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Lubrication and Adhesion by Charged Biopolymers for Biomedical Applications

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1. Introduction

Charged polymers (polyelectrolytes) are water-based lubricants that perform efficiently in biological systems where the charged hydrophilic surfaces provide an electrostatic "double-layer" repulsion, in addition to the "steric" repulsion of any protruding polyelectrolyte segments and the hydration layer of tightly bound water molecules, all leading to low friction (Urbakh et al., 2004). Polymer conformation and strength of attachment to surfaces also play essential roles in lubrication, and recent experiments (Raviv et al., 2003) indicate that brushes of polyelectrolytes grafted to surfaces rubbing across aqueous media result in superior lubrication (friction coefficient, $\mu < 0.001$) at low sliding velocities and pressures up to a few atmospheres. This suggests that some biolubricating systems, such as in the eyes, may be mediated by brushlike polyelectrolyte layers. However, other experiments (Lee et al., 2003; Benz et al., 2004) show that brushes may not function well at high pressures where wear (damage) and/or higher friction coefficients are usually measured, indicating that high-pressure, high-impact systems, such as in the hip or knee joints, are likely mediated by more complex mechanisms. In fact, no model system currently exhibits both low friction and good wear resistance at high pressure (and over a large-range of velocities); however, polyelectrolytes seem to be the best way to go. Most specifically, naturally occurring polyelectrolytes (charged biopolymers) have gained interest because of their (controlled) degradable capabilities, abundance in nature (low cost), and biocompatibility, essential requirements for biomedical applications.

In this chapter, we first review the challenges of biolubrication, including the need for controlling the properties of both the lubricant and the confining (shearing) surfaces. We then report the lubrication and adhesive properties of a variety of naturally occurring polyelectrolytes (from glycoproteins to polysaccharides) in particular, the potential use of (nano)thin films of those polymers (adsorbed from aqueous solutions, grafted, or free in solution) to improve the lubrication properties of tribological systems composed of molecularly smooth mica surfaces (a chemically inert inorganic aluminosilicate clay). We focus on the capacity of the biopolymers to carry high loads and pressures (up to hundreds of atmospheres) and their ability to resist wear when sheared over large distances (larger than the contact diameter)—two crucial requirements of most lubricating systems—in addition to exhibiting low friction forces and average friction coefficients, to ensure low energy dissipation.

2. Biolubrication challenges

Biotribology, namely the study of adhesion, friction/lubrication, and wear in a biological environment, relates to the relative motion of surfaces either manmade (and implanted), natural tissues or the combination of both. Finding the best compromise between tribological requirements (low friction coefficients, efficient load bearing, wear resistance, chemical stability) and biocompatibility (since the host response to a biomaterial is critical in determining the success of an implant) makes it a challenging yet exciting task.

The tribological behavior of any (not necessarily biological) system is complex because it is governed by interacting factors:

- surface properties (topography, crystallinity, chemistry),
- environmental "global" parameters (presence of lubricant, temperature, pH),
- external "local" parameters (applied load/pressure, displacement, shear).

Surfaces are defects of a material *per se*, having peculiar atomic organization and reactivity (surface energy) responsible for their interactions with other media. Many methods are currently employed to modify the surface properties of artificial or natural bodies. They can be functionalized with coatings or self-assembled layers, gradually modified (gradients) through e.g. ion implantation, surface chemical reactions, surface active bulk additives or etching (Ratner & Hoffman, 1996). A crucial parameter is the texture of surfaces, characterized by its roughness. It determines how an object genuinely interacts with its environment. Surface roughness not only distorts the adhesive forces, it also modifies the friction forces. The surface asperities limit the average distance of closest approach between the bodies, usually reducing their normal interaction (adhesion). However, the highest asperities will also deform elastically and/or plastically when pressed against other, modifying the original surface roughness and chemistry, which may generate wear debris upon shear, acting as a new compound, called the tribolayer (Schouwenaars et al., 2007).

In biotribology, and particularly in biolubrication, the absence of damage (wearless sliding) does not only translate into mechanical efficiency, it also prevents from further inflammation occasioned by wear debris. For example, premature wear of the ultra high molecular weight polyethylene (UHMWPE) acetabular cup of a total hip replacement will not only cause loosening of the implant leading to failure, but it will also produce toxic third body particles promoting serious inflammation. To prevent the formation of such tribolayer, postpone wear, reduce friction forces, and increase efficiency, lubricants are commonly introduced between the shearing surfaces. Those lubricants can be solid, oil-based or water-based. This review focuses exclusively on naturally occurring water-based lubricants as described in the section 3. Current approaches to assess biolubrication.

Together with the surface properties and the presence of a lubricant, environmental conditions such as pH, ionic strength, temperature, etc. will ultimately determine the strength of the interactions (adhesion and friction) between surfaces, in particular when the confined lubricant is a highly charged polyelectrolyte. Although those parameters are not the subject of the present study, they are mentioned later, when discussing the remarkable stability of polysaccharides (showing slow and controlled degradation) over a wide range of pH and temperatures.

