# Aquous Lubrication. Natural and Biomimetic Approaches

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2014. 284 Pages Hardcover
GBP 71.00 - US$108
ISBN 978-981-4313-76-6
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This book about water lubrication in nature, covers the current state of our understanding of the principles of aqueous lubrication with gels and materials. Organized in 8 chapters it covers the lubrication phenomena of natural articular joints as well as of Food and Cosmetic emulsions, Ceramics and Polymer Brushes, reported and discussed underlining their tribological and nano tribological effectiveness.

Tribology deals with friction, wear and lubrication, representing one of the least developed classical science to date. Nanotribology is a branch of tribology which studies friction phenomenon at the nanometer scale. Thus, it is concerned with experimental and theoretical investigation of processes ranging from atomic and molecular scales to the microscale, occurring during adhesion, function, wear, and thin-film lubrication at sliding surfaces.

The reason is that like nanoscience is neither truly to a single discipline nor well represented by steady state processes. However, the viscosity of the lubricating film is recognized as one of the most influential parameters for the film thickness and lubrication regime, so that it is reasonable to expect a beneficial effect on its tribological performance. Another important consequence of surface charge due to the repulsion and/or attraction between the surfaces and debris is the effect on the mechanical properties of the newly formed electro-tribochemical layers. In conclusion tribology like nanoscience involves all the complexities of nano-constrained materials that are experienced over a wide range of scales during a shear occurrence.

Tribology plays therefore a very important role in improving the design and making successful biomaterials for cosmetic and medical use. At this purpose, biomaterials used to date are metal ceramics with polymers, biopolymers and related composites.

Hyaline cartilage is a smooth, white tissue that covers the surface of all moving joints in the human body, playing an important role in determining the friction coefficient in different situations. The most abundant substance in cartilage is water, which makes up 70 to 80% of the weight. The remained material includes type II collagen, which forms the fibrous network, and the proteoglycans aggregate, a large complex comprising hyaluronan. The mechanical properties of cartilage are attributed to the highly hydrated aggregate trapped in a matrix of collagen, makes up approximately 50-75% of the dry weight of articular cartilage. Thus, articular cartilage coefficient plays a role in determining the friction coefficient. Therefore, in order to compare the friction coefficient in different

experiments, it must be considered not only the changes in the lubricant but also changes in the bulk cartilage or articular surface. Additionally, a change in the friction coefficient of this tissue indicates some changes in the tribological system, which may be the lubricant, substrate, environment and/or the tribological conditions.

On one hand, the articular surface seems to have special properties that, enhancing the cartilage lubrication, protects itself against wear; on the other hand, a number of other requirements may be part of the articular surface in order to fit its functions, such as the ability to allow nutrients to permeate, to show resistance to non-specific protein adsorption, and integration with the opposing cartilage surface.

The structure, surface, friction and wear of articular cartilage, together with lubricant studies and theories on the activities of the fluid films during the swing phase of walking, are all reported and discussed on the **Chapter 1:** *Tribology of Natural Articular Joints*.

**Chapter 2,** *Sticky and Slippery: Interfacial Forces of Mucin and Mucus Gels*, deals with natural lubricating mechanisms as found in mucous membranes. Mucosa plays a protective role by secreting slimy and adherent mucus layers, represented by hydrogel networks formed from macromolecules called *mucin*. Mucin, known as lubricant for biological systems, is a glycoprotein, which, accounting for 70-80% of carbohydrate chains, is responsible of the mucus-gel's hygroscopic nature.

In addition, mucin/mucus possess other biological functions, such as bioadhesion, cell signal transduction, diagnostic marker in cancer, bacterial inoculation, immune response, inflammation, and tumour genesis.

The chapter reports and discusses the recent studies on the characterization and understanding of interfacial forces arising and involving mucins/mucus gels. These studies, in fact, have been performed in the contest of researches that include mucoadhesion for drug delivery, understanding the lubricating properties of saliva in food science and ontology, masticatory food consumption in food science; smooth gliding of endoscopy in biomedical science, and fundamental understanding of mucin lubricating behaviour in biotribology.

At this purpose, the chapter is composed of two main parts, covering molecular mucins and mucus gels/mucosa. The molecular mucins offer an opportunity to understand the fundamental force-interaction mechanisms at interfaces, while mucus gels offer an opportunity to understand in systems the interacting forces of physiological relevance. However, unlike other biomolecules that are known to be responsible for the lubrication of biological systems, mucin/mucus gels have both adhesive and slippery characteristics.

