Nanotribology of Skin Cream Using AFM and Nanoindentation

Prof. Bharat Bhushan
Ohio Eminent Scholar and Howard D. Winbigler Professor
and Director NLBB
Bhushan.2@osu.edu

Nanotribology Laboratory for Information Storage and MEMS/NEMS
Micro/nanoscale studies
- Bio/nanotribology
- Bio/nanomechanics
- Biomimetics
  - Materials sci., biomedical eng., physics & physical chem.

Techniques
- AFM/STM
- Microtriboapparatus
- Nanoindentor
  - Numerical modeling and simulation

Materials/Device Studies
- Materials/coatings
- SAM/PFPE/ionic liquids
- Biomolecular films
- CNTs
  - Micro/nanofabrication

Collaborations

Applications
- MEMS/NEMS
- BioMEMS/NEMS
- Superhydrophobic surfaces
- Reversible adhesion
  - Beauty care products
  - Probe-based data storage

Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics
Laboratory Facilities

5700 sq. ft. of lab space (T&H controlled; part lab – class 100 clean room)

Major Equipment

- Scanning tunneling microscope & five Atomic force/Friction force microscopes
- Noncontact optical profiler and stylus profiler
- Microhardness and Nanohardness testers
- High vacuum tribotest apparatus equipped with mass spectrometer and Auger
- Microtriboapparatus for Micro/Nanoscale Devices
- Pin-on-disk type continuous/Reciprocating sliding test apparatuses
- Vapor and liquid deposition facilities for self-assembled monolayers and liquid lubrication
- Scanning ellipsometer
- Particle counters/Optical microscopes/Microbalance/Environmental chambers
- Micro/nanofabrication facilities for bio/nanotechnology and biomimetics research
- Access to various physical and chemical analyses facilities at OSU
Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics

Director: Prof. Bharat Bhushan

Senior/Visiting Scientists


2010- Usama Heiba, “Nanotribology of Contact Switches,” Ph.D. Mechanical Engineering

2010- Dr. Monalisa Mazumder, “AFM Characterization of Biologically Active Electrokinetically-Altered Fluids,” Ph.D. Chemical Engineering

Ph.D. Students

2006- Shrikant C. Nagpure, “Multiscale Characterization of Aging Phenomena in Li-Ion Batteries,” Department of Mechanical Engineering

2010- Daniel R. Ebert, “Biomimetics,” Department of Mechanical Engineering

M.S. Student

2009- Brian Dean, “Biomimetics,” Department of Mechanical Engineering


2010- Steven Englehaupt, “Tribology of Skin Cream,” Department of Mechanical Engineering.
Sponsors

**Industrial**
- Corning
- Revalesio
- MicroMed
- Technova

**Government Sponsors**
- National Science Foundation
- National Institute of Health
- Institute for Materials Research
- European Union

**Instrumentation Support**
- Veeco Instruments
Industrial Membership Fees

- Annual membership fee is an unrestricted annual grant to NLBB
- Three levels of membership
  - Member $25,000
  - Advisory Member $50,000
  - Senior Member $75,000
  - Corporate Member $100,000
- Members will have limited access to lab facilities. Advisory, senior and corporate members can initiate and guide research project.
- Contract research can also be initiated. The cost usually runs from $60 to $100 k per year.
Sponsor Benefits

• Access to all laboratory facilities

• Initiate and guide a research project (Advisory, Senior and Corporate members)

• Receive all written reports before they are submitted for external publication or are available for general distribution

• Attend Industry/University Technical Exchange meetings held once per year

• May send one representative to any short courses offered by NLBB

• May place a visiting Industrial Fellow for any period

• List of students available for employment
Ongoing Research Projects

Nanotribology and Nanomechanics
• Influence of Water on the Interaction Between Graphite and Carbon Nanotubes
• Nanotribological and Electrical Characterization of Ultrathin Wear-Resistance Ionic Liquid Films

Bio- & Nanotechnology
• AFM Characterization of Biologically Active Electrokinetically-Altered Fluids
• Nanolubrication of Sliding Components in Adaptive Optics Used in Microprojectors
• Charging/Discharging in Capacitive RF-MEMS Switches Using an AFM
• Morphology and Mechanical Properties of Block Copolymer Films for Bone Regeneration Applications (with Prof. S. Schricker, College of Dentistry)
Biomimetics
• Lotus Effect: Roughness-Induced Superhydrophobic Surfaces
• Mechanically Durable Superhydrophobic, Self-Cleaning, and Low-Drag Surfaces with Hierarchical Structure
• Shark-Skin Inspired Structures for Low Drag
• Gecko-Inspired Hierarchical Structures for Reversible Adhesion