Finally, external parameters such as applied load (pressure) and shear act as the local and transient *stimuli* controlling the instantaneous response of the tribological system. Among the harsh conditions encountered in the body are highly compressive loads (in the knee, hip or spine), large sheared distances (in the shoulder), a wide range of velocities (static, walking, running) and high fatigue strength cycles (in the heart and eyelids). In the next

sections, we evaluate the capacity of several charged biopolymers (HA, lubricin, chitosan, and a polysaccharide from the algae) to carry high loads and pressures, to resist wear when sheared over large distances and over a wide range of velocities, in addition to exhibiting low friction forces. We also introduce thick (non-biological) polymer brush layers, as they were found to function well in tribological systems subjected to low pressures, and therefore currently thought to be the best biomimetic lubricants.

3. Current approaches to assess biolubrication

The most efficient, energetically speaking, tribosystems are those found in nature, e.g. mammals joints. Natural joints have been the center of interest of biomedical research with the hope of mimicking such low energy dissipation and wear resistance in engineered systems: physiological coefficients of kinetic friction $\mu=0.002-0.006$, billions of cycles without wear (high fatigue limit), high-load carrying capacity and robustness, all hardly reproducible "macroscopic" natural lubrication achievements (Hills, 2000). Synovial fluid (SF), the natural thick and viscous lubricant of joints, has for long been believed to be responsible for such remarkable lubrication properties and is addressed in section 3.2. However, as mentioned earlier, some biolubricating systems (such as in the eyes where the pressure is low) may be mediated by brushlike polyelectrolyte layers. Because polymer brush layers are currently thought to be the best biomimetic lubricants (hence promising for future biomedical applications), we start our next section by reporting friction experiments performed with non-biological (charged and uncharged) polymer brush layers used to lubricate mica surfaces.

3.1 Polymer brushes

Polymer brushes (PB) have been proposed to be responsible for efficient lubrication in biological tribosystems subjected to low external pressures (Raviv et al., 2003; Gourdon et al., 2008) such as in the eye or in the respiratory system, mediating not only low friction, but also permeability and/or bacteria and dust adhesion. PB are in general, a dense array of polymer chains (neutral or charged) endgrafted to a surface. The vicinity between adjacent polymer chains forces the polymer to adopt more favorable conformations. When the polymer chains stretch and point out perpendicularly to the supporting surface, the array is named PB (Brittain & Minko, 2007).

To control the formation of dense brushes at the surface, specific conditions have to be fulfilled, i.e., a complex balance between molecular weight (M_w), surface density, quality of solvent, charge distribution, etc. Instead of brushes, the polymer chains may also adopt less desirable conformations, such as pancake or mushroom, see figure 1, leading to weaker stability and non functional properties of the coatings. Among the controlled properties achieved by brushes are wettability, adhesion and lubricity (Klein et al., 1993; Brittain & Minko, 2007). The ability to manipulate easily these properties makes brushes smart surfaces that have attracted attention for applications like biosensors, tissue engineering, drug delivery and lubricants (Dong et al., 2009).

An increasing number of groups have been clarifying the main parameters governing the tribological behavior of PB coated surfaces (Liberelle & Giasson, 2008; Zappone et al., 2008; Kampf et al., 2004; Hartung et al., 2008; Chen et al., 2009). It is well established that under low loads, almost any pair of polymer coated surfaces will slide with low friction coefficients, $\mu=0.01$ (Raviv et al., 2003; Liberelle & Giasson, 2008). An extreme case has been found to be of the order of $\mu=0.001$ (Raviv et al., 2003) when end-grafted charged polymers were sheared

at low pressure (0.5MPa), and across very small distances ($0.7\mu\text{m}$). This low friction behavior was attributed to the strong resistance to mutual interpenetration of the pressed brushes together with the presence of hydrated ions surrounding the long polymer chains, see figure 2 a) and c). In contrast, neutral brushes exhibited high friction due to chain interpenetration (figure 2 b) and d)) and a significant increase in viscosity upon shear rate, leading to solid-like friction behavior (Neelov et al., 1998). Thus, the friction coefficient could be directly correlated to the degree of interpenetration between the polymer layers, governed itself by solvent ionic strength and polymer ionization degree.



Fig. 1. Possible polymer conformations, depending on quality of solvent, polymer degree of ionization and grafting distance.

