Swollen, surface-attached hydrogel layers in sliding contact exhibit unusual friction properties. To study this phenomenon, hydrogel layers covalently bonded to solid substrates are generated by C–H insertion crosslinking. Brief UV irradiation of thin layers of photoreactive prepolymers leads to simultaneous crosslinking of the polymer chains and attachment of the network to the substrate. As the surface-attached hydrogel layers can only swell perpendicular to the surface, and the polymer subchains on the two sides of the friction pair cannot interpenetrate for entropic reasons, adhesion in such friction pairs is negligible. In this work, the tribological behavior of surface-attached hydrogel pairs is investigated as a function of load and sliding velocity. It is observed that for very thin films, the indentation and accordingly the friction is a strong function of the film thickness and the role of the chain confinement on the lubrication of surface-attached hydrogels is discussed. A model for the friction mechanism of such systems is developed.

1. Introduction

All surfaces in the human body which are in sliding contact with each other are made of soft, permeable tissues composed of hydrophilic biopolymers. A key feature in such systems is the low friction that reduces wear and ensures a long lifetime of surfaces sliding against each other. Extremely efficient lubrication in the human body (e.g., synovial joints and the eyelid–cornea interface) has inspired many studies on the tribology of artificial materials, and notably, hydrogels to mimic such behavior. Lubrication phenomena occurring in soft tissues or hydrogels differ from the friction mechanism when two hard surfaces lubricated by a fluid are sliding against each other as in such soft systems, the interaction between the swollen solid matrix and the fluid inside this matrix plays an important role in the determination of the frictional behavior.

Understanding the lubrication of hydrogels has attracted growing attention as they show great potential for the implementation of water-based lubrication. So far, there is no general theory concerning the relationship between hydrogel mechanics and frictional behavior. This lack of understanding arises from the complexity of the friction in such systems, where frictional properties are controlled by parameters such as deformation rate, applied load, permeability, confinement, and nature of the contacting surfaces (i.e., hydrogel–hydrogel contact or hydrogel–stiff slider contact).

Various scenarios have been proposed to explain the lubrication occurring between a hydrogel and an impermeable hard slider. Gong et al. described the frictional behavior of a hydrogel sliding against a solid counter surface by a repulsion–adsorption model based on a polymer–solid interfacial interaction. If the interaction of the solid surface with the polymer network is weaker than that of the solvent with the polymer, the formation of an interfacial layer of solvent leads to a friction force generated by the viscous flow of the solvent. When a strong interaction between the polymer and the solid surface occurs, the friction of a gel is caused by the elastic deformation of the polymer chains. According to the proposed model, surface adhesion is dominant at low sliding velocities, and hydration lubrication becomes the major mechanism at high velocities.

Shoaib et al. considered friction in such systems to be the result of adhesive and viscous dissipation. Below a
transition speed, where the minimum friction happens, the friction is caused by stick-slip phenomena. However, above the transition speed, the stick-slip effect starts to diminish and the friction increases as a result of increased viscous dissipation. It has been shown that the transition speed can be estimated by means of the hydrogel viscoelastic properties and the relaxation properties of the polymer.\[26,32\]

However, the situation is completely different for two hydrogel coated layers in friction contact with each other.\[5\] Pitenis et al. reported two lubrication regimes for the lubrication of “Gemini” contact.\[132\] At slow sliding speeds, in their experiments, friction coefficients were independent of the speed. In this regime, the friction force has been attributed to the thermal fluctuation of the polymer chains. Whereas, at high sliding speeds, the polymer chains have to be stretched and relax along the sliding direction that gives rise to the friction force. They proposed that parameters to describe the friction of “Gemini” contact are elasticity, mesh size of the network, and relaxation time of the polymer chain.\[26,32\] Accordingly, the transition between the two regimes occurs when the relaxation time is equal to the time it takes for the polymer chains at the interface to displace one mesh size.\[3\]