Beauty Care Products
• Adhesion, Friction, and Wear Characterization of Skin and Skin Cream Using Atomic Force Microscopy

Batteries Aging
• Aging Mechanisms in Lithium-ion Batteries (with Profs. S. Babu, G. Rizzoni, and Y. Guezennec, College of Eng.)

http://www.mecheng.osu.edu/nlbb/
Nanotribology of Skin Cream
Motivation

• Skin cream improves skin health and creates a smooth, soft, and moist perception by altering the surface roughness, friction, adhesion, elasticity, and surface charging characteristics of skin surface.
• The tactile perception of skin texture is mediated by skin vibrations which are highly dependent on the friction properties of the surface.
• A detailed study should include both friction and resulting skin vibrations.

Schematics of the application process of skin cream and the interaction between the skin vibration and the brain perception of the texture
**Background**

- Many studies have focused on the friction and triboelectrical properties of skin and skin cream on the macroscale.
- The study of the coefficient of friction, adhesive force, and surface potential on the nanoscale provides a fundamental understanding of the mechanisms behind how skin cream interacts with skin. Little data exists.

![Engineering Interface](image1)
![Tip-based microscope](image2)

- Viscosity of very thin liquid films increases exponentially with a decrease in thickness.

During rubbing of the cream over skin surface, it gets thinner, the person starts to apply it at increasing high interfacial speeds. This should lead to high friction towards the end due to high viscosity and high viscous shear rates. Understanding of the effect of thickness and shear rates is crucial.

- Skin is the outermost organ of the body and is easily affected by the environment (humidity, temperature, and surface charge).
Project Plans

Part I: Adhesion, friction and wear study of virgin skin and common cream treated skin
  - Surface roughness and friction force
  - Effect of film thickness, velocity and normal load on friction and adhesion at nanoscale
  - Effect of relative humidity and temperature
  - Durability study

  - Effect of film thickness, velocity and normal load on adhesion and friction, and durability at macroscale

Part II: Adhesion, friction and wear study of various creams treated skin and effect of humidity
  - Film thickness, adhesion, Young’s modulus maps at various humidities
  - Durability study
Part III: Triboelectrification of virgin skin and common cream treated skin
- Effect of Velocity, normal load, rubbing time, and relative humidity on electrostatic charging of virgin skin and treated skin

Part IV: Nanomechanical properties of skin and skin cream
- Nanoscratch
- Nanoindentation
- In situ tensile properties

Part V: Nanoscale characterization of synthetic skins for cosmetic science
- Surface texture
- Film thickness and adhesive force maps
- Friction force
- Nanoindentation
Experimental Samples

• Category of skin and skin creams
  - Rat skin with common cream (Vaseline Intensive Care)
  - Rat skin, pure lanolin, pure petroleum jelly, aqueous glycerin (weight fraction = 1/4), common cream and oil free cream
  - Two synthetic skins and rat skin, common cream
Experimental Techniques

- Nanoscale measurements were conducted using the AFM and nanoindenter.
- A homemade humidity control chamber and a temperature control system were used to study the effect of relative humidity and temperature.
- Macroscale tests were conducted to compare with nanoscale tests by using a ball-on-flat tribometer.
AFM

Schematic of a small sample
AFM/FFM

Schematic of a large sample
AFM/FFM

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Three-sided pyramidal (natural) diamond tip

Square pyramidal silicon nitride tip

Square pyramidal single-crystal silicon tip

Three-sided pyramidal (natural) diamond tip

Carbon nanotube tip

Various AFM tips
Optical micrographs of standard tip and microtips of different radii

Si$_3$N$_4$ - 0.05 $\mu$m
SiO$_2$ - 3.8 $\mu$m
SiO$_2$ - 14.5 $\mu$m

25 $\mu$m
Various AFM operating modes

Tapping mode (constant amplitude) is used for roughness measurements. Contact mode is used for adhesion, friction and durability studies. Torsional resonance (TR) mode (constant load) is used to measure in-plane (lateral) heterogeneity (elastic and viscoelastic properties).
• Film thickness, $F_{ad}$ and Young’s modulus mapping of various creams treated skin was obtained using the force calibration plot technique (force-volume mode).

- The film thickness is the sum of the travel distance of the piezo ($h_1$) and the deflection of cantilever ($h_2$).

- $F_{ad}$ is calculated from the force calibration plot by multiplying the spring constant with the vertical distance between point B and F.