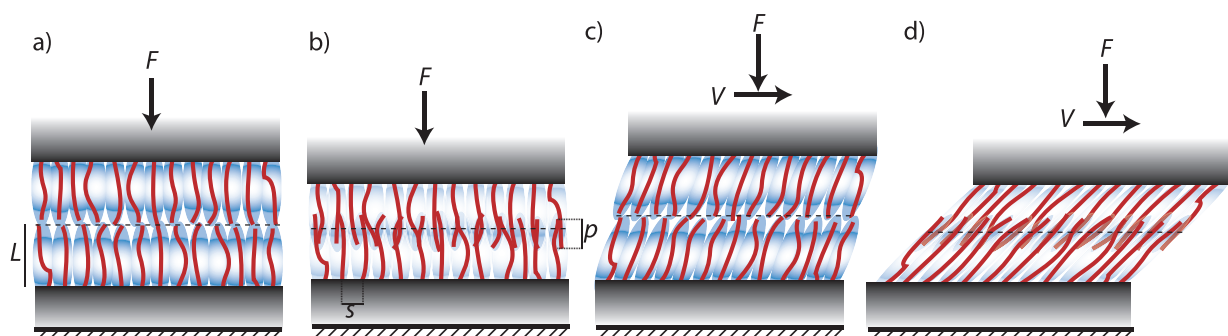


Fig. 2. a) Charged polymer brushes showing a strong resistance to mutual interpenetration, b) neutral brushes showing a weak resistance to mutual interpenetration. L , brush length; s , grafting distance; p , brush interpenetration; F , applied normal force, c) smooth sliding, consequence of (almost) no interpenetration, and d) dragging of brushes due to large interpenetration, yielding to high friction forces. V , sliding velocity.

PB appear to be efficient for modifying surface properties thus for controlling tribological behavior of shearing junctions, however, controlling the coverage density of brushes (and their attachment to surfaces) has been of great concern, especially to resist high pressures and large distances sheared. Highly packed synthetic PB have been used to successfully lubricate artificial joints at low pressures (Hartung et al., 2008). We next address another class of water-based lubricants, naturally occurring biological compounds, such as hyaluronan (the main component of synovial fluid), commonly used to heal degenerative joint diseases via direct injections at the site of inflammation.

3.2 Naturally occurring biological compounds

An intrinsic advantage of naturally occurring biological polymers is their similarity to macromolecules that biological systems are prepared to recognize, and handle metabolically. Thus, problems like toxicity or chronic inflammatory responses can be

excluded (Yannas, 1996). In this section, we review the lubrication and adhesive properties of four naturally occurring charged polymers (hyaluronic acid, lubricin, chitosan, and an algae polysaccharide), and report the potential use of (nano)thin films of those biopolymers to improve the lubrication properties of tribological systems composed of molecularly smooth mica surfaces. We particularly focus on the capacity of the biopolymers to carry high pressures (up to hundreds of atmospheres), to resist wear when sheared over large distances, and to exhibit low friction forces, all required for efficient biolubrication.

3.2.1 Hyaluronan

Hyaluronan or hyaluronic acid (HA), one of the main glycoproteins present in synovial fluid and connective tissues, is found in many different concentrations, depending on the physiological location. A concentration of $3.5 \frac{\text{mg}}{\text{ml}}$ is normally found in a regular adult knee (Tadmor et al., 2002). HA is a large, negatively charged and unbranched glycosaminoglycan (specialized glycoprotein with polysaccharide side-chains), having a high M_W , ranging from 6-7MDa for healthy to 3-5MDa for rheumatoid fluid (Dahl et al., 1985), with a polymer length $\approx 2\mu\text{m}$ (Toole, 2004; Mow et al., 1984). It also possesses an hydrophilic face, due to the presence of carboxyl groups, figure 3 a). A number of specific functions like lubrication, macromolecular filtering, cartilage surfaces protection, water homeostasis, selective binding of proteins (known cell-surface receptors) have been attributed to HA (Laurent et al., 1996). Over the last decades, HA has been thought to be responsible for the ultra low friction and wear rates in articular joints, until Radin et al. questioned such claim (Radin et al., 1970). Despite still open questions, HA has been used for the treatment of degenerative joint diseases and total or partial joint replacements (Kirchner & Marshall, 2006), providing temporary pain relief for patients (HA intra-articular injections are recommended every six months).

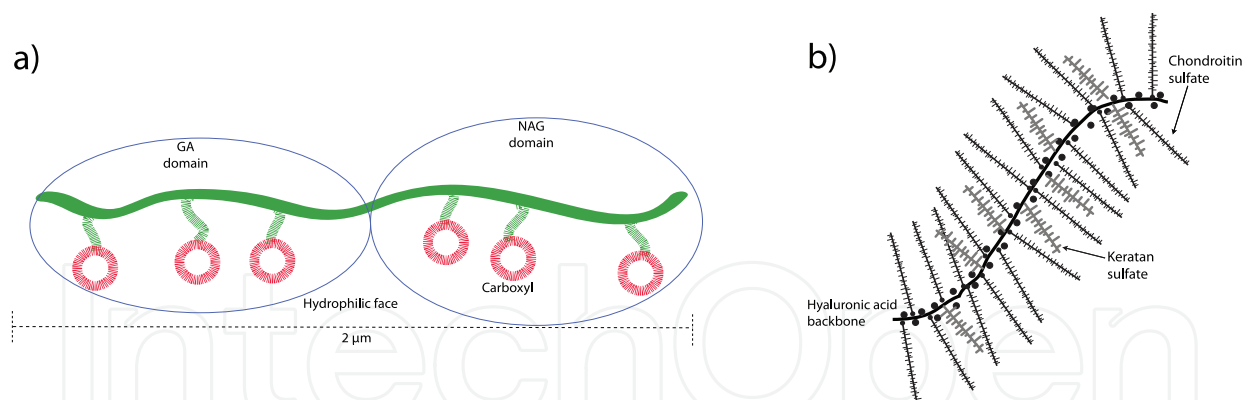


Fig. 3. a) Representation of a HA molecule. It is composed of a glucuronic acid (GA) domain and a *N*-acetylglucosamine (NAG) domain. b) Proteoglycan structures attached to a backbone of HA (adapted from (Neville et al., 2007)).