A special case is when the polymer chains are covalently anchored to the substrate surfaces.\[12–40\] Chemical bonding of the gels to a substrate results in 1D swelling which makes them impermeable by the chains of the opposing layer.\[19,42\] If interpenetration with incoming macromolecules would occur, the chains would become even more stretched, leading to a stronger loss of entropy.\[19,40,41\] This exclusion effect of surface-attached hydrogels is surprisingly even stronger than that of polymer brushes (“entropic shielding”). As the distance from the substrate increases, the segment density profile of brushes possesses a parabolic form (probably with an exponential tail due to polydispersity). In surface-attached networks, the segment density profile stays constant up to a certain distance from the substrate and then decreases suddenly, resembling a delta function. The delta-like segment density profile and the resulting very small chain interdigitation of the surface-attached polymer networks suggest that surface-attached hydrogel layers can be attractive candidates to generate superlubricious surfaces.\[34,42,43\]

A similar effect is observed in the lubrication of brush-bearing surfaces where strong repulsive forces of entropic origin largely prevent the interpenetration of polymer chains on opposing surfaces. As two polymer brush-coated surfaces are becoming compressed, only very small interdigitation of the polymer chains happens.\[41\] Due to configurational entropy effects, it is energetically favored for the two brush coated layers rather to be compressed than to interdigitate.\[132,41\] The repulsive interactions help with the formation of a thin layer of fluid at the interface, which is easy to shear, leading to extremely low friction. However, at high pressures, significant interpenetration occurs and the frictional drag rises correspondingly.\[41\]

In the present work, photoreactive poly(dimethyl acrylamide-co-methacryloyloxy benzophenone) (PDMAA-co-MABP) is used to produce surface-attached hydrogel layers.\[19\] In order to understand the lubrication mechanism of surface-attached hydrogels, we first examine different properties of surface-attached hydrogels that can influence frictional properties such as elasticity, permeability, and adhesion. To study the lubrication properties, we record the adhesion of the two layers at low loading and low shear rate. The frictional behavior is measured at high pressures close to the pressure in synovial joints and rather high shear rates. For surface-attached layers, the layer thickness is also an important parameter. Therefore, we study the influence of layer confinement, which is the ratio between penetration depth and thickness, by performing friction tests as a function of film thicknesses. Finally, a model for the lubrication mechanism of surface-attached hydrogel pairs is developed.

2. Results

2.1. Gel Layer Generation and Characterization

To generate the surface-attached hydrogel layers, thin films of the photoreactive precursor–polymer are deposited on both sliding partners. The dry films are then illuminated for varying durations of time. During illumination, the benzophenone units in the polymer become activated into a biradicaloid triplet state and subsequently the polymer crosslinks through C,H insertion reactions and the forming network become simultaneously covalently attached to the self-assembled silane layers on the surfaces as described previously.\[39,40,43\] We focus here explicitly on neutral hydrogel layers to avoid any complication due to the presence of charges. The water content inside the network is obtained by measuring the thickness in the dry state and swollen state and the ratio of the wet thickness to the dry thickness is then defined as the swelling ratio. The recorded swelling ratios for the samples with 1% crosslinker density and crosslinked under the conditions given in the Experimental Section, range from 4.5 to 5.4, which means the samples contain 70–82% water.

The swelling pressure of the hydrogel layers in the swollen gels was determined by placing the gel in a syringe and pressing with a constant speed while the squeeze out of the water was recorded. The swelling pressure was determined to \( \approx 60 \) kPa and 90 kPa for PDMAA-1% MABP and PDMAA-5% MABP, respectively. Water permeation of the swollen hydrogels was measured by placing the bulk gel in a syringe and compressing it with a constant compression velocity. The compression force was recorded as a function of time, that is, as a function of the displacement using a tensile test machine. To eliminate the influence of the internal friction of the syringe, the test was also performed without hydrogel and the recorded force was subtracted.