Lubrication is also an important factor in the oral processing of food. However, it is difficult to interpret the tribological response of food products due to their innate complexity in terms of rheology and microstructure, also because they contain multiple phases and components of emulsions that are interfacially active.

*Aqueous Lubrication and Food Emulsions are the topics focused on* **Chapter 3**. Emulsions are an important class of aqueous-based lubricants as they can be designed to deliver essentially the same lubricating properties as oils do, under low-temperature situations. However, although there is some general understanding and know how on food-emulsion lubrication, their predictive properties and surface characteristics are still in development.

Foods are also highly complex in terms of microstructure, rheology and composition so that more research is still needed to both characterize and understand the lubricative properties of complex

food systems under well-defined conditions and biosubstrates. Moreover, the influence of saliva on food-emulsion lubrication has to be better understood. In any way, the utilization of modern tribometers could provide fundamental insights into the mechanisms by which the friction coefficient is defined in a soft-tribological contact for a complex food or emulsion system, particularly when the system is well defined in terms of surface toughness and surface chemistry.

Lubrication and tribological issues are also involved in many cosmetic products, in which water plays not only an important role to deliver a particular activity or properties, but has to be considered also an active ingredient, improving, for example, skin hydration or hair feel. Thus, while creams are expected to improve texture and feel of skin, hair-styling lacquers improve adhesion between hair fibers to set a specific shape while nail varnishes decrease wear in nails. This is why lubrication and in general tribological issues are involved in many cosmetic applications. Therefore when dealing with biological surfaces, such as skin and hair, it is important to understand the importance of the substrate that cannot be underestimated.

Water, in fact, acts like a plasticizer on both skin and hair. Human hair is a nano composite biological fiber which, by the fiber-to-fiber interactions of its cuticle, plays an important role in fiber-assembly behaviour. The inter fiber forces play a significant role in hair combing and manageability, and therefore in the overall appearance of the whole head. Thus, friction coefficient tends to rise when hair is wetted or ambient humidity is high, as well as excess sebum can stick together several hairs to form little swatches, which characterize greasy hair.

Under wet conditions, the value of friction coefficient is nearly multiplied by 3, while with the addition of a *cationic surfactant* the coefficient drops drastically to the level of dry hair. This is why cationic surfactants and cationic polyelectrolytes are widely used in cosmetic treatments, to affect the maintenance and grooming processes. For these reasons, the nanoscale characterization of the cellular structure, and the tribological properties of hair are essential to evaluate and develop more effective cosmetic products and to advance the understanding of biological and cosmetic science. Hairstyle and manageability depend, in fact, on numerous parameters such as the geometry of the fibers, the topography of the hair coverage, the fiber-to-fiber interactions and, in other words, to a great extent on the surface properties.

In any way, many people who use hair/skin care products regularly might think that the tribology of hair and skin/mucous surface is more important than the lubrication of moving metal surfaces! These the topics focused on **Chapter 4**, *Aqueous Lubrication in Cosmetics*, which reports a general view of the hair surface properties, describing the current understanding of the lubrication mechanisms of the common ingredients used, evaluating also the effects on friction properties of specific conditioning ingredients.

**Chapter 5**, *Hydrogel a Friction and Lubrication*, covers the current status and principles governing the gels' aqueous lubrication. Sliding friction and frictional behaviour of polymer gels is one of the most important practical subjects in physics. It depends on the chemical structure, property and geometry of the gels, the surface properties of sliding counter surfaces with their measurement conditions.

A gel has many features in common with other soft cross-linked polymers in terms of its cross-linked polymer structure and viscoelastic properties. In contrast to a rubber, a gel contains a large amount of low molecular weight component and water. The water content in biological gels such as cartilage is, in fact, ~70-80wt% while, in synthetic gels, the water content can be as high as 99.9%.

Due to the large presence of water, strongly solvated to the polymer network, the internal friction of a gel is much less than that of a cross-linked polymer melt or rubbed. Moreover, the surface structure and, therefore, friction of a gel strongly depends on the substrate on which the gel is synthesized. Thus, when gels are synthesized between a pair of glass substrates they have a mirror-like smooth surface.

On the contrary, when synthesized between two different plates, one hydrophobic and the other hydrophilic, heterogeneous gelation occurs. In any way, the friction events in biological systems mostly occur between soft and wet tissues, mediated by viscoelastic polymeric gel fluids such as synovial fluid or mucus. Mucus, for example, adheres to many epithelial surfaces, where it serves as a diffusion barrier against contact with noxious substances and as lubricant to minimize shear stresses. Mucus is, therefore, an important component of lubricating saliva, as well as articular cartilage is a natural fiber-reinforced hydrogel that, contributing to the joint functions of the tissue, involves ultra-low friction, distribution of loads, and adsorption of impact energy.