HA has been proved to be non-adhering to negatively charged surfaces, thus acting only as a viscous and bulky lubricant. In its native environment, the huge molecules can be locked mechanically by the pores of the cartilage, rather than bound, giving rise to a mechanical entrapment instead of physical or chemical binding. Experiments using bare and functionalized positively charged mica were performed using the SFA to measure the normal (adhesion) and friction forces of an HA solution of $3.4 \frac{\text{mg}}{\text{ml}}$ ($M_W=540\text{kDa}$) (Tadmor et al., 2002).

The normal force profile of non adsorbing HA showed a short-range repulsive behavior. This was attributed to a decrease of the Debye length, consequence of the dissociated sodium cations from HA, and the squeezing of HA molecules out of the contact area. In the case of adsorbed polyelectrolytes to the surface (using Ca^{2+} as anchor), a steric, long-range repulsion was seen. At very short distances, the van der Waals and hydrophobic attraction forces increased (in comparison to the free HA solution), even though the system showed a more repulsive force. The weak binding of HA to the surface could be a consequence of the hydrated divalent cations that did not readily lose their water on binding to mica (Berg et al., 1993).

Friction experiments revealed an interesting behavior. While damage was always observed when shearing HA between bare mica surfaces, as indicated by a friction coefficient $\mu=0.25$ (a typical value for wear), Ca^{2+} bonded HA to mica surfaces could resist damage upon initial shear at low pressures (0.5MPa), although the measured friction was relatively high. These results indicate that HA is capable to sustain lubrication as long as it is well confined between surfaces. Upon prolonged shear, the free HA molecules are expelled from the high pressure zones in the junction. This also suggests that HA works more like a visco-additive to enhance and maintain hydrodynamic lubrication in joints rather than like a boundary lubricant.

It has recently been proposed that HA is not the real responsible for the remarkable lubrication properties of synovial fluid, in spite of the high concentrations found in it (Neville et al., 2007). Hydrodynamic modes of lubrication are known to be enhanced by highly viscous lubricants, preventing contact between cartilage surfaces (e.g., during walking). The capability of HA to "wet" the highly hydrophobic cartilage surfaces (in order to promote hydrodynamic lubrication) has been hypothesized to be HA's main function (Hills, 2000). Other proteins, like lubricin, should then be responsible for the outstanding joint lubrication under extreme conditions, e.g., when no synovial fluid is present after prolonged periods of rest. More recently, HA has been proposed to be used together with bone grafts in order to accelerate the integration process of exograft bone implants, since HA has shown to facilitate cell migration and differentiation during tissue formation and repair (Aslan et al., 2006). This supports the idea that HA may function more as a carrier of wetting agents (to enhance binding), see figure 3 b), rather than as a boundary lubricant.

3.2.2 Lubricin: an example of mucins

Lubricin is another glycoprotein present in the synovial fluid, and is believed to lubricate and protect the cartilage surfaces in boundary lubrication, preventing cartilage-cartilage contact, and thus, wear (Schaefer et al., 2004). Like any other efficient boundary lubricant, lubricin is capable of binding to the cartilage surface. Apart from lubricating, it also protects the cartilage surfaces from excessive protein adsorption and cell overgrowth, which is one of the causes of joint failure diseases (Rhee et al., 2005). Lubricin is a structureless flexible high M_W molecule, of the order of 230kDa and has an extended length of 210nm. The molecular structure, represented in figure 4, is composed of a large heavily glycosylated central domain, carrying the negative charges, and two end-domains that are not glycosylated, carrying the positive charges (Zappone et al., 2007). These somatomedin (SMB), heparin and homepexin (PEX) like-domains are of special interest, since they are known to play specific roles in cell-cell and cell-extracellular matrix interactions (Jay, 2004).

In order to obtain a complete picture of the possible interactions of lubricin with different surfaces at physiological concentrations ($250 \frac{\text{mg}}{\text{ml}}$ (Jay, 2004)), a variety of substrates under controlled physical and chemical properties have been used. While negatively charged

lipids, sulphated proteoglycans and glycoproteins were mimicked by hydrophilic, negatively charged mica surfaces, basic amine groups of proteins were simulated by positively charged physisorbed poly-lysine to the mica surfaces. Chemisorbed hydrophobic monolayers of alkanethiol on gold were used to mimic collagen below the cartilage surface. The hydrophilic negatively charged mica, the physisorbed and chemisorbed hydrophilic, as well as the hydrophobic surfaces, showed similar normal force behaviors: a purely repulsive force, showing always a reversible compression-decompression cycle for different contact times and compressive forces, i.e., no hysteresis. This behavior was achieved with a saturated surface, corresponding to "brush" thicknesses $L=70\text{nm}-100\text{nm}$, i.e., approximately one half of the length of stretched lubricin (Zappone et al., 2007).

