TECH BEAT

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Feel of skin cream

Three phases of friction are major factors where the skin cream is applied to the skin.

KEY CONCEPTS

- Selection of a skin cream is based in part on its effect on the tribological properties of the skin surface.
- Skin cream application moves through three phases: a hydrodynamic or mixed lubrication regime, boundary lubrication and reduction in the coefficient of friction.
- A number of parameters, including contact angle, change in skin roughness and friction, are evaluated to determine the tribological properties of the skin cream on the nanoscale.

As an old surfactant chemist, I found out early in my career that there is a direct relationship between the components used in personal-care products and in lubricants. Formulators in both markets share components such as emulsifiers and lubricity additives. The latter are known to the personal-care industry as emollients.

One personal-care product that we use everyday is skin cream. While we may not pay much attention to the product's content, skin creams are complex emulsions that contain such additive types as humectants (attract and hold water in the skin) and occlusives (form a layer on the skin surface and moisturize by retarding water evaporation). In a sense, a skin cream has comparable components to an emulsified oil used in metalworking applications.

STLE fellow Bharat Bhushan, professor and director of the Nanoprobe Laboratory for Bio- and Nanotechnology and Biomimetics at The Ohio State University in Columbus, Ohio, says, "Skin cream is used for a number of reasons. One of the main uses is to moisturize dry skin. Skin cream also helps to soften skin, as a rough feel is no good."

Bhushan maintains that there are a number of factors to consider in selecting a skin cream from a scientific viewpoint. He says, "Skin cream performs by altering the tribological properties of the skin surface. These include the roughness, friction and adhesion of the skin surface."

Friction is a major factor when the skin cream is applied. Bhushan says, "An individual places skin cream on his or her skin leading to the generation of friction between the cream and the finger, as shown in Figure 1. Sensations in the finger are sent to the brain indicating how the cream is perceived. Initially, skin vibrations will be produced that are minimized once the cream becomes smooth."

Bhushan indicates that there are three phases in this process. Initially, the skin cream film is quite thick so that lubrication is in the hydrodynamic or mixed lubrication regime. This means that the skin feels slippery, and the coefficient of friction is low. As the cream is thinned out on the skin, a boundary lubrication regime is created in the second phase. At this point, the skin becomes more moist and smooth, leading to high adhesive forces and friction. Finally, either through water evaporation or some other physical or chemical change in the skin surface, a reduction in the coefficient of friction and adhesive force is achieved in the third phase.

Bhushan summarizes, "The progression through the three phases of friction is dependent upon the thickness of the cream, time and finally the quality of the cream."

A better understanding of how skin cream interacts with skin at the nanoscale would provide greater insights into the three phases of friction and, as a consequence, determine which components in a skin cream provide better performance characteristics. Such a study has not been conducted until now.

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The contact angle for skin treated with skin cream is lower, which means that the cream imparts hydrophilic properties to the skin.

PARAMETERS EVALUATED

Bhushan and his research group evaluated the tribological properties of skin cream on the nanoscale at ambient temperature through the use of an Atomic Force Microscope (AFM). The skin cream examined is a well-known commercial product, Vaseline Intensive Care Lotion. Studies were conducted on the raw skin itself and on skin treated with the cream.