Using the results of water permeation measurements and Darcy’s law\[45\] which has been developed to describe the permeability of a fluid through a porous media, the hydraulic conductivity can be obtained:

\[
Q = \frac{kA}{\eta h} p \tag{1}
\]

In this equation, \( Q \) is the total discharge, \( k \) is the permeability, \( A \) is the cross-sectional area, \( p \) is the applied pressure, \( \eta \) is the viscosity, and \( h \) is the thickness of the sample.
As the viscosity of water in the hydrogel is different from that of the free bulk water, we considered the hydraulic conductivity \( K = \frac{1}{\eta} \) to describe how easily water can be displaced through the hydrogel. Hydraulic conductivity is the property of the whole system, including the porous medium and the flowing fluid. The average hydraulic conductivity of PDMAA-1%MABP is \( 3.53 \times 10^{-14} \) m\(^4\)/Ns.

The elastic modulus of the swollen film was obtained by fitting the Hertz equation to the force–indentation curves as the behavior was purely elastic and the approach and retract curves overlap. The indentation depth for the elastic modulus measurements was \( \approx 250 \) nm, which means the penetration depth was only \( \approx 0.3 \) % of the film thickness. The average measured elastic modulus for PDMAA-1%MABP with a 74.6 \( \mu \)m thickness was 49 \( \pm \) 20 kPa.

2.2. Adhesion Induced Friction

The contribution of adhesion to the friction force was measured between PDMAA-1% MABP pairs. For this purpose, the friction force was measured at low load (3 mN) and low sliding speed (0.001 mm s\(^{-1}\)), where the hydrogels were only slightly compressed and the penetration depth was close to zero. In this case, the friction force was mainly caused by the adhesion between the two hydrogel layers. The friction test under the above-mentioned conditions (i.e., small load and slow sliding speed) shows that the adhesion component is very small, as the friction force was below the detection limit of the setup (<3 \( \mu \)N). By taking the detection limit of the measurement setup and the applied load into account, it can be concluded that the coefficient of friction is below 0.001 and accordingly, that the adhesion is extremely low.

2.3. Influence of the Film Thickness on Coefficient of Friction

The influence of normal load, sliding speed, and confinement on the friction behavior was investigated by recording friction force during sliding of four samples having varying thicknesses (35, 47, 52.8, and 74.6 \( \mu \)m in the swollen state). Friction tests were carried out for normal loads of 100, 300, 500, 700, and 1000 mN. For each normal load, the friction force was recorded for sliding speeds from 0.006 \( \mu \)N up to 1.4 mm s\(^{-1}\). The coefficient of friction (obtained by dividing friction force by normal force) is plotted versus the sliding speed in Figure 1. For the sample with a thickness of 35 \( \mu \)m, the friction coefficient decreased as the sliding became faster. For the samples with an intermediate thickness (47 and 52.8 \( \mu \)m), the friction coefficient decreased slightly and started to increase after assuming a minimum at a specific sliding speed. For the thickest sample, the coefficient of friction rose continuously.

To understand this difference in the behavior of thin and thicker films, we compared the penetration depth of two extreme cases (thinnest sample 35 \( \mu \)m and thickest sample 74.5 \( \mu \)m). For both samples, by increasing the sliding speed,
the penetration depth decreased rapidly. For values higher than a specific sliding speed; however, the penetration depth stayed almost constant. As can be seen in Figure 2, the recorded difference in penetration depth between the experiments with the maximum and minimum load was for the thin sample smaller than that of the thick sample.

2.4. Friction Force

The common observation in all plots of Figure 1 is the reduction of the coefficient of friction at higher normal loads. Clearly, hydrogels exhibit a deviation from Amontons law. This has been reported also for other systems and has been attributed to the influence of adhesion.[28] However, as shown in Section 3.2, for surface-attached layers, the adhesion is negligible. In Figure 3, the friction force is shown versus the normal load for the 35 and 74.6 µm thickness samples. The friction force appears as non-linear functions for both samples and at high loads, it reaches an almost constant value (asymptotic behavior) but with different slopes depending on the sliding speed.