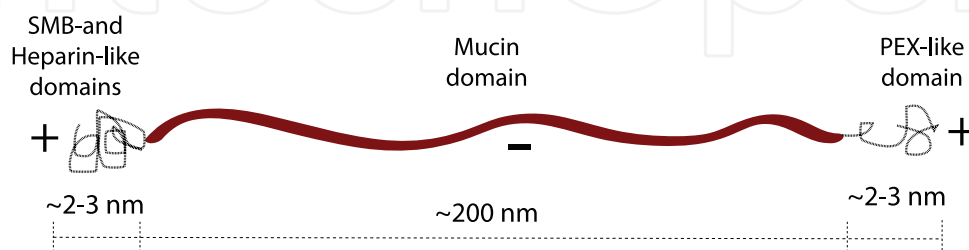


Fig. 4. Representation of lubricin. The end-domains of the molecule carry most of the positive charges and hydrophilic groups, while the central domain carries the negative charges, adapted from (Zappone et al., 2007).

The frictional properties of lubricin have been shown to be highly pressure-dependent. For contact pressures up to 0.4MPa , the friction coefficients were as low as $\mu=0.02-0.04$, but increased abruptly by one order of magnitude ($\mu=0.2-0.6$) at higher pressures (Zappone et al., 2007). This high friction eventually led to wear of the lubricin monolayer, but no damage of the underlying mica was reported. The hydrophobic surfaces showed a substantial different behavior in their tribological properties, exhibiting high friction coefficients even at low pressures, $\mu=0.3-0.5$ (Zappone et al., 2007). Wear of the lubricin monolayer could also be seen, but when reaching much higher loads ($P\approx 1\text{MPa}$) than those needed to cause wear in the hydrophilic samples ($P\approx 500\text{kPa}$).

Since the semilogarithmic normalized force runs ($\frac{F}{R}$) versus surfaces separation (D) can be well described by the Alexandre-deGennes model, lubricin is believed to form a monolayer of brushes arranged in the various conformations shown in figure 5. This simple model can explain the low friction coefficients ($\mu\approx 0.03$) found at low pressures, and the sudden change to higher friction coefficients ($\mu\approx 0.4$) measured when increasing pressure. Similar behavior has been previously reported for charged polymer brushes (Raviv et al., 2003), and attributed to weak interpenetration of opposing brushes occurring at high pressures.

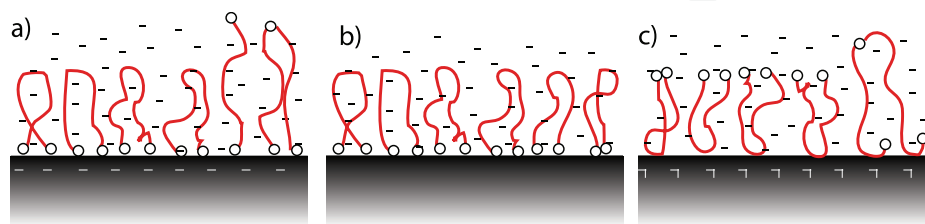


Fig. 5. Likely configurations of lubricin when physisorbed to a) negatively charged surfaces, b) hydrophobic surfaces and c) positively charged surfaces as proposed by Zappone et al. End-domains of lubricin carry most of the positive charge of the molecule.

These experiments suggest that the elongated lubricin molecules can attach to the mica surface by both its positively charged end-domains (leading to high repulsion as a consequence of entropic resistance to confinement). They also indicate that lubricin alone may not be responsible for the ultra low friction found in joints, although it is able to ensure good protection of the "contacting" surfaces against damage, even at high pressures.

The naturally occurring polyelectrolytes described so far (HA and lubricin) are both found in the human body. We now report the lubrication and adhesion properties of polyelectrolyte extracted from other natural sources (crustaceans or algae). Those have also been used successfully in specific biomedical applications, and they deserve our interest as complementary approaches to assess biolubrication.

3.2.3 Chitosan

Chitosan is a linear polysaccharide produced from chitin, the structural element in the exoskeleton of crustaceans and some unicellular organisms. It has gained considerable attention due to its biological properties, uses in food industries (water filtration), agricultural fields (biopesticides) and potential uses in medicine (antihemorrhagic agents). On controlling the M_w , pH , ionic strength and degree of deacetylation, one is able to drastically change its properties (Claesson & Ninham, 1992). Chitosan has a peculiar property; it is the only cationic polysaccharide occurring in nature in abundant quantities. Its cationic nature comes from the presence of amino groups at acidic to neutral pH , adopting an extended conformation at low ionic strengths, see figure 6, due to strong electrostatic segment-segment repulsion, in contrast to the large majority of polysaccharides that carry a negative charge or are neutral. It is composed of a relatively large backbone, that is not very flexible due to the presence of bulky sugar rings. Solutions containing the appropriate concentration of chitosan are capable of forming very stable layers (with varying pH), as well as gels in the presence of cross-linking agents, such as carboxylic acid or polyphosphates. Being hypoallergenic and having antibacterial properties, chitosan has also been successfully used as an antihemorrhagic agent (Pusateri et al., 2003). Because of so many potential applications, Claesson & Ninham initiated the investigation of the molecular mechanisms of chitosan adsorption to surfaces.