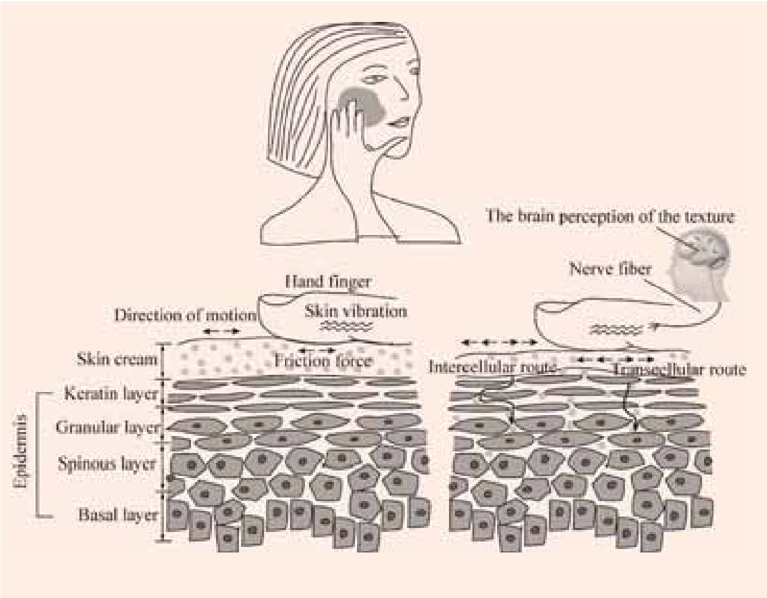

Figure 1 | **Application of skin cream onto skin is a complicated process in which the friction generated between the skin and the individual's finger is a major factor in determining how the cream is perceived.** *(Courtesy of The Ohio State University)*

The first parameters evaluated are how the contact angle and the roughness of the skin change when the cream is applied on the skin. Bhushan says, "Contact angle is a very important factor because it measures how readily the skin repels water. The key angle is 90 degrees because contact angles above this figure indicate skin is sufficiently hydrophobic to repel water, while a lower angle indicates that the skin attracts water."

The contact angle for skin treated with skin cream is lower, which means that the cream imparts hydrophilic properties to the skin. Surface roughness is also lower, indicating that the cream improves the condition of the skin surface.

Friction increases upon application of the skin cream because of its impact on the AFM probe. Bhushan says, "As the probe encounters the skin cream film, the hydrodynamic drag rises as the tip tries to move through the cream, leading to an increase in friction. This force is not seen with the skin itself.

The thickness of the cream on the skin surface also is a factor in influencing the magnitude of friction seen. The researchers applied skin cream with a thickness between 80 and 450 nanometers. These values are approximate because the cream is continuously being absorbed by the skin.

There is a direct correlation between cream thickness and friction. Bhushan says, "Cream thickness is directly related to viscosity, which means that a greater value leads to higher friction."

Two important external factors, humidity and temperature, also affect the tribological properties of skin cream. Intuitively, the goal is to moisturize skin, which would suggest that higher levels of humidity are helpful. But in actuality, humidity is a negative factor.

Bhushan explains, "In a high-humidity environment, a meniscus force is formed between the condensed water and the lipids constituting the surface of the skin. This increases the thickness of the film present on the skin, resulting in an increase in friction."

Friction is higher with cream-treated skin because some of the components used to prepare the cosmetic are humectants that attract water. Result: A higher concentration of water is hydrogen-bonded to the humectants, leading to a thicker film.

When asked about the properties of a good skin cream, Bhushan indicated that viscosity, thickening and rate of applications all must be considered. He adds, "The key element is how long the skin remains smooth or moist. A superior skin cream will maintain this effect for more than a day, while an inferior product may last for less than an hour."

Bhushan intends to do further evaluation of other skin creams and their components. Additional details can be found in two recent articles[1,2] or by contacting Bhushan at **bhushan.2@osu.edu.**

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Smart metal foam

A new class of materials lighter than conventional metal alloys still retain excellent mechanical properties.

KEY CONCEPTS

- **Metal foam is a relatively new class of materials that is lighter in weight than conventional metal alloys yet retains excellent mechanical properties.**
- **A smart metal foam has been developed based on a combination of nickel, manganese and gallium that changes shape in the presence of a magnetic field and retains the shape when the field is removed.**
- **One potential application for this smart metal foam is in micropumps.**

Foam is usually considered to be a negative factor if not a curse when present in lubricant applications. This phenomenon occurs due to the entrainment of air in either an aqueous or oil medium. In the case of metalworking fluids, the presence of foam deprives the fluid from actually contacting the surface of a cutting tool and a workpiece during a metal-removal operation. This factor leads to inferior performance.

