ABSTRACT: Biological tissues subjected to rubbing, such as the cornea and eyelid or articular cartilage, are covered in brushy, hydrated mucous structures in order to reduce the shear stress on the tissue. To mimic such biological tissues, we have prepared polycrylamide (PAAm) hydrogels with various concentrations of un-cross-linked chains on their surfaces by synthesizing them in molds of different surface energies. The selected molding materials included hydrophilic glass, polyoxymethylene (POM), polystyrene (PS), polyethylene (PE), polypropylene (PP), and polytetrafluoroethylene (PTFE). After synthesis, demolding, and equilibration in water, the elastic modulus at the hydrogel surface decreased with increasing water contact angle of the mold. The softer, brushier surfaces did not completely collapse under compressive pressures up to 10 kPa, remaining better hydrated compared to their denser, cross-linked analogs. The hydrogels with brushier surfaces displayed an order of magnitude lower coefficient of friction than the cross-linked ones, which is attributed to the ability of their near-surface regions to retain larger amounts of liquid at the interface. The characteristic speed-dependent friction of the denser, cross-linked hydrogel surface is compared to the speed-independent friction of the brushy hydrogels and discussed from the perspectives of (elasto)hydrodynamic lubrication, permeability, and shear-induced hydrodynamic penetration depth.
their surfaces reduces interfacial friction. However, in order to create supportive substrates with increased amounts of water at the surface, brush-decorated hydrogels appear to be a key combination, which has already been successfully used in the contact-lens industry. For example, polyacrylamide (PAAm) chains grown from within the surface-near region of a denser polyhydroxyethyl methacrylate (PHEMA) hydrogel was shown to reduce friction by almost two orders of magnitude. Another way of creating lubricious hydrogels with a brushy, high-water-content surface layer is by the inhibition of polymerization close to the surface during the synthesis of a hydrogel. This can be achieved by oxygen inhibition as described recently. A straightforward way of creating brushy hydrogels was also introduced by Gong et al., where a polymer-depleted surface layer is formed during synthesis close to a hydrophobic molding material. They showed, for example, that a poly-2-acrylamido-2-methyl-1-propane-sulfonic acid (PAMPS) hydrogel synthesized against a Teflon or a polystyrene (PS) surface has significantly lower friction compared to the same hydrogel molded against hydrophilic glass. According to their theory and experiments, a homogeneously dense and cross-linked hydrogel surface is formed close to hydrophilic surfaces such a glass; however, the thickness of the soft surface layer increases when more hydrophobic molds are used. Despite the observed correlation between the hydrophobicity, or rather surface energy, of the molding material and the thickness of the sparser hydrogel surface, no systematic comparison between the mold surface energy, hydrogel surface properties, and friction has been shown.

In order to systematically study the link between the surface properties of brushy hydrogels and their friction, we have prepared polycrystalline hydrogels with different surface properties by synthesizing them against materials with different surface energies. We have measured water contact angles and performed infrared (IR) spectroscopy of the molding surfaces before and after polymerization to check for the presence of any chemical interactions during the synthesis. Elastic moduli of the obtained hydrogel surfaces were measured following swelling and equilibration in water. To check for the ability of the sparse surfaces to remain hydrated under load, polymer densities near the surface of different samples under compressive stress were compared by means of IR spectroscopy. Finally, the coefficient of friction was measured as a function of sliding speed for the different hydrogel surfaces sliding against an identical hydrogel surface in water. Self-mated hydrogels were chosen to bring the experimental sliding against an identical hydrogel surface in water. Self-function of sliding speed for the different samples under different conditions close to those of an actual biological system. Possible mechanisms for the substantial differences in friction of different hydrogel surfaces are presented and discussed.