Chitosan is a polyelectrolyte that fully dissociates at low pH , having a $pK_a=6.5$. Its interactions with surfaces are therefore highly pH dependent. At very acidic values, the system presented a steric repulsive force starting at 10nm. The smallest measured distance (hard wall), D , was 1.5nm, indicating that the layer on each surface was of the order of 0.7-0.8nm. In spite of pure repulsion during approach, a small adhesive force during receding was measured, suggesting the formation of weak polyelectrolyte bridges. Adsorbed chitosan dissolves poorly in free polyelectrolyte solution, once reached the surface saturation. Free cationic polymer molecules in solution could not contribute to the lubricating behavior, because the molecules were squeezed out when the surfaces approached, as indicated by changes in the refractive index. Changing the pH to less acidic environments, the approach/receding experiments showed similar behavior, decreasing only the Debye length and preserving a small 1 nm-thick polymer layer (Claesson & Ninham, 1992). When approaching to the pK_a value, $pH=6.2$, no double-layer force repulsion was present, leaving only the attractive van der Waals forces. Beyond this critical value (at higher pH values) the double layer repulsion reappeared and the layer thickness increased to 1.6nm (the force needed to reach the hard wall was also larger than at lower pH values). Chitosan has a strong positive charge at low pH , being therefore attracted to the negatively

charged mica surface, forcing the polysaccharide to adsorb in a flat conformation. The likely conformations of chitosan at various pH are shown in figure 6. Gelled (cross-linked) chitosan using sodium hexametaphosphate as linking agent showed some differences: hysteresis was observed between compression and decompression, increasing the repulsion force and range. Besides these differences, the behavior of the cross-linked chitosan was similar to the non cross-linked one.

Friction forces were measured for both free adsorbed and gelled chitosan layers. Friction forces, in the former case, could only be detected at distances, $D=20\text{nm}$ and increased monotonically when decreasing D , being slightly above the noise level of the system ($2\mu\text{N}$). After gellation, friction was large even at large D , showing a sharp initial rise but final (steady state) friction could not be achieved because of the very small distances sheared. (Kampf et al., 2004). The friction forces between freely and gelled chitosan were also investigated as a function of velocity. Freely adsorbed chitosan showed little frictional force dependency on velocity, in contrast to what was seen in crosslinked chitosan, where a significant increase in the friction force (with increasing velocity) was observed. For a shearing velocity of $200 \frac{\text{mm}}{\text{s}}$, an effective friction coefficient, $\mu_{ef} = 0.003$ was measured for non cross-linked molecules, increasing up to $\mu_{ef} = 0.5$ for the cross-linked gel (Kampf et al., 2004).

3.2.4 Algae polysaccharide

Algae polysaccharides have diverse biological functions and physicochemical properties and are increasingly being used in various fluid formulations. They dissolve easily in aqueous solutions, increasing their viscosity, and controlling their rheological properties that ultimately define the various applications of the biopolymers (Geresh & Malis, 1991). Biological properties of the polysaccharides include anti-inflammatory, anti-oxidant and anti-viral activity (Gourdon et al., 2008). They also own chemical and biological inertness (high stability) under extreme conditions of salinity, pH, temperature, light and dehydration (Geresh & Malis, 1991). Tribological studies at the macroscopic scale showed that their friction coefficients were lower than the ones found in HA, making them excellent candidates for biomedical applications. The naturally occurring polysaccharide studied is synthesized by the algae *Porphyridium* sp. and is composed mainly of three sugars: xylose (38%), galactose (24%) and glucose (22%), and glucuronic acid units (10%) (Percival & Foyle, 1979). It is an anionic high M_W (2.3MDa) molecule. Surprisingly, this polysaccharide is able to adsorb even to negatively charged surfaces, despite its anionic nature, showing a stable low friction coefficient, robustness (high load carrying capacity), good wear protection and a weak dependence of the friction force on sliding velocity (Gourdon et al., 2008).

Atomic force microscopy (AFM) imaging of mica surfaces in polysaccharide solution indicated that physisorbed small polysaccharide globular domains could built on the surface, increasing in number but neither in size nor height with increasing incubation time. These globules were measured to be 10nm in diameter and $\approx 1.1\text{nm}$ in height and appeared to remain highly mobile at the surface (easily dragged upon shearing with the AFM tip). Normal forces measurements carried out with the SFA (at room temperature) revealed that, in polysaccharide solution, the forces during approach were exponentially repulsive, due to the large-range double layer force. Below 10nm, an additional short-range repulsive hydration force could be seen (Gourdon et al., 2008). In contrast, adhesion was measured during receding. Such adhesion was found to increase with the maximum load applied

during each compressive cycle, before reaching a maximum at $W \approx 6 \frac{\text{mJ}}{\text{m}^2}$.