But foam can impart beneficial properties to a metal alloy. Metal foams are a relatively new class of materials that have the potential to be used in structural applications because they are lighter in weight than conventional metal alloys but can retain excellent mechanical properties. Now a collaborative research program between Northwestern University in Evanston, Ill., and Boise State University in Idaho has led to some very unusual metallic foams.

David Dunand, the James N. and Margie M. Krebs professor of material science and engineering at Northwestern, describes how metal foams are prepared. “Instead of just casting by pouring molten metal into an empty mold,” he says, “the metallic melt is cast onto an aggregate of inorganic oxide particles (such as sodium aluminate) under vacuum. After cooling and cutting the alloy/oxide composite with a saw, the oxide is removed by dissolution in a mineral acid such as hydrochloric acid. The result is a metal alloy sponge or foam with voids replicating the shape, size and connectivity of the original oxide particles.”

Dunand indicates that the trick is finding a suitable mineral acid that will not dissolve the metal and an oxide that is heat-resistant but still dissolves in acid.

Certain metal alloys have been known to change states when placed in a magnetic field. In a previous TLT article, the concept of magnetic refrigeration was examined as an alternative to gas compression.[1] An exotic metal alloy based on manganese, iron, phosphorus and germanium is described that moves reversibly from a disordered paramagnetic state to an ordered ferromagnetic state in a magnetic field. During this process, heat is absorbed from a refrigerator and then expelled.

Certain metal alloys have been known to change states when placed in a magnetic field.

Metal alloys based on nickel, manganese and gallium also exist that change their shape in the presence of a magnetic field and retains the shape when the magnetic field is removed. These materials then revert back to their original shapes when the magnetic field is rotated by 90 degrees.

Peter Mullner, professor of materials science and engineering at Boise State, says, “This shape memory effect occurs when the direction of the magnetic field is changed. Alternatively, the magnetic-shape memory effect occurs if the metal works against an external load such as a spring. The metal alloy expands when the magnetic field is applied and then contracts when the magnetic field is removed. Metal alloys receptive to this process can expand and contract hundreds of times per second.”

Magnetic-shape-changing alloys generate stretching and shrinking, which is expressed as a parameter known as magnetic field induced strain.

One of the problems in working with these magnetic-shape memory alloys is that the effect is only seen with single crystals, which are difficult to work with and too expensive to be commercially viable. An example of a single crystal is a gem such as a diamond. It is more desirable to prepare magnetic-shape memory alloys out of polycrystalline alloys that are much easier and cheaper to prepare. Such an approach has not been successful until now.

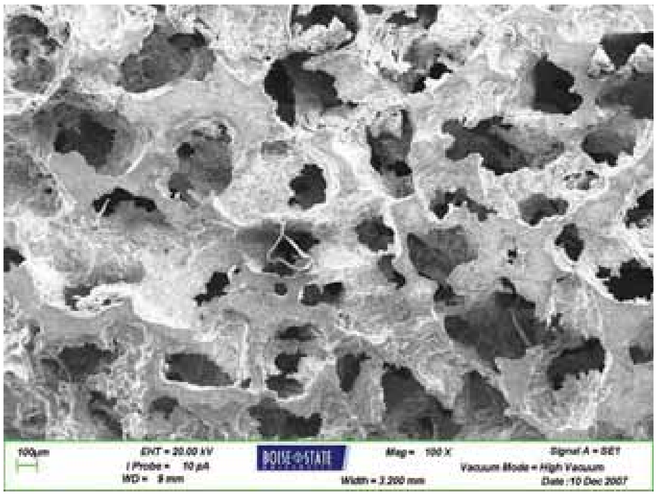

Figure 2 | **The two-tier structure of the smart metal foam enables the material to change shape in the presence of a magnetic field and retain that shape when the field is removed.** *(Courtesy of Boise State University and Northwestern University)*

POLYCRYSTALLINE METAL FOAMS

Dunand and Mullner have developed polycrystalline metal foams that function as a magnetic-shape memory alloy. The metal alloy used is also a combination of nickel, manganese and gallium.

