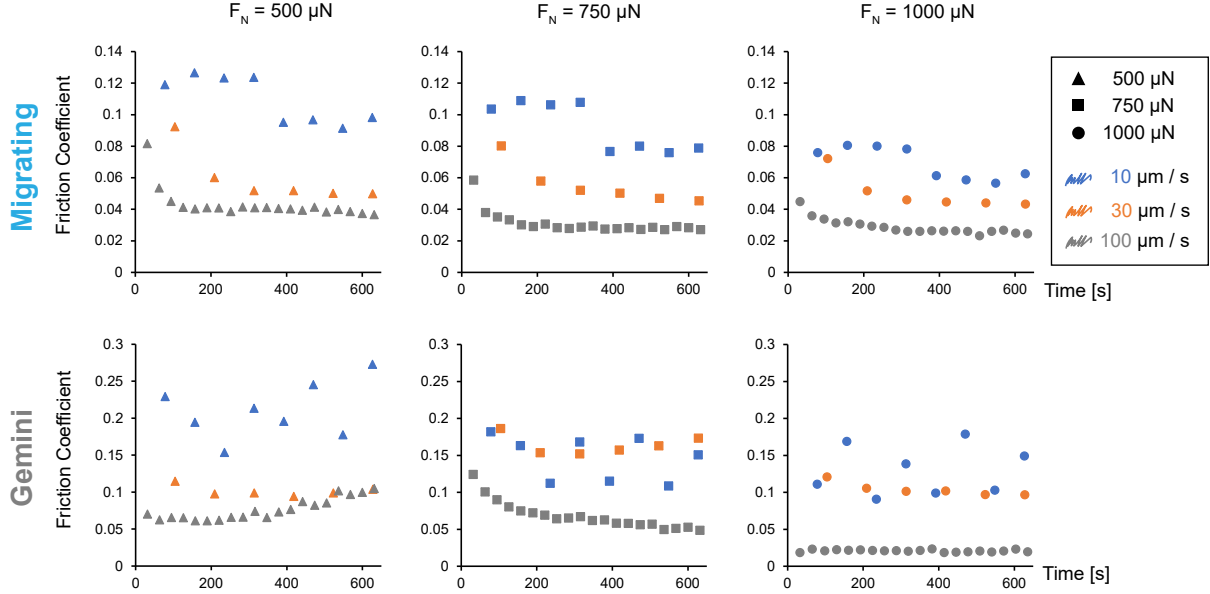


Figure 43: Composition 5 (R15). Friction coefficient versus time for applied normal loads of $[500, 750, 1000] \mu\text{N}$ at sliding speeds of $[10, 30, 100] \mu\text{m/s}$.

A.4 Special Compositions

A.4.1 M20,R100

A composition with $M = 20$ and $R = 100$ was polymerized against polystyrene to induce the gradient layer. Indentation testing was performed reaching a peak load of $3000 \mu\text{N}$. The stiffness of the composition was 65.4 kPa , which was larger than all but composition 4 of the original five compositions. Despite having $M = 20$, we see that crosslinker is still influential on the stiffness of the composition. The thickness of the gradient layer was $34.1 \mu\text{m}$, which produced a linear stiffness change per gradient thickness of $E/\Delta d = 1.92 \text{ kPa}/\mu\text{m}$. This was at least 23% lower than values for compositions 3-5. Sliding was conducted at speeds of $[10, 30, 100] \mu\text{m/s}$ under a normal load of $3000 \mu\text{N}$ for at least three minutes. The power fit exponent obtained from the shear stress versus the pseudo-Sommerfeld parameter was -0.212 . This says that the shear stress stability is higher, in large part due to the thickness of the induced gradient layer.

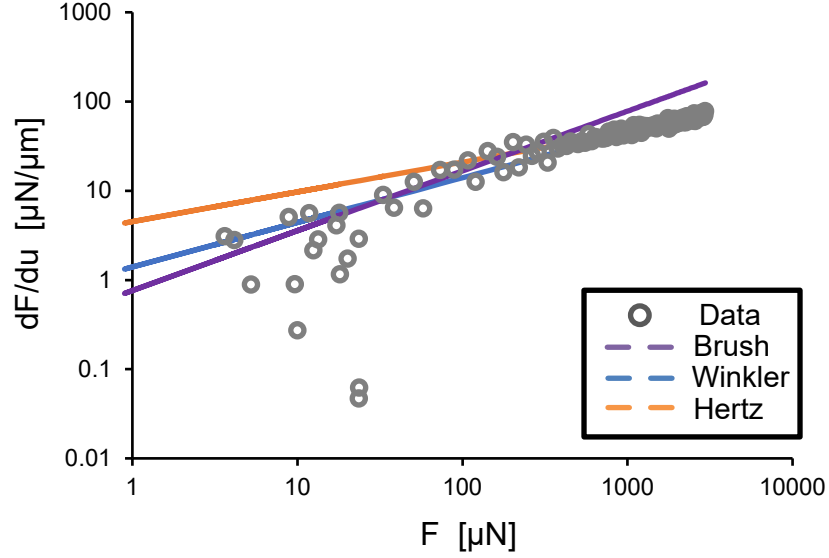


Figure 44: Migrating contact indentation with a maximum normal load of $3000\mu\text{N}$.

Elastic Modulus [kPa]	Gradient Layer Thickness Δd [μm]	Shear Stress Power Exponent
65.4	34.1	-0.212

Table 9: Contact areas of each sliding experiment could be consolidated to produce an average contact pressure across the entirety of each experiment. These pressures were generally smaller than the corresponding initial creep pressure, with their percent increase compared to the initial creep pressure shown in parentheses.