MATERIALS AND METHODS

Materials. Acrylamide (AAm, Sigma-Aldrich, St. Louis MO, U.S.A., > 99%), N,N'-methylenebis(acrylamide) (bis-AAm, Sigma-Aldrich, > 99.5%), and 2,2'-azobisis(2-methylpropionamidine)-dihydrochloride (98%, Acros Organics, New Jersey) were used as monomer, cross-linker, and initiator, respectively, for the free-radical polymerization reaction. Milli-Q water was bubbled with nitrogen for 30–45 min in order to remove the oxygen and then used to dissolve 7.5 wt % of the monomer, 0.3 wt % of the cross-linker, and 0.3 wt % of the initiator by gentle stirring. The solution was carefully poured into molds to an approximate thickness of 3 mm. The molds, filled with the solution, were put in a UV cross-linker (Stratalinker UV Cross-linker 2400, Stratagene Corp., La Jolla, CA, U.S.A.) and polymerized for 7 min by a UV light with an intensity of about 1 mW/cm² at a wavelength of 365 nm. After polymerization, the gels were removed from the molds and immersed in a large amount of Milli-Q water for at least 48 h to remove unreacted species and allow swelling of the gels.

The materials of the molding surfaces were glass, polyoxymethylene (POM, Kern GmbH, Germany), polystyrene (PS, TTP Techno Plastic Products AG, Switzerland), polyethylene (PE, common low-density PE zip-loc bag, Minigrip, Alpharetta, GA, U.S.A.), polypropylene (PP, Entegris Inc., Billerica, MA, U.S.A.), and polytetrafluoroethylene (PTFE, Kern GmbH, Germany). For the glass and the PS mold, common glass and PS Petri dishes were used, respectively. The other materials (POM, PE, PP, and PTFE) were obtained as thin sheets that were glued into a PS Petri dish. All the molding materials were rinsed and sonicated for 10 min in isopropanol prior to use. Chemical structures and water contact angles of the selected materials are presented in Table 1.

| Material | Chemical structure | Contact Angle (°) | Surface Tension (mN/m) | Measured Surface Roughness Rq [nm] |
|----------|--------------------|------------------|------------------------|-----------------------------------|
| Glass    | SiO₂               | < 5              | 64                     | < 1                               |
| Polyoxymethylene (POM) | | 77               | 37                     | 18 ± 1                           |
| Polystyrene (PS) | | 87               | 34                     | 4 ± 1                             |
| Polyethylene (PE) | | 96               | 32                     | 35 ± 5                           |
| Polypropylene (PP) | | 102              | 31                     | 14 ± 6                           |
| Polytetrafluoroethylene (PTFE) | | 109              | 19                     | 300 ± 100                        |

*Presented surface-roughness values are averaged values obtained by atomic force microscopy in tapping mode and by optical profilometry (see Supporting Information).

Contact Angle. In order to check the initial state and any polymerization-induced degradation of the molds, the static water contact angles with the mold surfaces were measured with a NRI CA goniometer (model 100–00–230, Rame-Hart Inc., NJ, U.S.A.) before and after the polymerization. Before the contact-angle measurements, the molds were sonicated in isopropanol for 10 min. The contact angle was measured on both sides of the droplet on at least five different locations of the mold surface. The contact angle of glass was too low to be measured and was therefore assumed to be less than 5°.
degrees before and after the polymerization. All measurements were performed at a room temperature of 22 ± 1 °C.

**Infrared Spectroscopy.** In order to further verify the initial state of the molds and possible polymerization-induced degradation, attenuated-total-reflection Fourier-transform infrared (ATR-FTIR) spectroscopy of the mold surfaces was performed. The measurements were carried out with the Alpha-P ATR-IR (Bruker, Billerica, MA, U.S.A.), equipped with a diamond ATR crystal and a DTGS detector. The spectra were recorded from 500 to 4000 cm\(^{-1}\) with 64 scans at a resolution of 4 cm\(^{-1}\) for each sample.

ATR-IR spectra were also recorded for the surfaces of hydrogels molded against different molds as shown in Figure 1. Round discs of 10 mm diameter were punched out of 4–5 mm thick hydrogel slabs and attached to 10 mm flat-ended steel pins using a thin layer of cyanoacrylate-based superglue (Pattex, Henkel AG & Co. KGaA, Düsseldorf, Germany). The pins with the gels were then pressed with the side of interest against the diamond ATR crystal using the normal loads of 0.1, 0.5, and 1 N, which corresponds to contact pressures in the range of 1 to 14 kPa. Before each measurement, the ATR crystal was cleaned with isopropanol and the background was recorded in pure Milli-Q water. The measurements were repeated three times at each condition and then averaged.