The magnetic-shape memory effect is related to a temperature-dependent phenomenon in which the metal alloy transitions during cooling from the austenite phase at elevated temperature to the martensite phase at lower temperature. Mullner explains, "This phase transition is similar to a substance moving from a liquid to a solid. In our case, movement of the single crystal version of the alloy to the martensite phase leads to the formation of crystallographic twins, which shear back and forth in the presence of a magnetic field. This shearing effect gives the alloy its memory capability."

Magnetic-shape-changing alloys generate stretching and shrinking, which is expressed as a parameter known as magnetic field induced strain (MFIS). Single crystals exhibit high MFIS values up to 10%. Dunand says, "Single crystals are not constrained by neighboring grains, which makes it easy to shear twins and, as a result, readily change shape."

Polycrystals are much easier to prepare from a molten state than single crystals. But twinning in polycrystals is canceled because neighboring grains deform in incompatible directions and hinder each other.

The researchers overcame this problem by introducing porosity into the structure, making it foam-like. This reduced the number of neighbors for each grain, which could behave much more like a single crystal. Initial efforts led to the creation of a bamboo grain structure in the struts, which contain grains that span their whole width, 200 to 300 microns, and are connected at nodes. This arrangement does allow the struts to display a small MFIS due to the added freedom introduced by the pores.

The researchers decided then to mix two sizes of oxide particles to prepare a foam with two different pore sizes. Dunand says, "We processed the molten metal alloy into a metal foam, leading to a material that has a porosity of 62%. The presence of the two different pore sizes enabled the formation of struts and nodes on two size levels. Besides the big struts and nodes seen previously, a network of finer struts and nodes is developed among pores that are 50 micron in length."

This finer structure enables twinning to occur in the presence of a magnetic field to change the shape of the metal foam. MFIS for this polycrystalline, magnetic-shape memory metal foam can reach up to almost 10%.

An image showing the two-tier structure of the metal foam is shown in Figure 2. Mullner says, "Now that we have developed this polycrystalline material, the porosity will enable it to be used in applications such as a micropump. The metal foam will be able to move liquids in the presence of a magnetic field without any moving parts. One advantage of a magnetic-shape memory foam as compared to other smart actuator technologies is a large work output, making these materials suitable for micropumps."

Other applications include sonar devices, precision actuators and magneto-mechanical sensors. Future work will involve optimizing the architecture of the foam to achieve better performance. Dunand adds, "We also need to understand what is going on in the nodes and then apply this idea to other alloys."

The researchers have filed a patent application, and further information can be found in a recent article.[2]

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Facile olefination of aromatic derivatives

An alternative technique can prepare carbon-carbon bonds and synthesize more substituted aromatic molecules.

A large number of diverse additive and basestock technologies are used in the preparation of automotive and industrial lubricants. Many of these components are organic molecules that have been prepared by standardized reaction processes for many years.

Derivatives of aromatic compounds such as benzene, xylene and cumene are used as lubricant additives. Among the examples are alkyl phenols that can be used as antioxidants or precursors for detergents used in automotive lubricants. Alkylbenzene sulfonates are another member of this class and are used as detergents, corrosion inhibitors and emulsifiers in both automotive and industrial lubricants. A third example is aromatic amines such as alkylated diphenylamines that are widely used as antioxidants in automotive lubricants.

Derivatization of basic aromatic molecules has been difficult to achieve because it is not very easy to replace a hydrogen on an aromatic ring with a carbon chain. Jin-Quan Yu, associate professor from The Scripps Research Institute in La Jolla, Calif., says, "The main method used currently is known as the Mizoroki-Heck reaction. This process involves the addition of an olefin to an alkyl or aromatic halide in the presence of a base and a palladium catalyst."

Direct olefination of aromatic derivatives is an alternative approach that has been examined since the 1960s.

The Mizoroki-Heck reaction has proven to be an indispensable tool in organic synthesis. It relies on the need to utilize an organic halide molecule as an intermediate. Yu says, "Extra steps are required to halogenate the substrate and then remove it. This can lead to excessive waste, both in terms of the labor and energy needed to conduct these steps."