For these reasons, it is important develop specific gels as therapeutic agents and substitutes of synovial fluid for the damaged cartilage, a tissue extremely difficult to regenerate. Thus, design and production of hydrogels with a low surface friction and high mechanical strength are crucially important in the biomedical applications such as contact lens, catheter, artificial articular cartilage, and artificial oesophagus.

Nature's effective lubrication mechanisms are mostly based on sugar-decorated polymers-glycoproteins- that utilize the facility with which they can be hydrated in order to hold a significant amount of water at the surface to be lubricated.

Charge, hydrophobicity, and hydrogen bonding all play significant roles in the behaviour of natural lubricant molecules. Brush coating, for example, is a way to control the friction in skin and teeth product interactions thus, in attempting to mimic the lubricating function of the natural molecules, a class of polymer brushes has been produced. They appear to function by means of their ability to separate hard, sliding counter surfaces while presenting a solvent-rich, low-shear-strength interbrush layer, providing fluid-film lubrication without the need for hydrodynamic forces.

Brush coating represent, in fact, polymer layers developed on a supporting surface by tethering long polymer chains with a sufficiently high grafting density. Because of the main challenge, facing polymer brushes, appear to be resistance to wear, inter penetration of polymer brushes, response to applied load, effect of pressure on the lubricity of surface-grafted polymers, and macro-micro-nanotribological measurements on different charged systems, all phenomena reported and discussed on **Chapter 6**, *Aqueous Lubrication with Polymer Brushes*.

Moreover, the efforts to apply aqueous lubrication are focused on **Chapter 7**, *Water-like Lubrication of Hard Contacts by Polyhydric Alcohols*.

Water has a low viscosity so that it isn't a good lubricant for hard steel contact. However, liquid and vapour water is known to have some ability to lubricate diamond and amorphous carbon materials in the boundary regime at high contact pressure and slow speeds. It is also interesting to notice that ceramic materials are easily lubricated by water and that tribochemical reactions lead to smooth surfaces and subsequent water hydrodynamic lubrication.

This chapter reports the tribological results obtained with glycerol and other polyol molecules on steel and diamond-like coatings. All these molecules, small and with different shapes such as spherical, crab shape or spider shape, seem to be progressively dissociated under the effect of pressure

shearing and liberating water. Thus, the formation of water molecules may be an important mechanism for friction reduction by polyhydric alcohols and glycerol. They, however, do not contain aliphatic chains, distinguishing them from most of the amphiphilic molecules used as traditional lubricant additives.

**Chapter 8** reports how the electrochemical parameters ,such as surface charges and the associated pH, zeta-potential or solubility, affect the properties of the surface layer, the physicochemical and load-carrying properties of the lubricating film, together with the tribochemical reactions and the tribolayer failure modes of water-lubricating contacts. It is, however, suggested that a more complete set of tribo-electro-chemical effects should be considered and controlled in the aqueous lubricating film of ceramic systems, and that more refined models should be developed to enable a more accurate prediction of the contact conditions in future aqueous, boundary-lubricated-ceramic tribosystems.

At this purpose several groups of parameters that directly influence the properties of the lubricating film and the severity of the contact conditions have been suggested.

In this interesting book, where the mechanisms of aqueous lubrication in nature are reported and discussed for trying to understand and imitate them for practical purposes, various cellular structures of human hair and body have been described. Friction and lubrication of skin, for example, play a major role in product development for cosmetics, textiles, artificial turf, medical devices, floor cleaning, etc. Characterizing the friction and wear properties of hair and skin is, in fact, essential to develop more effective shampoos and conditioners that leave hair untangled and skin hydrated looking natural while feeling smooth.

Thus, nanomechanical properties such as hardness, elastic modulus, tensile deformation, fatigue, and scratch resistance have been discussed, as well as nanotribological properties such as roughness, friction, adhesion and wear have been presented. All these tribological properties are essential to evaluate and develop cosmetic and biological products, and to advance the understanding of cosmetic and biological science. During all the pages of the book the remarkable properties of water as the main and important lubricant in nature is continually discussed and explained in simply way so that its lecture is to be considered useful for all the scientists, such as dermatologists, biologists, gynaecologists, paediatricians, marketing managers, and also students of both the chemical and medical community who wish to better understand the biological and biomimetic role the water has for the human body and for many human activities involved in producing smart textiles, innovative cosmetics, medical devices and other innovative products where skin represents one of the interacting surfaces in relative motion.

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