**Nanoindentation.** Nanoindentation experiments were performed on hydrogel surfaces that were molded against the selected molds, using an atomic force microscope (AFM, MFP-3D, Asylum Research, Santa Barbara, U.S.A.). The Sader method was applied to determine using an atomic force microscope (AFM, MFP-3D, Asylum Research, Santa Barbara, U.S.A.), equipped with a diamond ATR crystal and a DTGS detector. The spectra were recorded from 500 to 4000 cm\(^{-1}\) with 64 scans at a resolution of 4 cm\(^{-1}\) for each sample.

The spectra were recorded from 500 to 4000 cm\(^{-1}\) where

\[ L \] with a radius of 11 μm (GP0083, Whitehouse Scientific, Waverton, UK) with a radius of 11 μm was glued to the end of the tipless cantilever with a 2-component epoxy resin adhesive (UHU GmbH, Germany) by means of a home-built micromanipulator. The spring constant was then corrected for the colloid position on the cantilever as

\[ k' = k \left( L / L' \right)^3 = 1.98 \text{ N/m}, \]

where \( L \) is the cantilever length and \( L' \) is the distance from the base of the cantilever to the colloid position.\(^{24}\) Indentation speed was set to 1 μm/s, which was slow enough to avoid significant contributions from the visco- or poro-elasticity of the hydrogel samples. The very minor hysteresis between the approach and retraction parts of the indentation reflects the insignificance of such contributions. All measurements were performed at room temperature of 22 °C ± 1 °C with samples completely immersed in milli-Q water in order to minimize any capillary forces between the probe and the investigated surfaces. Prior to the measurements, the optical-lever sensitivity \( S \) was calibrated by pressing the probe against a hard surface of a silicon wafer in water to obtain the relation between the cantilever deflection and the photodiode signal. An acquisition rate of 2000 Hz was used. Force maps of 3 × 4 force curves were obtained over an area of 40 × 40 mm\(^2\) at three different locations on a sample.

For the data analysis, the background slope and the offset that were calculated for the signal away from the surface were subtracted from the entire curve. The root-mean-square value of the noise away from the surface was determined to be \( \sigma \approx 50 \text{ pN} \). The exact contact point was therefore determined on the approach curve as the last data point lying within 2\( \sigma \) from the zero-force line. The indentation depth was calculated as \( d = Z - \theta = Z - SU \), where \( Z \) is the measured piezo position, \( \theta \) is the cantilever deflection, \( S \) is the optical sensitivity, and \( U \) is the measured photodiode signal. The force was calculated as \( F = k \theta \), and the results are presented as force indentation (\( F-d \)) curves.

**Friction.** The coefficient of sliding friction of the gels was measured using a tribometer (CSM, Needham, MA, U.S.A.) in reciprocating configuration. The schematic of the friction experiments is shown in Figure 2. Similarly to the FTIR experiments, flat discs of 10 mm diameter were punched out of 4–5 mm-thick hydrogel slabs and glued to flat-ended steel pins of the same diameter. The pin with the hydrogel was pressed against the surface of a larger slab of a similar hydrogel that was glued into a polystyrene Petri dish. In this way, the hydrogel surfaces that were synthesized against the same molding surface were brought into contact. The normal load was set to 0.5 N (6 kPa) and the range of sliding speeds was 0.1–15 mm/s in the middle of the stroke.

The friction loop appeared symmetrical, indicating only negligible transient effects upon reversal of the sliding motion (Figure S3 in Supporting Information). The average friction coefficient was calculated over the last 5 cycles. The tests were performed at 22 °C ± 1 °C with samples fully immersed in pure milli-Q water.

**RESULTS AND DISCUSSION**

**Contact Angle.** Figure 3 shows water contact angles of the molding surfaces according to the literature\(^{21}\) as well as before

---

**Figure 1.** Schematic of ATR-IR experiments with hydrogels showing a flat hydrogel disc attached to a flat stainless-steel pin and pressed against a diamond ATR crystal at various loads. The intensity of the characteristic peaks in the IR spectrum depends on the polymer density close to the hydrogel surface and the applied load.