Yu also points out that positioning the halide group on the organic substrate in the right position represents a challenge. Depending upon the target molecule, additional reaction steps may be required just to synthesize it properly.

Direct olefination of aromatic derivatives is an alternative approach that has been examined since the 1960s. This technique has not been fully utilized because of problems with controlling selectivity, utilizing versatile substrates and the need to develop simple and practical reaction conditions.

There is need for a technique that improves upon direct olefination of aromatic derivatives yet complements the Mizoroki-Heck reaction. Such a technique has not been devised until now.

KEY CONCEPTS

- Derivatives of aromatic compounds are widely used in lubricants as antioxidants, corrosion inhibitors, detergents and emulsifiers.
- A new synthetic technique has been developed to directly add olefins to aromatic molecules under relatively low temperatures and short time frames.
- This process may provide a more efficient and economical way to develop new aromatic derivatives for use as lubricant additives.

DIRECT METHOD

Yu and his research group have now shown that an olefin can be directly added to

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a diverse group of aromatic derivatives under simple reaction conditions. He says, "This direct approach to prepare carbon-carbon bonds in place of carbon-hydrogen bonds is a key discovery that will enhance the ability to synthesize more substituted aromatic molecules."

Figure 3 | **A direct olefination process has been developed that enables olefins to be easily inserted into aromatic ring systems under relatively mild conditions over a short time frame.** *(Courtesy of The Scripps Research Institute)*

The researchers focused on using phenylacetic acid derivatives as the substrates because they are readily available and reasonably priced. Figure 3 shows the scheme for the reaction of a substituted phenylacetic acid with an olefin. A sodium salt (such as table salt—sodium chloride), a palladium (II) catalyst, amino acid ligand and oxygen are used in the process.

Yu says, "Two key discoveries have been achieved in our work. We found that a sodium salt can coordinate to the carboxylic acid group to accelerate the reactivity, and there is good selectivity to direct the olefin to a specific site on the aromatic ring. A second finding is that coordination of amino acid ligands to the palladium catalyst does not kill the reaction but, rather, controls the regiospecificity of the process."

Without using the sodium salt, the reaction does not occur. From a selectivity standpoint, as the example in Figure 3 shows, the reaction conditions enable the olefin to become attached mainly in a position adjacent (or ortho) to the carboxylic group.

One of the more interesting aspects of this process is that the researchers found it was beneficial to run in the reaction in an oxygen environment. Oxygen works well as an oxidizing agent.

Benzoquinone also is employed to prevent a second olefin from being inserted onto the aromatic ring. Yu adds, "We want the process to be very selective and use benzoquinone to prevent the formation of difunctional species. This prevents the production of mixtures with the desired monofunctional adduct."

Initial work to establish reaction conditions was conducted on 4-methoxyphenyl acetic acid and ethyl acrylate. Excellent yields were found when the reactants were heated at 90 C for 24 hours. Yu says, "These results met our goal of developing a process that is cost-effective and does not need to be run at temperatures above 100 C. In more recent work, we have evaluated a new amino acid ligand that is even more effective. We can achieve 100% yields when the reaction is run at a lower temperature (80 C) for only 20 minutes. Another benefit is only 0.2% palladium is required."

Yu indicates that this combination of reactants and conditions enables the process to work quite well. The researchers are still working to better understand the reaction mechanism.

Yu says, "We believe that the amino acid coordinates to the palladium complex, which then attaches to the olefin substrate and the phenylacetic acid species. We are still working on better understanding the transition state at this time."

The researchers have used these reaction conditions to develop complex molecules that are intermediates in the manufacture of pharmaceuticals. Yu indicates that the researchers have now determined how to activate sp^2 unsaturated species very well. The future challenge is to find ligands that can be used to react with saturated sp^3 moieties.

This process provides a more efficient and economical way to insert unsaturated organic groups onto aromatic ring systems. It has the potential to provide lubricant additive suppliers with additional options to develop new molecules that may provide better performance in the future.

Further information can be found in a recently published article[1] or by contacting Yu at **yu200@scripps.edu**.

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