- Young’s modulus can be determined using Hertz analysis:

$$ F + F_d = \frac{4}{3} \sqrt{RE\Delta z^{3/2}} $$

A typical force distance curve for cream treated skin.
• **Surface potential** was measured using Kelvin probe method with the Multimode III AFM.

• Skin samples were rubbed with polystyrene as it is known that it creates a charge on skin surface. They were rubbed on the microscale with 45 µm φ polystyrene microsphere mounted on the AFM tip and on the macroscale with a polystyrene plate in a tribometer. Surface potential map of skin samples (electrically isolated from ground to prevent quick discharge) were obtained.
  – Before rubbing
  – After rubbing

Before rubbing, skin surface is negatively charged because the epithelial cells in skin carry a negative charge.
In-Situ Tensile Measuring Setup

- In situ tensile measurements are made using a custom-built tensile stage attached to the AFM base and uses a linear stepper motor to load a sample in tension.
Nanoindentation

Schematic of nanoindentation and nanoscratch test on hair

SEM imaging
- Philips XL-30 ESEM
- Hair sample sputtered with thin gold coating prior to SEM measurements
Tribometer with an environmental chamber
Part I: Adhesion, friction and wear study of virgin skin and common cream treated skin

Surface roughness and friction force on virgin skin and common cream treated skin at nanoscale

<table>
<thead>
<tr>
<th>Skin type</th>
<th>Surface roughness statistics</th>
<th>contact angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Virgin skin</td>
<td>160 ± 28</td>
<td>983 ± 156</td>
</tr>
<tr>
<td>Cream treated skin</td>
<td>119 ± 20</td>
<td>730 ± 125</td>
</tr>
</tbody>
</table>

- After the application of skin cream, the surface roughness and contact angle decrease and friction force increases.

Representative surface roughness and friction force AFM images

Effect of Film Thickness

- The coefficient of friction (COF) and $F_{ad}$ increase as film thickness increases.
Effect of Velocity

- For both virgin and treated samples, when the velocity is below 1000 μm/s the COF decreases (decreasing meniscus contribution) with an increase of velocity. When it is higher than 1000 μm/s the COF increases due to increasing asperity deformation and viscous shear (in the case of treated).
- Φ_ad for both decreases with an increase in velocity due to reduced meniscus contribution.
Effect of Normal Load

- The COF increases above a critical load, due to large asperity deformation.
- The critical load in the cream treated skin increases from ~ 250 to 500 nN, which suggests that the cream film serves as a protective layer on the skin surface.
- For both samples, $F_{ad}$ increases slightly with load.
Effect of Relative Humidity and Temperature

- For virgin and treated samples, the COF and $F_{ad}$ increase as the relative humidity increases. Adsorbed water molecules increase film thickness leading to higher COF and $F_{ad}$.
- For both samples, COF and $F_{ad}$ decrease as the temperature increases. Desorption of water molecules in both is believed to be responsible. Reduction in viscosity at higher temperatures also should lead to a decrease in friction.
**Durability study**

- For virgin skin, COF and $F_{ad}$ remain constant during the initial few cycles and then increase and decrease, respectively. This is due to removal of the lipid film on virgin skin.
- For treated skin, COF and $F_{ad}$ decrease with the sliding cycles. This is primarily due to adsorption of the skin cream by skin and more uniform distribution.
- Damage observed from AFM profiles of worn area shows scratches created by the sharp tip.
Macroscale Studies

Film thickness, velocity, normal load, and durability study

- Magnitude of COF is higher on the macroscale than on the nanoscale.
- COF increases with the cream thickness increasing up to 1.4 μm, and then it decreases with the further increase of cream thickness.
- Velocity has no effect on COF for virgin skin, but a higher velocity leads to a lower COF for treated skin (shear thinning).
- COF decreases as the normal load increases.
- COF of virgin skin during sliding remains constant. For treated skin, COF increases when the sliding cycle increases up to about 400, after which it decreases slightly and then remains constant.
Summary

• Skin cream reduces the surface roughness and increases the hydrophilicity of skin.

• For a thicker film, the larger meniscus at the contact interface results in larger meniscus forces leading to larger COF and $F_{ad}$.

• Menisci shear and alignment of molecules affect COF and $F_{ad}$ under low velocity and viscoelastic shear affect under high velocity.

• Cream film exhibits a larger load carrying capacity and serves as a protective covering to the skin surface.

• Increase of humidity increases adsorbed water molecules leading to high COF and $F_{ad}$.

• Desorption of water molecules and reduced viscosity with an increase in temperature is responsible for decrease in COF.