**Figure 2.** Schematic of the friction experiments, where a flat hydrogel pin of 10 mm in diameter was sliding reciprocally over a larger flat piece of a hydrogel with a matching surface. The normal load was 0.5 N (6 kPa) and the range of sliding speeds was 0.1–15 mm/s in the middle of the stroke.
and after the polymerization of the gels. The obtained contact angles before the polymerization agreed with the literature data, confirming the chemical structures and cleanliness of the molding surfaces in this work. The water contact angles also did not change significantly after the free-radical polymerization of the gels in the molds, which indicates that no significant chemical interaction with the mold occurred during the polymerization. Similar observations were also made by Gong et al.,18,19 who proposed that the heterogeneous polymerization at the surface occurs due to the differences in surface tension of the polymerizing solution and the molding surface. According to Gong et al., the surface-tension difference increases during the polymerization. Due to the higher surface tension of the polymer solution compared to the monomer solution, the entangled polymer network is pushed away from the surface by osmotic pressure and replaced by a monomer-depleted solution close to the surface in order to decrease the Gibbs free energy of the system. This causes a formation of a loose polymer network close to the surface without any chemical interactions with the molding surface itself. Our results cannot confirm Gong’s proposed mechanism, although they are consistent with the absence of chemical interaction and show that the molds can be reused after the polymerization process.

Infrared Spectroscopy. To further verify the absence of chemical interactions of the polymerizing solution with the molds, ATR-IR spectra of the molding surfaces were recorded before and after the polymerization. Figure 4 shows the corresponding spectra for all the polymeric molds. The obtained spectra match the expected spectra of the used molds and show no significant changes following polymerization of the hydrogels. The results agree with those of the water-contact-angle analysis presented above.

Figure 5a shows a characteristic transmission IR spectrum of a glass-molded PAAm hydrogel surface pressed against an ATR-IR crystal with a pressure of about 8 kPa. Since pure water was used for the background spectrum, the broad peak that corresponds to the water O−H stretch at 3700–3000 cm$^{-1}$ should appear above 100% transmission due to the lower amount of water within the hydrogel compared to pure water. However, the peak is superimposed with symmetric and asymmetric N−H stretching vibrations of the acrylamide in the...
same region. More intense peaks appear in the C=O stretching region, with the amide I band at about 1660 cm\(^{-1}\) and the amide II band at about 1610 cm\(^{-1}\) (N–H bend) being the most pronounced (Figure 5b).

In order to evaluate the selected peak intensities obtained from different samples and at different contact pressures, the amide I and amide II bands were deconvoluted using a linear combination of Gaussian and Lorentzian functions. The integrated area of the deconvoluted amide II (N–H bending) band positioned at 1610 cm\(^{-1}\) is presented for variously molded gels as a function of contact pressure in Figure 6. The results for amide I (C=O) band were qualitatively similar and only differed in their peak intensities. Peak intensities correspond to the amount of polymer concentration within the first few microns of a hydrogel surface. Therefore, the higher the intensity, the denser the polymer network at the hydrogel surface. All the other more hydrophobically molded hydrogels had much sparser polymer networks at the surface. As expected from the theory of heterogeneous polymerization presented by Gong, the hydrogel molded against the most hydrophilic (glass) mold showed the highest polymer concentration at the surface. All the other more hydrophobic molds resulted in much sparser polymer networks at the surface. Small differences in water contact angles (surface tensions) of the hydrophobic, polymeric molds resulted in rather small differences in hydrogel polymer densities. However, hydrogel surface polymer density tended to decrease with decreasing surface tension of the mold. For example, POM with its relatively high surface tension yielded a denser hydrogel surface compared to the more hydrophobic molds such as PP or PTFE.

Increasing the contact pressure from less than 2 kPa to more than 13 kPa resulted in an increase in peak intensities and thus hydrogel polymer density in all the cases, which is due to the compression of the hydrogels and migration of water from the surface region. Therefore, all the hydrogel surfaces were observed to densify upon compression. Interestingly, however, none of the hydrogel surfaces showed a complete exudation of water from the surface region even at the highest applied contact pressure. In the case of complete dehydration, the intensity of the peaks corresponding to the PAAm polymer would have increased well above the intensities observed for the glass-molded gel, which are assumed to represent the bulk of an equilibrated, swollen gel. This means that the affinity to water was sufficient to keep even the sparsest hydrogel surfaces relatively well hydrated at these contact pressures. Therefore, even at increased contact pressures, the water content was higher for the gels that were molded against more hydrophobic molds. This is an important finding also for the tribological tests that were performed at a contact pressure of about 6 kPa, which is close to the middle of the contact-pressure range used in the ATR-IR experiments.