For the thin sample (35 µm) at a low normal load, the friction force is almost the same regardless of the sliding speed. As the applied load is increased, the sliding speed dependence becomes stronger. In contrast to this behavior of the thin films, the friction force of the thicker sample seems to be only rather weakly dependent on the applied force.

To investigate the coupled influence of applied load and penetration depth, the maximum pressure is calculated by Hertz theory:

$$p_{\text{max}} = \frac{3F_n}{2\pi R \delta}$$  \hspace{1cm} (2)

Here, $F_n$ is the normal load, $R$ is the radius of the slider, and $\delta$ is the penetration depth. Then, in Figure 4a,b, the coefficient of friction is presented as a function of this calculated pressure for the thin (35 µm) and thick (74.6 µm) samples, respectively. In both situations, the coefficient of friction decreases as higher pressures are applied. This can be attributed to the rather weak increase in the penetration depth by increasing the pressure. However, looking at the data more closely, differences appear: for the thin sample (Figure 4a), the highest COF is observed at the lowest sliding speed. In contrast to this for the thick sample, the highest COF appears at high sliding speed (Figure 4b). Furthermore, it can be seen in Figure 4b that the coefficient of friction of the thick sample remains constant over a relatively large range of pressures for the slow sliding speeds. However, at higher velocities, the COF decreases very strongly with the applied pressure.

![Figure 2](https://example.com/fig2.png)

**Figure 2.** Penetration depth as a function of sliding speed in a scratch test for two samples with different thicknesses (35 and 74.6 µm).

![Figure 3](https://example.com/fig3.png)

**Figure 3.** Friction force versus applied load at different sliding speeds for samples with a thickness of a) 35 µm and b) 74.6 µm.
3. Discussion

3.1. Friction in Hydrogels

Hydrogels are composed of an immobile phase (polymer matrix) and a mobile phase (water). When hydrogels are compressed, the overall deformation is the result of polymer matrix deformation and simultaneous displacement of water out of the polymer network. The friction force between two contacting hydrogel layers is thus the coupled outcome of the interaction between the solid, swollen films on the opposing surfaces and the interaction between the solid phases and the fluid phase. If we consider the forces that contribute to the friction force when two hydrogel-coated surfaces slide against each other, the forces are (schematically shown in Figure 5):[33]

- Adhesion between the two opposing surfaces \( F_A \) is the result of van der Waals interactions[46] and entanglement[48] of polymer chains with those on the opposite contacting surfaces. Adhesion becomes the dominating component of the friction force at small applied load and penetration depth.
- Upon compression of the hydrogels, the polymer matrix undergoes deformation, resulting in a polymer deformation force \( F_p \). The force required to deform the polymer matrix is a function of the penetration depth and assumed to be independent of the sliding velocity. The overall deformation is caused by the difference between the swelling pressure of the gel and the applied pressure and yields an apparent elastic modulus. The apparent elastic modulus or contact stiffness is not a material constant but depends on the confinement and crosslinker density. The polymer deformability is a thermodynamic property. However, fast compression and relaxation can give it a strong kinetic component.
- Water as an incompressible fluid is squeezed out of the network under compression. The resistive force opposing the squeeze-out depends on the geometry of the slider, the penetration depth/confinement, and the viscosity of the water inside of the hydrogel or, in other words, the permeability of the network. The drag force \( F_D \) described here is the resistance of water in the network against movement.[47]

Accordingly, the overall friction force that can be written is:

\[
F_f = F_A + F_p + F_D
\] (3)

