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Summary

All surfaces in the human body which are frequently in sliding contact with each other are made of soft, permeable tissues. To reduce wear and ensure that they last for a lifetime they evolved to exhibit low friction. The common feature of such interfaces is that they are composed of hydrophilic biopolymers. This has inspired many studies on tribology of tissues, artificial materials, and notably hydrogels. Most of the studies performed so far were conducted using hard sliders and a soft tissue or hydrogel sample as a countersurface, whereas both sides of the contact in the lubricated surfaces in the body are made of soft, permeable surfaces.

It has been proposed that friction of twinned bulk hydrogel samples (“*Gemini*” contact) where the two contacting surfaces are identical is controlled essentially by parameters such as the energy of hydration and the crosslink density (and in case of polyelectrolytes the effective charge density in gel). These parameters govern the polymer network mesh size which in turn determines the permeability and, to some extent, also the stiffness of the hydrogels [1–3]. It has been shown that the frictional behavior of “*Gemini*” interfaces changes by varying the sliding speed. The transition in frictional properties is related to the polymer relaxation time and the ratio of the mesh size to the sliding speed [4]. Most of the measurements in the previous studies have been done in a low-pressure range below 100 kPa since the soft hydrogel samples might be damaged under higher pressures.

To ensure the long term stability of the polymeric coatings, it is often desirable to attach the polymers to the surfaces through covalent bonds. Chemically attached polymers are stable even in good solvents and at high ionic strengths, while a physisorbed polymer layer could be dissolved or detached [5].

In this thesis, we investigated the lubrication between the surfaces coated with surface-attached hydrogels. In such a system, interpenetration between the two counter surfaces is prevented due to entropic shielding and size exclusion, which differentiates surface-attached gels from bulk gels. This concept is not unlike that of polymer brushes that have been recently intensely investigated in tribology [6–8]. The ultra-low friction between two brush coated surfaces arises from very small interpenetration due to an unfavorable increase in segment-segment repulsions when the polymer brush layers are compressed. Polyelectrolyte brushes, however, are unstable as they are endangered against entropic death [9,10].

Compared to such brushes, the profile density of surface-attached hydrogels decreases sharply within a very small range at the outer periphery of the layer so that the segment density decreases like a delta-function [3]. Thus surface-attached polymer networks exclude chains coming from solution in a much stronger way. Smaller interpenetration, the possibility to create thicker layers and better mechanical stability make surface-attached hydrogels attractive candidates for tribological studies.

Frictional behavior between two hydrogel coated surfaces can basically be described by three main components: forces generated by adhesion, polymer deformation, and drag. Pull-off tests with the AFM and a nano-indenter showed that when two highly hydrated hydrogel coated surfaces were in contact, adhesion was extremely low and it was not recordable with either of the aforementioned techniques. To study the adhesion induced friction, friction tests were carried out in sliding experiments at a very low sliding speed (0.001 mm/s) under a small load (3 mN), where the deformation was mostly zero. These tests with the nanoscratch setup confirmed that adhesion can be considered to have a negligible contribution to friction (COF <0.001). Hence, the main components of the friction force when these layers are strongly compressed are the polymer deformation force and the drag force. The application of a load leads to the squeezing out of the water from the polymer layer and the deformation

of the polymer network. The friction force depends on the volume of the water that has to be displaced, which in turn depends on the extent of the water squeeze out. The compressibility of the layers is strongly a function of the thickness of the layer, or in other words, the extent of the layer confinement. Thus, the friction behavior of such hydrogel layers is also highly thickness dependent.

In friction tests, it was observed that the friction force does not depend linearly on the normal load. The deviation from Amanton's law is caused by the limited compressibility of these layers. The limited compressibility leads to a friction force that becomes independent of the applied load at some point, meaning that the COF reduces as the applied load becomes larger. This limited compressibility is the result of several parameters such as nonlinear behavior of polymer chains at high extensions, the incompressible fluid phase in the polymer matrix and the confinement. Furthermore, the compressibility depends strongly on the osmotic pressure in the gel, which in turn depends (for a given chemical composition of the gel) on the crosslink density and the degree of charging of the polymers. By increased osmotic pressure through charged polymers, the load-bearing capacity of hydrogels is expected to increase. The influence of the charges on the lubrication properties of hydrogels remains to be seen.