• Magnitude of COF is higher on the macroscale than on the nanoscale.
Part II: Adhesion, friction and wear study of various creams treated skin

Friction and Adhesion of various Skin Creams

- Among the five kinds of skin cream, pure lanolin and pure petroleum jelly have the highest coefficient of friction and adhesive force (highest viscosity), and aqueous glycerin has the lowest coefficient of friction and adhesive force.

Friction, adhesion, dynamic viscosity and durability of various skin creams


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• There is a good correlation between coefficient of friction and dynamic viscosity.

Dynamic viscosity measured using a rheometer with parallel plate configuration.
Film thickness, $F_{ad}$ and Young’s modulus maps of various creams treated skin at various humidity

- Film thickness and $F_{ad}$ increase as the humidity increases; Young’s modulus decreases as the humidity increases (adsorption leading to compliance).

- The cream film is unevenly distributed on skin surface.
• For the five kinds of creams, film thickness and $F_{ad}$ increase as the humidity increases; Young’s modulus decrease as the humidity increases.

• Relative changes in the film thickness, adhesive force, and effective Young’s modulus of pure lanolin, pure petroleum jelly treated skin, and virgin skin are less than the oil free cream, common cream, and aqueous glycerin treated skin.

Relative change (wrto 55% RH) in film thickness, $F_{ad}$ and effective Young’s modulus of various creams at various humidity.
Summary

• The cream film unevenly distributes on skin surface.

• Pure lanolin and pure petroleum jelly have high durability and sticky tactile perception compared with other skin cream. The higher viscosity results in higher friction (stickiness) and longer durability.

• Adsorption of water molecules increases the film thickness and $F_{ad}$, softens the skin surface.

• Lanolin and petroleum jelly is less sensitive to the change of humidity compared to others.
Virgin skin and treated skin both before and after rubbing with polystyrene plate (5 × 5 mm) at two velocities

- Virgin skin has larger absolute surface potential compared to cream treated skin.
- For virgin skin, the absolute surface potential decay with time. For cream treated skin, it is more constant.

Samples scanned top to bottom. Relative surface potential is absolute surface potential minus average value.
Virgin skin and treated skin both before and after rubbing with polystyrene microsphere (d = 45 μm) at two velocities.

- For virgin skin, the absolute surface potential increase with time. For cream treated skin, it is more constant.

**Summary of effect of velocity, normal load, and rubbing time on surface potential of virgin skin and treated skin**

- Charge build up in treated skin is less than virgin skin.
- The surface potential increases with an increase of velocity, normal load, and rubbing time when skin is rubbed with polystyrene plate and decreases when rubbed with microsphere.
- Compared with virgin skin, the surface potential of cream treated skin does not change much with an increase of velocity, normal load, and rubbing time.
For all skin samples, the surface potential increases at low humidity, decreases at high humidity. (Data shown only for common cream.)

Compared to oil free cream, common cream, aqueous glycerin, and virgin skin, pure lanolin and pure petroleum jelly have lower relative change in surface potential at RH 8%.

Summary

• Cream treated skin significantly reduces the charge buildup on skin surface.

• Electrostatic charge on skin can dissipate rapidly. The cream treatment can increase the rate of dissipation.

• The increasing of velocity, normal load, and rubbing time increase the electrostatic charging on skin surface.

• Low humidity increases the surface potential, and high humidity increases it.
Part IV: Nanomechanical properties of skin and skin cream

**Nanoscratch**

- Virgin skin could be scratched at a normal load of 3 µN and 15 cycles. The average scratch depth increases almost linearly with an increase in the normal load.
- For cream treated skin, the scratch depth increases little until a critical normal load of 15 µN is reached, above which the scratch depth increases rapidly.

AFM topographical images of scratch, and (b) scratch depth as a function of normal load

Nanoindentation

- At 1000 nm indent depth, the load on virgin skin is about 35 µN, and load on cream treated skin is about 22 µN.
- The hardness and elastic modulus of treated skin is lower than virgin skin, indicating that the skin cream can moisten and soften the skin surface.
In situ tensile properties

- During low strain, the stress-strain curve ascends according to an exponential function. Afterward an almost straight section is reached.
- For virgin skin, the number of patches present on skin surface at around 10% strain increase as the strain increases.
- For treated skin, there are few patches present on skin surface at around 20% strain.
- The patches occur due to interlayer shear force and consequent separation between inner and outer keratin layer.

