following on the excellent biotribology article published in the December 2003 TLT issue, I thought it might be interesting to relay some very exciting research aimed at determining the mechanisms by which human biolubricants work.

A team of researchers from the University of Oxford (U.K.) and the Weizmann Institute of Science (Rehovot, Israel) with support from the University of Montreal (Québec, Canada) and the University of Liège (Belgium) has been looking at why our eyelids don’t stick to our corneas and why our knees bend smoothly.

Human and animal biolubricants are water-based, but water is not a particularly good lubricant. A polysaccharide called hyaluronan (also known as hyaluronic acid), a long-chain molecule that can bind up to a thousand times its weight of water, has been thought for many years to play a key role in biolubrication. Several tribologists have speculated that hyaluronan molecules might attach to the surfaces of cartilage to form a lubricating layer, much like lubricity additives on steel surfaces.

The synovial fluid found in joints such as knees and elbows is markedly thixotropic. Its viscosity, which is higher than that of water, decreases with increasing shear force, but its elasticity increases with increasing velocity of the fluid. The thixotropy of synovial fluid is thought to be due to the hyaluronan that it contains. Functionally, synovial fluid lubricates and nourishes the articulating parts of cartilages.

Researchers have developed a method of mimicking the possible actions of hyaluronan on cartilage. Mica surfaces, which are usually negatively charged and hydrophilic, were made hydrophobic by coating them with a layer of stearic trimethyl-aminium iodide. A diblock poly(methylmethacrylate)-block-poly(sodium sulphonated glycidyl methacrylate) (PMMA-b-PSGMA) copolymer was then coated onto the ‘hydrophobised’ mica surfaces. This copolymer is hydrophobic at one end (PMMA), hydrophilic at the other (polyelectrolytic PSGMA). The copolymer must be attached to the mica by the hydrophobic PMMA end because polyelectrolytic PSGMA does not adsorb onto hydrophobic surfaces.

As a result, the ‘hydrophobised’ mica surfaces became coated with a long-chain polymer that had the polyelectrolytic end sticking out. Researchers describe these as “PE-brush-bearing mica surfaces.” According to the researchers, the ends of the ‘bristles’ of these PE-brushes become negatively charged and attract water molecules in clusters or ‘shells’ around them. Although these shells are held quite firmly by the bristles, they are also very fluid.

Normal and shear forces between opposing mica surfaces immersed in various liquids were measured using a surface force balance. The opposing surfaces were then progressively compressed together by increasing the load on the top surface. The shear (frictional) forces between them were measured while the top surface was made to slide over the lower surface at different sliding velocities. Control measurements on normal mica surfaces were performed in salt-free water.

PE-brush-bearing mica surfaces immersed in water were found to have much lower coefficients of friction than the same surfaces immersed in other liquids, including organic solvents. Researchers believe PE-brushes provide good lubrication for two reasons:

- Mutually compressed PE-brushes in a good solvent resist interpenetration due to excluded volume effects arising from chain configurational entropy.
- The configurational excluded volume effect is augmented by the large osmotic pressure exerted by mobile counterions within the PE-brush.

This implies that a given load can be supported with less mutual interpenetration of the PE-brushes than for neutral brushes, thereby reducing the extent of the sheared interfacial region when the opposing surfaces slide over each other. Charged brushes reduce the friction much more than uncharged ones. This combination of charge and steric effects is absent in most other forms of polymeric surface-active chemicals such as conventional lubricity and boundary lubrication additives on metal surfaces.

Researchers suggest that lubrication in living systems may be mediated by brush-like PE lubricants. The next piece of research will be to determine if hyaluronan-cartilage combinations have similar properties to PE-brush-mica.

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