The attachment of hydrogels to a stiff substrate not only reduces adhesion between the contact counterparts but also decreases the swelling/increases the segment concentration in the film leading to smaller penetration depth. As the zone, in which complete relaxation can occur, becomes larger than the thickness of the hydrogel layer (strong confinement), the hydrogel layer cannot relax completely. Incomplete relaxation of the sample and high segment density results in a higher effective modulus of the gel layer, a smaller penetration depth and a lower coefficient of friction.f

Friction tests showed that lubrication of surface-attached hydrogels depends on two parameters: the extent of penetration of the slider into the gel and the drag force induced by the movement of water. The penetration depth decreases with increasing sliding velocity, while the drag increases – leading in many cases to a minimum in the friction coefficient at intermediate velocities. How pronounced this behavior depends on the degree of confinement, i.e., the layer thickness. Thus the frictional behavior of such hydrogels can be described in two regimes, namely a polymer deformation controlled regime and a drag force controlled regime. Polymer deformation governs the lubrication when the sliding velocity is low. Drag control occurs when most of the fluid is still in the network and does not have enough time to be displaced.

All friction force curves can be superimposed onto each to form a master curve by normalizing the data by a force characteristic number. The force characteristic number is defined as a dimensionless number that is proportional to the sliding speed and the contact radius and it is inversely proportional to the permeability and elastic modulus. In some publications, it is considered as similar to a Peclet number. It has to be pointed out that for the surface-attached gels, as confinement plays an important role in the determination of the contact stiffness and permeability, effective elastic modulus and effective permeability have to be taken into account. The film thickness plays a role when the layers are confined and no complete stress relaxation can occur. High confinement of the polymer (sub)chains in the gel results in a lower penetration (and thus a slightly smaller contact area) and a higher effective modulus, thus leads to a smaller force characteristic number.

When channels are introduced, the system consists of the swollen hydrogel and bulk water inside of the channel. The water squeezed out from the gel can now flow easily through the channels as the viscosity of bulk water is much lower than that of water in a hydrogel. This decreases the water resistance against sliding, especially when the sliding is in the same direction as the channels. The lower friction of the textured hydrogels comparing to the flat layers is due to the fact that the distance through which water has to be transported to be squeezed out is much shorter in the case of the patterned hydrogels. However, decreasing the structure width of patterned hydrogels does not always lead to smaller friction comparing to the ones with wider structures, as narrow and high stripes are more susceptible to large deformation under the same applied load. Thus, the friction force of textured hydrogels depends not only on in the presence of channels but also on the ability of the structures to support the load.

A significant improvement of the friction properties was noticed by combining the hydrogel-hydrogel system with liquid lubricants. Similar behavior was observed when a low molecular weight alkylgluconat or the polymer polyvinylpyrrolidon was used. In both cases, extremely low friction in a broad range of sliding speeds was obtained, indeed so low that the COF could not be measured which means that the COF is lower than 0.001. The penetration depth of the slider into the gel was smaller with both PVP and C8 in comparison to the purely water-swollen sample. This implies that a part of the applied load is supported by the fluid phase and induces hydrodynamic lubrication

Friction systems in which both sides are coated with a hydrogel and are swollen in water are extremely interesting lubricant systems, at least in a pressure range which is roughly the same as that occurring in human joints. The hydrogel-hydrogel systems show extremely low coefficients of friction, which can be even lowered through microstructuring or through the addition of polymeric viscosity enhancers. The COF were among the lowest reported for macroscopic systems so far and even in some cases below the detection limit of the measurement setup (COF < 0.001). The results for textured surface-attached hydrogels and the additivated systems are very attractive and make further investigations in this direction promising.

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