Stress-strain curves, and (b) AFM topographical images of a control area showing progress of damage with increasing strain.
Elastic modulus, ultimate tensile strength, and ultimate strain, obtained using in situ tensile tester

<table>
<thead>
<tr>
<th></th>
<th>Virgin skin</th>
<th>Cream treated skin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic modulus (MPa)</td>
<td>31±11</td>
<td>22±7</td>
</tr>
<tr>
<td>Ultimate tensile strength (MPa)</td>
<td>11±2</td>
<td>10±2</td>
</tr>
<tr>
<td>Ultimate strain (%)</td>
<td>59±3</td>
<td>62±5</td>
</tr>
</tbody>
</table>

- It shows that there is a slight decrease in the tensile properties of treated skin. The elastic modulus is a little lower than virgin skin, and ultimate strain is a little higher than virgin skin.
Summary

• Cream treated skin exhibits better scratch resistance up to a normal load of 15 µN. Once the normal load exceeds the value of 15 µN, the protection of cream film fails.

• The hardness and elastic modulus of cream treated skin is lower than virgin skin, indicating that the skin cream can moisten and soften the skin surface.

• The stress-strain curves show a characteristic shape, which is related to the deformation of the collagen fibers of the dermis.

• Skin cream moistens and softens the skin surface which increases the extensibility of the keratin layer and reduces the generation of fractions (patches) as the strain increases.
Part V: Nanoscale characterization of synthetic skins for cosmetic science

Preparation Procedure

Synthetic Skin -1 – Dragon Skin®
High performance cast silicone rubber used for applications including medical prosthetics and cushioning applications.

Synthetic Skin -2
Mixture of gelatin from porcine skin, glycerol, formaldehyde, prolipid, and water cast on a replica of human skin make of silicone (originally developed for dental implants) (Lir et al., 2007).

Measure surface roughness, contact angle, adhesive force, friction force, and mechanical properties of the two synthetic skins and compare with rat skin.
Apply skin cream to the synthetic skins and compare various properties with that of rat skin.

Surface texture

- Rat skin surface has some hair follicles and fraction of hairs on the skin surface.
- The surface of the two synthetic skins are different with rat skin and there are no hair follicles and hairs present on skin surface.

SEM images of the surface of virgin synthetic skin-1, synthetic skin-2, and rat skin
Typical surface roughness AFM images, and (b) RMS and P-V distance

- In the case of various skin, before and after treatment, the RMS and P-V distance of the two synthetic skins and rat skin are comparable.
Contact angle

- In the case of virgin skins, the contact angle of the two synthetic skins and rat skin are comparable.
- After treatment, the contact angles of the two synthetic skins and rat skin remain comparable and dramatically decrease as a result of treatment, indicating cream improves the hydrophilic properties of skin surface.
Film thickness and adhesive force maps, and (b) film thickness and adhesive forces of virgin skin and cream treated skin.

- In the case of virgin skins, the film thickness and adhesive force of the two synthetic skins and rat skin are comparable.
- After treatment, the trends of film thickness and adhesive force remain comparable, and both of them increase.
Friction properties

- In the case of virgin skins, the coefficient of friction of the two synthetic skins and rat skin is on the same order.
- After treatment trends of the friction force are similar but the values increase.

Typical friction force AFM images of skin samples, and (b) coefficient of friction of skin samples.
Nanoindentation

- In case of virgin skins, the hardness of synthetic skin-1 is higher than synthetic skin-2 and rat skin, indicating its hard texture. The hardness of rat skin and synthetic skin-2 is comparable. The effective Young’s modulus of synthetic skin-2 is lower than synthetic skin-1 and rat skin.
- After treatment with skin cream, hardness and effective Young’s modulus of synthetic skin-1 show a slight decrease.

Typical load versus displacement plots for the virgin, and (b) hardness and effective Young’s modulus of virgin skin and cream treated skin
Summary

• Based on surface adhesion and friction properties, synthetic skins are good simulations of rat skin. However, the hardness of synthetic skin-2 is comparable to rat skin and can be a better simulation.

• After treatment with cream, the trends of the properties of the two synthetic skins and rat skin are comparable.

• The methodology presented here can act as a good reference for researchers to evaluate the surface, frictional, and mechanical properties of synthetic skins.
Overall Summary

- Nanotribology of skin cream and role of operating condition have been studied using an AFM.
- Skin cream reduces the surface roughness and increases the hydrophilic properties of skin.
- The cream film unevenly distributes on skin surface.
- The higher viscosity results in higher friction and longer durability.
- Cream treated skin significantly reduces the charge build up on the skin surface.
- Skin cream moistens and softens the skin surface.
- Synthetic skin provides a good simulation for the skin and can be used in nanotribology research.

Future Plans

- Study the nanotribology of cream treated damaged skin
- Develop a AE sensor to measure interface vibrations during sliding on nanoscale and macroscale. Correlate vibration data to friction
References


http://www.mecheng.osu.edu/nlbb/