As observed in our experiments, the adhesion between two surface-attached gel layers is very small and does not contribute significantly to the friction force. The reason for such extremely low adhesion values can be that the opposing contact surfaces are mostly composed of water. As the polymer layers used in this study are strongly swollen and the polymer–water interactions are stronger than the polymer–polymer interactions, van der Waals forces between polymer chains do not contribute to the adhesion, especially as the polymers do not contain any charges \( \Delta H \approx 0 \). In addition, polymer interdiffusion cannot occur as (sub-)chains on the opposing gel layers cannot penetrate each other; thus, generating an easily shearable water-based interface (Figure 6). The reason for this is on the one hand that the already strongly stretched chains would become more strongly stretched when additional chains would come in, leading to a strong loss of entropy. On the other hand, the entropy of mixing for macromolecules is very small. This way the free energy would become positive when additional chains come in, rendering it energetically unfavorable. Therefore, at very small loads and slow sliding speeds, superlubricious
behavior is observed. This is in contrast to other studies where for contact between a solid slider and a hydrogel layer, the occurrence of stick–slip motion, especially at higher sliding speeds or applied loads has been reported. This demonstrates that hydrogel–hydrogel contact is very different from hydrogel–solid slider contacts.

At higher loads and higher sliding velocities, polymer deformation and drag forces are the main force components of the friction force. The main factor governing the friction force is the displacement of water. This depends on the indentation depth, or in other words, the water volume to be displaced and the rate of displacement, that is, the viscosity of the water in the gel. Both are directly related to the compressibility of the hydrogel layer where the polymer chains are deformed under the applied load. Upon compression, the surface-attached hydrogel layers become stiffer as a result of an increase in the segment density. This phenomenon renders the very thin polymer layers almost incompressible at high applied pressures. Accordingly, the friction force also assumes an almost constant value with increasing load, as can be seen in Figure 3. As a consequence of the only slightly increasing friction force with increasing normal load, the COF decreases with increasing load and becomes less dependent on the sliding speed, which is reported in Figure 1.

3.2. Lubrication Regimes

The lubrication mechanism of surface-attached hydrogels can be explained in light of the contributions to polymer deformation and drag forces, on the background of the fact that the contribution by adhesion is negligible. When the sliding is slow, the permeability is high (i.e., low dynamic viscosity of water in the network), or the sample thickness is small, the water in the network can be displaced easily, so there is not a significant resistance of water against sliding. Therefore, the dominant force at low sliding speed is that required for polymer deformation. This force depends on the penetration depth and apparent elastic modulus. As the sliding speed increases, the penetration depth becomes smaller and at values higher than a specific sliding speed, it depends only weakly on the sliding speed, as shown in Figure 2. This reduction in penetration depth leads to smaller friction force; and thus (as the normal force remains constant); smaller coefficient of friction.

Similar to the approach described for the time-temperature superposition, a universal behavior with the parameters that control the viscoelastic behavior of hydrogels, which are governed by gel compression and water transport, can be obtained. In order to displace water out of the compressed area, mechanical energy input is required. The energy input to displace water in hydrogels depends on the volume fraction of the polymer in the network and the compressibility of layers.

Accordingly, we take the thinnest sample (35 µm) as a reference and shift the curves measured for the other three samples (47, 52, and 74.6 µm) by a shift factor as schematically shown in Figure 7a and normalize the coefficient of friction and the sliding speed to the value corresponding to the minimum COF value (COF/COFmin). This way we obtain a master curve, which describes the friction behavior of hydrogel films of varying thickness under varying loads and at varying sliding speeds (Figure 7b). These master curves allow summarizing a couple of hundred friction experiments in one single curve.

3.3. Influence of Confinement

Penetration depth and thickness of the sample directly affect the contact stiffness or effective elastic modulus of the system. Upon compression, the segment density is increased locally and will relax more or less slowly. The size of the zone, which is influenced by the applied stresses, might be called relaxation zone. If the sample is thick in comparison to the penetration depth, the compressed layers can relax properly. In other words, when the relaxation depth is smaller than the film thickness (δr < h) (Figure 8b), no thickness dependence of the elastic modulus should be observed. In contrast to this, in a thin layer, the deformed network does not have the chance to relax properly and as the relaxation depth becomes larger than the film thickness (δr > h), a higher apparent modulus is observed (Figure 8a).