**Nanoindentation.** Figure 7a shows force–distance curves obtained during the colloidal-probe nanoindentation of variously molded hydrogel surfaces in water. The glass-molded gel showed the stiffest response with the shape of the force–distance curve following Hertzian contact mechanics, indicating a homogeneous structure right from the surface. The other hydrogels showed much softer response at the initial indentation that then gradually stiffened with increasing indentation. The shaded area in Figure 7a depicts the range of indentation depths within the first 2 \(\mu m\) that was used for the analysis of the elastic modulus. Hertzian contact mechanics
were used to fit the indentation part of the force–distance curves in that range, and the obtained elastic moduli are shown in Figure 7b as a function of the mold contact angle. The glass-molded sample had the highest elastic modulus. For the hydrogels molded in more hydrophobic molds, the elastic modulus at the surface decreased with increasing contact angle (decreasing surface tension) of the molds. The obtained elastic moduli of the hydrogel surfaces produced in molds with water contact angles above 87° or surface tension below 34 mN/m were below 1 kPa and therefore more difficult to differentiate. However, looking at the force–distance curves and comparing indentation depths at a certain force, it appears that the thickness of the soft top layer increased with decreasing mold surface tension. The only exception seems to be the PS mold, which, despite having a surface tension that falls in the middle of all the molds used, yielded the softest and likely also the thickest hydrogel surface layer. Since the Hertzian fit to the data is an integrated value over a gradient of properties, the low elastic modulus in this case could be due to a different shape of the density gradient of the PS-mold hydrogel surface. The molds had indeed substantially different surface roughness values, which could affect the surface of the hydrogels to some extent. One could assume that increasing the surface roughness of a mold would increase the surface roughness of a hydrogel, thus making it appear softer upon indentation. In our case, however, the glass and PS molds had the lowest and comparable roughness values but yielded hydrogels with the most different surface moduli. Besides, the PS mold was substantially smoother than any other polymeric mold in this work and still yielded the softest hydrogel surface. Moreover, the elastic moduli were determined from a depth range that greatly exceeds the surface roughness values. Therefore, mold surface roughness should have only a negligible effect on the surface modulus of the hydrogels and we believe the surface chemistry is the dominant parameter affecting hydrogel surfaces in our case.

Friction. Figure 8 shows the coefficient of friction as a function of sliding speed for variously molded hydrogel surfaces sliding against an identical hydrogel surface in a flat-pin-on-disc configuration. Figure 8b is a full logarithmic plot of Figure 8a to highlight the speed-dependent scaling of friction and for reasons of clarity in the low-friction regime.

Glass-molded hydrogel surfaces displayed the highest friction over the whole range of sliding speeds ranging from relatively low values of ~0.06–0.08 at low sliding speeds to over 0.5 at the highest sliding speed. The speed-dependent friction increase scaled with sliding speed to the power of 1/2 (Figure 8b). Similar speed-dependent behavior was also observed in other recently published papers. According to de Gennes, the mean hydrodynamic film thickness should scale with sliding speed as $h \propto U^{0.5}$. The above equation would thus yield a coefficient of friction that scales as $\mu \propto U^{0.5}$, as also observed in this work.

The isoviscous-elastic case of the soft EHL theory, developed by Hamrock and Dowson, returns film thicknesses in the order of hundreds of nanometers and thus friction coefficient values that are significantly below our measured values, as also observed by Uruèña et al. According to the soft EHL theory, the film thickness should scale with sliding velocity as $h \propto U^{0.65}$. Considering this relationship, the coefficient of friction would then scale with speed as $\mu \propto U^{0.35}$. This is indeed less than the observed power of 1/2; however, the difference could also come from the viscoelastic and/or poro-elastic dissipation of the migrating deformation. Poroelastic flow due to deformation could also contribute to the speed-dependent friction increase for the hydrogel with the denser surface structure. However, for the different surface layers, as in our case, the exact contributions of the mentioned dissipation phenomena remain unclear.

