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Polyelectrolyte interactions at the interface as a model for biolubrication

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Over the recent years we have investigated several model systems related to polymers that are confined between two surfaces across aqueous solution. Some of those bio-mimetic systems were composed of adsorbed or brush-like polymers present in confinement and pressures similar to those present in joints, moving tissues and cells. We primarily used surface force balance technique in order to determine the normal and shear forces between the surfaces.

One of the latest examined systems consisted on polyelectrolyte brushes (diblock copolymers namely: poly(methylmethacrylate)-*block*-poly(sodium sulfonated glycidyl methacrylate)) self-assembled on a hydrophobized (using: (stearic trimethyl ammonium iodide - STAI)) mica surface across aqueous solution (see Raviv et al. 2003 and Fig. 1). Strong hydrophobic attraction between the STAI coated mica surfaces was observed across water, but following overnight incubation aqueous solution of the diblock, polyelectrolyte brushes formed on the hydrophobic surfaces, leading to strongly-repulsive normal forces between them. The corresponding shear forces on sliding the surfaces, at shear rates up to order 100 s^{-1}, were extremely low, and the effective friction coefficients (μ_{eff}) with polyelectrolyte brushes in water were found to be lower than about 0.0006–0.001 even at low sliding velocities and at pressures of up to several atmospheres (typical of those in living systems).

We extended the former measurements between two such brush layers to the case of normal and shear forces measured between one mica surface coated with STAI or a STAI-diblock layer and a bare mica surface. This system is resemble to confined biological systems that on one side have an extended charged polymer opposing to flat charged surface. When the surfaces are coated only with hydrophobic STAI layer they exhibited long range attraction (from ca. 100nm) that resulted in flat adhesive contact. A very different behavior was seen after assembly of the polyelectrolyte brush on the STAI-coated surface. The long range attraction was replaced by repulsion, and on compression a weak attraction to adhesive contact was observed. While applying shear, extremely low friction (μ_{eff} ca. 10^{-4}) between polyelectrolyte-brush and bare

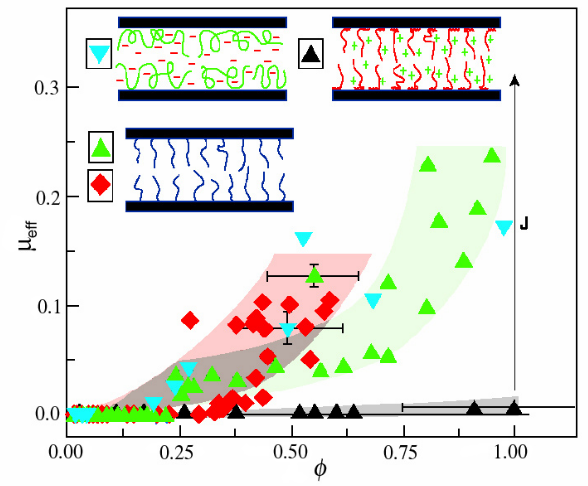

Fig. 1 *Variation of the effective friction coefficient* μ_{eff} *with volume fraction* ϕ *of confined polymer for different polymer lubricants. Volume fractions are based on absolute adsorbance values determined for the respective polymers from in situ refractive index measurements. Red and green symbols are for neutral brushes in non-polar and in aqueous good solvents respectively, with respective bands indicating the range of the scatter. Blue symbols are for an adsorbed cationic polyelectrolyte, chitosan, in an aqueous solution at pH 3.5. The black symbols and corresponding grey band are from the PMMA-b-PSGMA brushes study. Shear velocities for all data are in the range 250–500 nm* s^{-1}*. The cartoons illustrate the different charged and uncharged polymer lubricant configurations, with positive or negative charge signs indicating the counterions.*

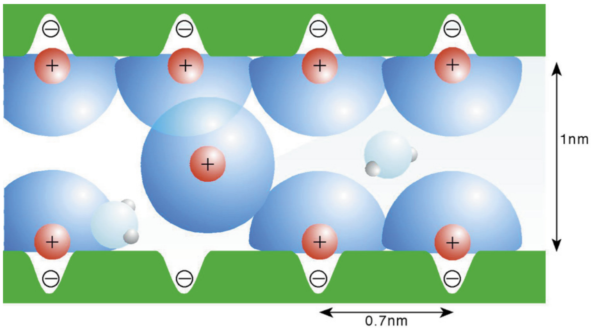

Fig. 2 *A cartoon demonstrating approximately to scale relative to the mica surface separation D = 1nm, the spacing of the ionizable mica surface lattice sites (~0.7nm) and the size of a free hydrated Na^+ ion (roughly 0.75-nm diameter). Water molecules (diameter ~0.25 nm) are indicated for comparison.*

charged mica surface was observed, similarly to what was observed between the two opposing polymer brush layers.

For both uni- and double- sided polyelectrolyte brush layers, we attribute the low friction effect to the high osmotic pressure within the counterion-swollen brushes, together with the fluidity of the hydration layers surrounding the charged segments in polyelectrolytes. Such counterions effect has been recently shown to act like molecular ball bearings when the compressed surfaces confining them slide past each other (see Raviv and Klein 2002 and Fig. 2). It is also well known that when brush-bearing surfaces slide past each other, the interfacial region remains very fluid and low friction results (see Klein et al. and Fig. 1). The combination of the two mentioned phenomena can be found in living systems and serve to protect and extent the viability of biological tissues.

A comparison between this unique brush-like structure to adsorbed positively charged polyelectrolyte (chitosan) was also made (see Kampf et al. and Fig. 1). The later system exhibited strong resistant to compression and friction coefficient of μ_{eff}=ca. 0.003 at low compressions, increasing to ca. 0.07 at pressures of some atmospheres measured while the surfaces slide past each other. Frictional forces between the rubbing crosslinked layers were much higher than for the non-crosslinked chitosan, an effect we attribute to increased segmental friction arising from attractive interactions between the crosslinking points.

In conclusion, polyelectrolytes can orient themselves in various configurations on a surface. We found that surfaces possess extended charged polymers are contributing to a very low friction that can increase in adsorbed or crosslinked adsorbed polyelectrolytes on charged surfaces. We also found that the presence of counterions near the surface play an important role in lubrication systems confined to the nanometric scale. The need of high or low friction in natural systems can be tuned by different configuration and conformations of polyelectrolytes assemblies on the surface, demonstrates the meet to the need of the biological adaptation. Learning the nanometric to the molecular level of polyelectrolyte interactions can help not only to understand the mechanism involved in biolubricating systems but also enable to use the knowledge for medicinal proposes such as designing of lubricated surfaces in artificial implants.

Selected Publications

Klein, J., Kumacheva, E., Mahalu, D., Perahia, D. and Fetters, L. J. (1994) Reduction of frictional forces between solid-surfaces bearing polymer brushes. Nature, 370, 634-636.

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Kampf, N., Raviv, U. and Klein, J. (2004). Normal and shear forces between adsorbed and gelled chitosan layers. Macromolecules, 37(3); 1134-1142.

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