In order to investigate how the confinement (i.e., the presence of the substrate) affects the apparent elastic modulus, a stiffer colloidal cantilever (CP-NCH-PS-C-5 NanoandMore GmbH) with a spring constant of 42 N m⁻¹ was used so that indentation tests could be performed at higher penetration depths. In Figure 8c, the apparent elastic modulus is shown as a function of penetration depth for a thin sample (10.8 µm). When the penetration depth to thickness ratio (confinement) was below 3%, no influence of the underlying
rigid substrate was observed. However, the confinement effect became prominent beyond this point. For a penetration depth above 300 nm, the apparent elastic modulus increased as the indenter penetrated further. As the confinement reached 0.1, the apparent elastic modulus increased to \( \approx 3 \) MPa, which demonstrates clearly that the contact became progressively stiffer as the penetration depth to thickness ratio got larger. The contact stiffening of hydrogels as a result of increased penetration depth is in good agreement with a study by Simič et al.\(^4\)

Drag force starts to add up to the polymer deformation force when the slider moves faster than the relaxation rate of the compressed zone. In this case, water displacement becomes the limiting factor of the friction process. The dynamic viscosity of water in the gel imposes a resistance against sliding, which results in a higher friction force at higher sliding speed. As the applied load increases in this regime, the coefficient of friction becomes less speed-dependent because the water in the interface is becoming reduced.

### 3.4. The Characteristic Force Ratio

To describe the overall behavior and especially describe the influence of confinement onto the friction behavior, we must take the extent of compression onto the stiffness (modulus) of the gel and onto the viscosity of the water inside of the gel into consideration. These factors influence the shift factor used to describe all friction measurements by single master curves as shown in Figure 7b. In the following, we try to develop a characteristic parameter describing the friction regime:

In order to estimate the polymer deformation force, Hertz theory is helpful. This theory predicts the force required to compress the elastic material to specific penetration depth \( \delta \) by an indenter with radius \( R \). Hertz theory is originally developed for the static contact; thus, for the sliding contact, we assume that the lateral force component is proportional to the normal force component. Consequently, the polymer deformation force can be written according to:

\[
F_\text{deform} = \frac{2}{3} \pi R^2 F_n \delta
\]
In this equation, $E_{\text{eff}}$ is the effective elastic modulus or contact stiffness, which is a function of confinement and sliding speed. The penetration depth is also a function of sliding speed (see Figure 2) and confinement, which are included here in the form of the contact stiffness.

The drag force that is observed as a result of the fluid phase present in the polymer matrix can be assumed to be proportional to the component obtained from Darcy’s law for sliding contact which can be written as:

$$F_d \propto \frac{4}{3} E_{\text{eff}} R^{1/2} \delta^{3/2}$$  \hspace{1cm} (4)

Here, $v$ is the sliding speed, $K$ is the hydraulic conductivity ($k/\eta$), and $\delta$ is the penetration depth. Due to the effect of confinement, the equation for the drag force has to be modified. In comparison to a semi-infinite case, the hydraulic conductivity of the hydrogel will be continuously lowered with increasing compression. Stronger confinement will result in a higher segment density; and therefore, lower effective conductivity ($K_{\text{eff}}(v, \delta / R)$).