Two POM-molded hydrogels in contact, however, had in general lower friction than the glass-molded hydrogels. At the same time, the friction showed a smaller increase with increasing sliding speed (i.e., $\mu \propto U^n$; $n \sim 0.33$) compared to the glass-molded gel (Figure 8). The lower friction could be explained by the lower amount of polymer in contact
compared to the case of the glass-molded hydrogel, as shown in Figure 6. The sparser surface of the POM-molded hydrogel, and thus the larger pore size, could allow for an enhanced poroelastic diffusion of water close to the surface driven by the interfacial shear. Such hydrodynamic penetration depth would effectively increase the region of “interfacial” shearing of water resulting in a speed-dependent increase in shear could cause the hydrodynamic penetration depth to increase with sliding speed, which would result in a friction coefficient with a lower degree of speed dependency \( (\mu \propto U^n; n < 1/2) \) compared to the glass-molded case.

All the other hydrogel surfaces that were molded against more hydrophobic molds (i.e., PS, PE, PP, PTFE) showed even lower coefficients of friction, which were in the range of \( \sim 0.01-0.05 \). The friction of all these hydrophobically molded hydrogels was almost independent of the sliding speed. Considering the even sparser surface structures of these gels compared to the glass- and POM-molded hydrogels, the shear-induced increase of the hydrodynamic penetration depth could be almost linearly proportional to the sliding speed \( h \propto f(U) \sim U \), which would yield a more speed-independent coefficient of friction \( \mu \propto U/h \sim U^0 \).

According to these results, hydrogels with a dense, cross-linked surface appear to behave like an impermeable body, resulting in a speed-dependent friction increase that follows the common (elasto)hydrodynamic theory (Figure 9). Sparser, brushy hydrogel surfaces may allow shear-driven diffusion within the soft surface layer, increasing the hydrodynamic penetration depth and thus reducing the speed dependency of the friction coefficient. However, in order to better verify these statements, further experiments are needed.

**CONCLUSIONS**

PAAm hydrogels have been synthesized by free-radical polymerization in molds of various surface energies, ranging from hydrophilic to hydrophobic. We have confirmed that the mold material indeed affects the surface of a hydrogel. This appears to occur in the absence of a chemical interaction that would alter the structure of the mold. Hydrophilic molds such as glass resulted in the densest surface structure of a hydrogel, whereas the hydrogel surfaces became softer and sparser with the use of more hydrophobic molds such as PS, PE, PP, and PTFE. Although the elastic modulus at the hydrogel surface in principle decreased with increasing hydrophobicity of the molds, the water contact angle and thus the surface tension or the surface energy seem not to be the only important parameters. We have also shown that sparser and presumably brushier hydrogel surfaces do become compressed but do not collapse completely under contact pressures up to 10 kPa. Below this contact pressure, the polymer density near the surface of the brushy hydrogel remains lower compared to that near the densest, glass-molded hydrogel surface. Such different hydrogel surfaces also present different frictional behaviors during sliding against matching surfaces at nominal contact pressures of about 6 kPa in water. The densest, glass-molded hydrogel surfaces showed the highest coefficients of friction, which increased with sliding speed to the power of 1/2. Sliding faster, brushier hydrogel surfaces reduced the friction and progressively decreased the speed dependency. While the polymer density in a sliding contact might affect the friction at low sliding speeds, the fluid-film formation presumably dictates the friction at higher sliding speeds. The friction behavior of the dense, glass-molded hydrogel surface could be explained in terms of the (elasto)hydrodynamic lubrication theory, assuming impermeable surfaces. The decrease in speed dependency with decreasing surface polymer density could be a consequence of the progressively increasing hydrodynamic penetration depth within the sparser surface.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b01636.

Topographic images of mold surfaces and representative friction loops (PDF)

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: rok.simic@mat.ethz.ch.