The friction behavior was recorded as a function of applied load/pressure, shearing velocity and shearing distance at different polysaccharide concentrations. At early stages of shear, the measured friction force was high and proportional to the contact area (indicative of adhesion-controlled friction). However, further shear drastically modified the frictional regime, showing an abrupt transition to low and stable (load-controlled) friction: average friction coefficients as low as $\mu \approx 0.015$, and no wear observed up to pressures of 10MPa and upon shearing over 3 decades of velocity. This tribological transition was attributed to the reorienting capability of the polysaccharide, similar to the one seen in nanoparticle systems when the particles minimize their energy via shear-induced alignment (Gourdon et al., 2004). Experiments performed over shearing distances greater than the contact area revealed that the polysaccharide could be carried out to new unsheared areas, capable of expanding the low friction and wear resistances domains. One of the most outstanding properties of the polysaccharide lubricating films is that only a subnanometric (0.5-1nm) monolayer was enough to provide such efficient lubrication and wear protection. Figure 7 shows the likely molecular mechanisms, involving confinement and shear-induced alignment of the polysaccharide molecules, allowing them to act as both good lubricants and adhesives. Such dual behavior can be explained by the highly flexible polysaccharide backbone, allowing for the rapid formation of hydrogen bonds between the biopolymer sugar moieties and the mica surfaces. Damage could only be observed when shearing over distances larger than twice the contact diameter, at pressures of 11MPa (higher than any pressure found in healthy human joints under normal daily activity).

The remarkable properties of the *Porphyridium* sp. polysaccharide should not be surprising, since it is found in the extracellular matrix of the algae cells, tightly bound to the outer membrane surface, and functions simultaneously as a lubricant and as a protecting film for the algae. In summary, the most notable properties exhibited by the naturally-occurring polyelectrolyte were:

- steady low friction
- stability at high pressures
- stability at high and low velocities
- wear protection
- stability at large shearing distances

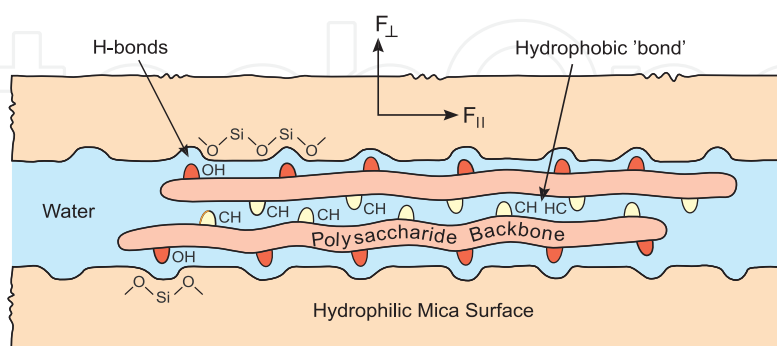


Fig. 7. Likely molecular mechanisms, involving confinement and shear-induced alignment of the polysaccharide molecules, allowing them to act as good lubricants and adhesives.

Adapted from (Gourdon et al., 2008).

None of the biopolymers investigated so far has been able to combine *at once* these five characteristics. However, the algae polysaccharide is the one fulfilling most of the

tribological requirements for efficient biolubrication. In such a context, polysaccharides seem to be the best way to go and further investigation (experimental and numerical) of this class of polyelectrolytes is needed to identify the crucial sequence(s) that determine the lubricating functionalities of the biopolymers.

4. Experimental methods

The surface forces apparatus (SFA) and the atomic force microscope (AFM) have proven to be ideal tools for combining nano-, micro-, and macroscale tribological experiments as well as for nanoscale imaging and characterization of surfaces in presence of lubricants. These two techniques are briefly described below.

4.1 Surface forces apparatus

The surface forces apparatus (SFA) was developed in the 70's and optimized in the 90's of last century to measure the normal and friction forces at the molecular and atomic scale, on a wide variety of systems, such as colloids, amorphous polymers, and metals. Details of the SFA can be found in (Israelachvili & McGuiggan, 1990). Two cylindrical silica lenses of radius R ($R=1\text{cm}$), wearing a thin sheet of back-silvered and atomically smooth mica, face each other and used as preliminary surfaces (these surfaces can be modified before being mounted into the SFA). The surfaces separation, D , is obtained by multiple beam interferometry, together with surface shape, contact radius, contact area and refractive index in both static and dynamic conditions. Normal and friction forces are measured by means of double cantilever springs while shearing is ensured by a piezoelectric bimorph slider allowing large displacements. A scheme of the SFA is shown in figure 8 a). Two enormous advantages of the direct visualization of the contact region with multiple beam interferometry using fringes of equal chromatic order (FECO) are: 1) the contact area is measured rather than calculated and 2) any damage of the surfaces can be easily detected, as well as undesirable particles/contaminants. A typical normal force $F(D)$ profile is presented in figure 8 b), for both, repulsive and adhesive behaviors.