The ratio of the two forces ($F_d$ and $F_p$) gives a dimensionless characteristic number which describes the lubrication mechanism (analogous to the Sommerfeld number in the Strieber curve).[51,52] In some investigations on the lubrication of articular cartilage,[59] a characteristic number has been used to describe the lubrication mechanism, namely the Peclet number:[35,50,53] This number usually describes in fluidic systems, the ratio of the rate of advection to the rate of diffusion. This corresponds in the hydrogel system to drag (induced movement) and compression/relaxation, which is essentially a diffusion process. According to articular cartilage studies,[55] interstitial lubrication is dominant when $Pe \gg 1$. The load supported by the fluid phase becomes reduced as the fluid transport out of the tissue occurs. Therefore, most of the load is supported by the solid phase when $Pe \ll 1$.[15]

As shown in Figure 7a, the ratio of the two forces can determine the main component of friction. The minimum of the friction force occurs at different sliding speeds as the applied force is increased. We call the ratio of forces the “force characteristic number” which is proportional to the Peclet number defined in other studies.[9,15,50]

$$\frac{F_d}{F_p} \propto Pe = \frac{va}{K_{\text{eff}} E_{\text{eff}}}$$  \hspace{1cm} (6)

The force characteristic number is directly proportional to the sliding speed, contact radius while it is inversely proportional to hydraulic conductivity and contact stiffness. It should be noted that both hydraulic conductivity and elastic modulus are functions of confinement and sliding speed: $K_{\text{eff}} = f(v, \delta / R)$ and $E_{\text{eff}} = f(v, \delta / R)$. Therefore, the change in penetration depth. When the layer is strongly compressed and the sample is highly confined, the effective elastic modulus is higher than that of the sample with low confinement.

**4. Conclusion**

The lubrication process between two surfaces identically coated with surface-attached hydrogels follows a unique friction behavior. Frictional mechanism of such systems can basically be described by three main components: forces generated by adhesion, polymer deformation, and drag force. Sliding tests at very slow speeds and pull off experiments by AFM show that adhesion of the two surface-attached, water-swollen layers has a negligible contribution to friction (COF < 0.001). A key component is here the prevention of any interpenetration and interlocking of polymer chains from the two contacting networks, which has been shown in the past to be even stronger than that of polymer brushes. This is a consequence of the 1D swelling behavior of such surface-tethered layers.
Hence, the main components of the friction force when these layers are compressed by the load are polymer deformation and drag force induced by water displacement. The application of a load leads to the squeezing out of the water from the polymer layer and the deformation of the polymer network. Consequently, the friction force depends on the volume of the water that has to be displaced/squeezed out and how fast this water displacement can occur. As the deformation is limited, the penetration depth of the slider shows a less than linear scaling with the load. This in turn leads to an according change in the displaced volume and non-linear behavior of the friction force; and thus, a decrease of the friction coefficient with increasing load.

When the sliding velocity becomes higher, the rate of water displacement becomes the limiting factor. With increasing sliding speed, the drag increases strongly while the penetration depth decreases slightly, leading to an increase in friction and coefficient of friction. Thus, in many cases, a minimum in the friction coefficient is observed at intermediate velocities.

An important aspect for the frictional behavior of such surface-attached gels is the confinement of the polymer chains within the thin film during the contact. When the (swollen) layers are so very thin that the zone in which network compression occurs cannot relax completely throughout the film, the contact stiffness of the gels increases with decreasing thickness and increasing load, leading to lower penetration depths, smaller volumes of displaced water; and thus, reduced coefficients of friction. In a follow-up communication, we will report on how an increased swelling pressure in the gel influences the load-bearing capacity; and thus, the frictional properties of the hydrogels, and how the size of the slider influences the friction behavior.