ORCID

Kaihuai Zhang: 0000-0002-7353-4180
Nicholas D. Spencer: 0000-0002-7873-7905
Rok Simic: 0000-0002-5258-6192

Notes

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This project has received funding from the European Research Council (ERC) under the European Union’s Horizon 2020 research and innovation programme (grant agreement No 669562). The financial support of the ETH Research Commission and the ETH Foundation are also gratefully acknowledged. The authors also want to thank Dr Kirill Feldman for his suggestions on mold selection and preparation. The authors would also like to express their gratitude to Dr Juliette Cayer-Barrioz and Dr Denis Mazuyer for the fruitful discussions about hydrodynamic friction.
REFERENCES

(1) Bansil, R.; Stanley, E.; LaMont, J. T. Mucin biophysics. Annu. Rev. Physiol. 1995, 57, 635–657.

(2) Pitenis, A. A.; Uruēña, J. M.; Hormel, T. T.; Bhattacharjee, T.; Niemi, S. R.; Marshall, S. L.; Hart, S. M.; Schulze, K. D.; Angelini, T. E.; Sawyer, W. G. Corneal cell friction: survival, lubricity, tear films, and mucin production over extended duration in vitro studies. Biotribology 2017, 11, 77–83.

(3) Lee, S.; Spencer, N. D. Sweet, hairy, soft, and slippery. Science 2008, 319, 575–576.

(4) Crockett, R.; Grubelnik, A.; Roos, S.; Dora, C.; Born, W.; Trosler, H. Biochemical composition of the superficial layer of articular cartilage. J. Biomed. Mater. Res., Part A 2007, 82, 958–964.

(5) Müller, M.; Lee, S.; Spikes, H. A.; Spencer, N. D. The influence of molecular architecture on the macroscopic lubrication properties of the brush-like co-polylelectrolyte poly (L-lysine)-g-poly (ethylene glycol)/(PLL-g-PEG) adsorbed on oxide surfaces. Tribol. Lett. 2003, 15, 395–405.

(6) Drobek, T.; Spencer, N. D. Nanotribology of surface-grafted PEG layers in an aqueous environment. Langmuir 2008, 24, 1484–1488.

(7) Lee, S.; Spencer, N. D. Aqueous lubrication of polymers: Influence of surface modification. Tribol. Int. 2005, 38, 922–930.

(8) Klein, J.; Kamacheva, E.; Mahalu, D.; Perahia, D.; Fetters, L. J. Reduction of frictional forces between solid surfaces bearing polymer brushes. Nature 1994, 370, 634–636.

(9) Klein, J. Molecular mechanisms of synovial joint lubrication. Proc. Inst. Mech. Eng., Part J 2006, 220, 691–710.

(10) de Gennes, P. Conformations of polymers attached to an interface. Macromolecules 1980, 13, 1069–1075.

(11) Rudy, A.; Kulia, S.; Schuler, J.; Sue, J.; Schulze, K. D.; Stewart, D.; Angelini, T.; Sawyer, W.; Perry, S. S. Lubricious hydrogel surface coatings on polydimethylsiloxane (PDMS). Tribol. Lett. 2017, 65, 3.

(12) Uruēña, J. M.; Pitenis, A. A.; Nixon, R. M.; Schulze, K. D.; Angelini, T. E.; Sawyer, W. G. Mesh size control of polymer fluctuation lubrication in gemini hydrogels. Biotribology 2015, 1, 24–29.

(13) Pitenis, A. A.; Sawyer, W. G. Lubricity of High Water Content Aqueous Gels. Tribol. Lett. 2018, 66, 113.

(14) Roba, M.; Duncan, E.; Hill, G.; Spencer, N.; Tosatti, S. Friction measurements on contact lenses in their operating environment. Tribol. Lett. 2011, 44, 387.

(15) Dunn, A. C.; Uruēña, J. M.; Huo, Y.; Perry, S. S.; Angelini, T. E.; Sawyer, W. G. Lubricity of surface hydrogel layers. Tribol. Lett. 2013, 49, 371–378.

(16) Pitenis, A. A.; Uruēña, J. M.; Nixon, R. M.; Bhattacharjee, T.; Krick, B. A.; Dunn, A. C.; Angelini, T. E.; Sawyer, W. G. Lubricity from entangled polymer networks on hydrogels. J. Tribol. 2016, 138, 042102.

(17) Zhang, K.; Simic, R.; Yan, W.; Spencer, N. D. Creating an Interface: Rendering a Double-Network Hydrogel Lubricious via Spontaneous Delamination. ACS Appl. Mater. Interfaces 2019, 11, 25427–25435.