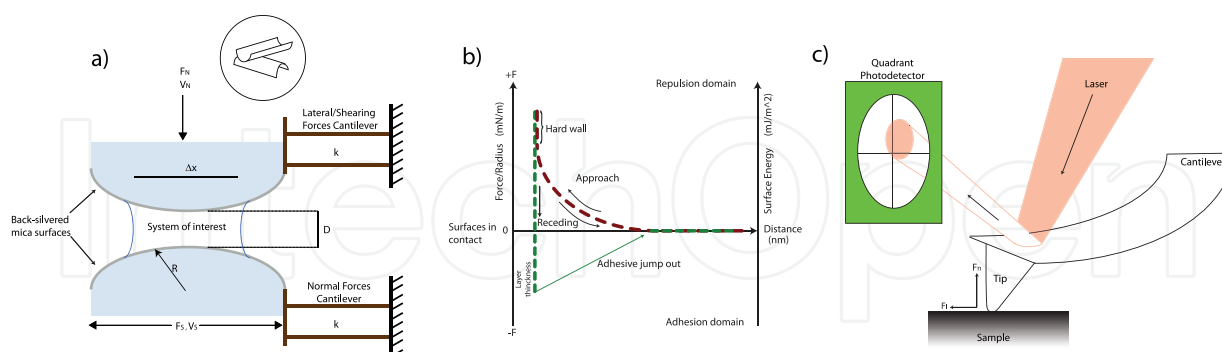


Fig. 8. Scheme of a) the SFA, where F_N is the normal applied load; V_N , approach speed of surfaces; F_S , the shear force; V_S , the shearing velocity; k , spring constant; Δx , shearing distance; R , curvature radius of the optical lenses, b) typical distance-force curves obtained with the SFA and the AFM. In sepia shown a purely repulsive behavior, during approach and receding of the surfaces. An induced adhesive behavior can be seen in the approach (sepia) combined with receding (green), extending the force to the negative (adhesion) domain, and c) the AFM, where F_N is the normal force between the tip and sample, and F_L , is the lateral friction force, adapted from (Caprick & Salmeron, 1997).

4.2 Atomic force microscope

Another useful tool for tribological studies is the atomic force microscope (AFM), developed in 1986. The AFM can be used to measure normal and frictional forces as well as to image samples with atomic scale resolution, and has been implemented for applications ranging from semiconductors to biological samples. Details about the AFM can be found in (Carpick & Salmeron, 1997). In this instrument (scheme shown in figure 8 c)), a tip of radius R ($R=30\text{nm}$) mounted onto a compliant cantilever is brought into contact with the surface of a stationary sample. Adhesion and friction forces are measured by recording the normal and lateral deflections of the cantilever beam. For that, a laser beam is reflected off the back of the cantilever into a quadrant photodiode detector, which records changes in the vertical and horizontal deflection of the probe.

5. Conclusions and future work

Although thick polymer brush layers are currently thought to be the best biomimetic lubricants, we have found that subnanometer-thick monolayers of of an algae polysaccharide can exhibit stable low friction and good wear protection, up to 11MPa and over a 1000-fold range of sliding velocities. Such remarkable tribological behavior is attributed to the ability of the polysaccharide to adhere weakly to the surfaces (ensuring that the lubricant is not easily squeezed out of the shearing junction) and to be flexible and mobile enough to be shear-aligned and transferred into new unsheared areas. However, despite the superior lubrication demonstrated by the algae polysaccharide compared to HA, lubricin, and chitosan, we conclude that none of the systems investigated so far possesses the ideal combination of friction and adhesion properties when subjected to cyclic loading, high pressures, high impact, and large sliding distances, as found in natural tribological systems such as in the hip or knee joint. Indeed even the algae polysaccharide monolayer breaks down when sheared (at high pressures) over distances larger than twice the diameter of contact between surfaces.

Hence, the best candidate for use in water-based lubricant fluids and/or as potential additives to synovial fluid in joints and other biolubricating fluids still needs to be identified. By further investigating this class of polysaccharides but also other natural polysaccharides and synthetic peptides, we expect to be able to identify the crucial chemical groups and/or sequences that determine their different functionalities, with obvious potential for biomedical (medical synthesis) and/or simply biomimetic applications.

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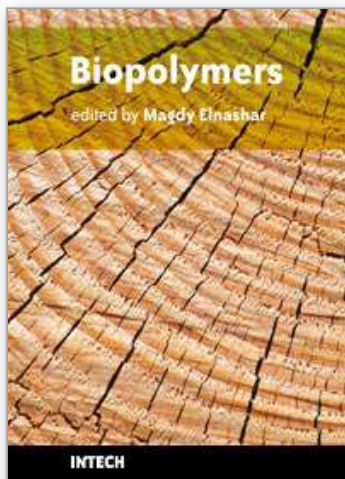
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