5. Experimental Section

Sample Preparation: In order to produce hydrogels that are chemically bonded to a substrate, glass microscope slides (Duran Company) were functionalized with a monolayer of triethoxy benzophenone silane via dip coating. The dip coating was done in a 50 mm solution diluted in toluene using a Zwick Z 2.5 (Zwick GmbH) at a rate of 100 mm min\(^{-1}\). The substrates were annealed on a hot plate at 120 °C for 30 min. Subsequently, the functionalized glass substrates were coated with the polymer either by dip coating or by doctor blading. The maximum concentration used for dip coating was 100 mg mL\(^{-1}\) as higher concentrations result in rather inhomogeneous films. With the doctor blade, it is possible to use higher concentrations of 200 mg mL\(^{-1}\). In both coating methods, the coating was repeated several times to reach the desired thicknesses. The films were dried in between the coating steps under ambient conditions. The slides were subsequently crosslinked in a Stratagene UV Stratalinker 240 UV-chamber at a wavelength of 365 nm at a cumulative intensity of ~24 J cm\(^{-2}\). Afterward, the films were immersed in methanol for 24 h to extract uncrosslinked polymer chains from the network. As a slider, a glass lens with a radius of 25.94 mm (Edmund optics) was used which was coated via dip coating (100 mm min\(^{-1}\)) using 50 mg mL\(^{-1}\) polymer solution and crosslinked as described above.

Indentation Tests for Elastic Modulus Measurements: To determine the elastic modulus of the hydrogel samples, an atomic force microscope (IPK Nanowizard 4) was used in contact mode (force mapping mode). The AFM colloidal cantilevers (CP-CONT-PS-C-5, NanoAndMore Company) used in these measurements had a polystyrene bead with a diameter of 6.1 μm attached to them. In order to avoid local strains that exceeded the linear material regime and ultimately might have even plowed into the sample, a spherical indenter geometry was preferred. The obtained sensitivity and spring constant from the calibration of the cantilever were 33.2 nm V\(^{-1}\) and 0.42 N m\(^{-1}\), respectively.

Force-indentation curves were recorded on three different spots of a sample with 74.6 μm thickness on an area of 100 × 100 μm\(^2\). For each spot, 64 force-distance curves were recorded.

Permeation Measurements: Water permeation through the swollen hydrogels was measured by placing the hydrogel in a syringe with a diameter of 8 mm and measuring the water flow through the gel during compression. During this test, the compression velocity was 60 μm min\(^{-1}\) to maintain a constant flow rate. The compression force was recorded as a function of time and displacement using a tensile test machine Zwick Z 2.5 (Zwick GmbH) with a constant compression rate. To eliminate the influence of the internal friction of the syringe, the test was repeated without hydrogel and the recorded force was subtracted from the force recorded with the hydrogel. In these experiments, the hydrogel sample was kept always in contact with water in order to allow it to completely swell to an equilibrium state.

Friction Tests: Friction tests were performed using a CSM nanoscratch setup (Anton Paar GmbH) on a hydrogel coated glass slide using a glass slider with a radius of 25.94 mm which was also coated with a thin layer of the same hydrogel. All friction tests were carried out while slider and sample were immersed in water. During unidirectional sliding tests, the sample was moving perpendicular to the slider at a specific sliding speed and normal force. Each test was performed by applying a constant normal load and sliding speed. The friction force and penetration depth were recorded at a stroke length of at least three times longer than the contact diameter. The friction tests were carried out for five different contact forces (100, 300, 500, 700, and 1000 mN), and the sliding speed was altered for more than two decades in the range of 0.006–1.4 mm s\(^{-1}\). Before and after the sliding test, the profile of the sample along the sliding path was recorded to make sure that no permanent deformation occurred. Moreover, the sample surface was checked by optical microscopy after each test. To ensure that there was no extra force on the slider due to measurement in water in our friction tests, one test was performed in pure water and the force was below the detection limit of the nanoscratch test setup. The presented results are the average of three measurements on the same path of a sample.

Acknowledgements

Financial support from the German Research Council (DFG) through the International Research Training group (IRTG 1642) Soft Matter Science is gratefully acknowledged. Partial support by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany’s Excellence Strategy – EXC-2193/1 – 390951807 and by the ZEISS Research Cluster IPROM is gratefully acknowledged. The authors are thankful to the micro–nanomechanic platform of Institut Charles Sadron, Strasbourg.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.
Keywords
friction, hydrogels, lubrication, surface-attached networks

Received: July 19, 2022
Revised: September 19, 2022
Published online: October 28, 2022

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