(18) Gong, J. P.; Kii, A.; Xu, J.; Hattori, Y.; Osada, Y. A possible mechanism for the substrate effect on hydrogel formation. J. Phys. Chem. B 2001, 105, 4572–4576.

(19) Kii, A.; Xu, J.; Gong, J. P.; Osada, Y.; Zhang, X. Heterogeneous polymerization of hydrogels on hydrophobic substrate. J. Phys. Chem. B 2001, 105, 4565–4571.

(20) Gong, J. P.; Kurokawa, T.; Narita, T.; Kagata, G.; Osada, Y.; Nishimura, G.; Kinjo, M. Synthesis of hydrogels with extremely low surface friction. J. Am. Chem. Soc. 2001, 123, 5582–5583.

(21) Critical surface tension and contact angle with water for various polymers, https://www.accudynetest.com/polytable_03.html, (accessed Feb 5, 2019).

(22) Sader, J. E.; Chon, J. W.; Mulvaney, P. Calibration of rectangular atomic force microscope cantilevers. Rev. Sci. Instrum. 1999, 70, 3967–3969.

(23) Cannara, R. J.; Eglin, M.; Carpick, R. W. Lateral force calibration in atomic force microscopy: A new lateral force calibration method and general principles for optimization. Rev. Sci. Instrum. 2006, 77, 053701.

(24) Shaw, A. J.; Collins, M. J.; Davis, B. A.; Carney, L. G. Eyelid pressure and contact with the ocular surface. Invest. Ophthalmol. Visual Sci. 2010, 51, 1911–1917.

(25) Pitenis, A.; Uruēña, J.; Schulze, K.; Nixon, R.; Dunn, A.; Krick, B.; Sawyer, W.; Angelini, T. Polymer fluctuation lubrication in hydrogel gemini interfaces. Soft Matter 2014, 10, 8955–8962.

(26) Shoabi, T.; Heintz, J.; Lopez-Berganza, J. A.; Muro-Barrios, R.; Egner, S. A.; Espinosa-Marzal, R. M. Stick–slip friction reveals hydrogel lubrication mechanisms. Langmuir 2018, 34, 756–765.

(27) Kurokawa, T.; Tominaga, T.; Katsuyama, Y.; Kuwabara, R.; Furukawa, H.; Osada, Y.; Gong, J. P. Elastic–Hydrodynamic Transition of Gel Friction. Langmuir 2005, 21, 8643–8648.

(28) de Beer, S.; Miser, M. H. Friction in (im-)miscible polymer brush systems and the role of transverse polymer tilting. Macromolecules 2014, 47, 7664–7673.

(29) Uruēña, J. M.; McGhee, E. O.; Angelini, T. E.; Dowson, D.; Sawyer, W. G.; Pitenis, A. A. Normal load scaling of friction in gemini hydrogels. Biotribology 2018, 13, 30–35.

(30) Kagata, G.; Gong, J. P.; Osada, Y. Friction of gels. 6. Effects of sliding velocity and viscoelastic responses of the network. J. Phys. Chem. B 2002, 106, 4596–4601.

(31) De Gennes, P.-G.; Brochard-Wyart, F.; Quéré, D. Capillarity and wetting phenomena: drops, bubbles, pearls, waves. Springer Science & Business Media: 2013.

(32) Hamrock, B. J.; Dowson, D. Elastohydrodynamic lubrication of elliptical contacts for materials of low elastic modulus I—fully flooded conjunction. J. Lubr. Technol. 1978, 100, 236–245.

(33) Delavoipie, J.; Tran, Y.; Verneuil, E.; Chateauminois, A. Poroelastic indentation of mechanically confined hydrogel layers. Soft Matter 2016, 12, 8049–8058.

(34) Delavoipie, J.; Tran, Y.; Verneuil, E.; Heuttefeu, B.; Hui, C. Y.; Chateauminois, A. Friction of poroelastic contacts with thin hydrogel films. Langmuir 2018, 34, 9617–9626.

(35) Reale, E. R.; Dunn, A. C. Poroelasticity-driven lubrication in hydrogel interfaces. Soft Matter 2017, 13, 428–435.