Lessons from Nature and Bioinspired Fabrication: Mosquito Bite and Lotus Leaf

Inspired Superliquiphobic Leather

Thesis

Presented in Partial Fulfillment of the Requirements for the Degree Master of Science in
the Graduate School of The Ohio State University

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2018

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Abstract

Bioinspiration is an emerging field of study. Commercially-available bioinspired products have already affected industries including water treatment, energy conservation and storage, transportation, and data and computing. Bioinspired products are estimated to impact the United States GDP by the order of $400 billion by 2030. The field of bioinspiration is highly interdisciplinary and it involves learning lessons from biological functions, structures, and principles of various objects found in nature. Using the lessons learned, fabricating products and/or surfaces of commercial interest can be produced.

In this research, a chapter on lessons learned on painless mosquito bite is presented first. The chapter starts with providing an overview on bioinsipiring attributes of mosquitoes, which are standing on water, sticking to any surface, flying in rain, and painless piercing. The first three attributes are a result of superhydrophobic legs, dry adhesion in the foot, and hydrophobic wings and antifogging eyes, respectively. The understanding of the fourth attribute—painless piercing—is further elucidated by investigating nanomechanical properties of its mouthpart. The mouth is a bundle of seven coherently functioning subparts. Based on experiments and available literature, it was hypothesized that mosquitoes painlessly bite using a combination of pre-bite numbing, the frequency-dependent-gradient in its labrum’s mechanical properties, its serrated-
design, and vibratory actuation. At end of the chapter, based on the hypothesis, a set of mosquito-inspired microneedle design guidelines has also been proposed.

A second chapter presented is on bioinspired fabrication of water- and oil-repellent leather. Leather is a flexible, yet strong material, which has found applications including footwear, furnishing, automotive, clothing, gloves, sports, and bags. For many applications, the leather should have properties such as liquid-repellency, self-cleaning, low adhesion at high temperature, and anti-smudge. In this study for the first time, artificial leather has been reported to achieve high water- and oil-repellency by using multi-layered nanocomposite coating structure. The coated surface exhibited self-cleaning, low adhesion up to 70°C, and high mechanical durability.
Dedication

Dedicated to my family and friends.
Acknowledgments

The accomplishments presented in this dissertation would not have been possible without the support of many people in my life. First I would like to thank my advisor, Professor Bharat Bhushan, who tirelessly provided guidance and feedback throughout the entire process. I would also like thank my doctoral committee member Professor Carlos Castro at The Ohio State University.

Furthermore, I would like to express my sincere love and appreciation to my family who have been constantly supporting and enduring throughout. I would also like to thank Lal and Sinha families who have been a moral support. Separate thanks to Dr. Mrs. Bhavna Lal.
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Chapter 1: Introduction

Albert Einstein once said, “Look deep into nature, and then you will understand everything better”.

Two of the world-known products, Velcro® and bullet trains, are inspired from burdock plants’ bur and kingfisher bird’s beak, respectively. Velcro® has found its application in even NASA and US Army. And bullet trains are responsible for 40% of the world’s train traffic, with 820,00 commuters per day, covering about 1500 miles of the total network (Mestral, 1964; McKeag, 2012).

Bioinspiration, or biomimetics, is an emerging field of study. Unlike traditional ways of developing a product, it provides an unparalleled opportunity for companies to create products and processes inspired by naturally-proven designs. Today, commercially-available bioinspired products have already affected industries including water treatment, materials, energy conservation and storage, optics and photonics, thermoregulation, transportation, and data and computing (Smith et al., 2015). Bioinspired products are estimated to impact the United States GDP by $425 billion in 2030 (Reaser, 2013).

The field of bioinspiration is highly interdisciplinary and can be divided into two parts. First part involves learning lessons from biological functions, structures, and principles of various objects found in nature by biologists, physicists, chemists, and
material scientists. Nature has gone through evolution over 3.8 billion years (Gordon, 1976). It has evolved species with desired functionality using commonly found materials and routine fabrication methods. The second part involves, using the lessons learned, fabricating products and/or surfaces of commercial interest, by engineers, material scientists, chemists, and biologists (Bhushan, 2016).

1.1 Lessons from Nature

About 7 to 9 million species of animals are known to exist (Resh and Carde, 2009; Mora et al., 2011; Barthlott et al., 2016). Figure 1 provides an overview of various species, organs, and systems with their functions of commercial interest (Bhushan, 2016). The list includes bacteria; plants; insects, spiders, lizards, and frogs; aquatic animals; birds; sea shells, bones, teeth; spider web; moth eye; fur and skin of polar bear; and biological systems.
Figure 1: An overview of various species, organs, and systems with their functions of commercial interest (Adapted from Bhushan, 2016)
Figure 2 presents a montage of some examples from living nature along with their working mechanism behind the properties of interest (Bhushan, 2016). Many bacteria propel themselves using a nanoscale electrical-motor-look-alike flagellum motor, which is driven by the proton flow caused by the electrochemical potential difference across the cell membrane. Leaves of lotus plant are known to be superhydrophobic, self-cleaning, and antifouling, which is due to nano-textured micro-bumps and the hydrophobic wax on top of it. Pitcher plants catch insects using their slippery rims, which is formed due to secreted-nectar and rainwater wetting the radially-oriented microstructures. Water striders are able to stand on water, due to nano-textured micro-hairs on their legs, which are also covered with wax. Butterfly wings exhibit superhydrophobicity, self-cleaning, antifouling, and low drag, due to micro-grooved scales. The wings also provide structure-coloration due to nanostructures on top of the micro-grooves. Geckos’ feet can provide high, dry adhesion, due to van der Waals forces applied by multi-level hierarchical structures on their foot. Shark-skin provides low-drag characteristics, due to longitudinally-grooved scales on their skin. Flexible feathers of bird wings help them in reducing drag when landing. Seashells, and other biomaterials, are strong and resilient, which is due to nanocomposite of thin elastic biomaterial covered with brittle platelets. Spider web is strong and tough, due to nanocomposite of crystalline regions separated by amorphous linkages (Bar-Cohen, 2011). Moth-eyes are antireflective due to hexagonally organized nano-pillars.
Figure 2: Montage of some examples from living nature along with their working mechanism behind the properties of interest (Adapted from Bhushan, 2016).
1.2 Bioinspired Fabrication

After understanding how nature does it, it is crucial to get inspired from it and fabricate structures, devices, and surfaces, using smart materials fabrication techniques. With advancing nanotechnology, the nano- and micro-fabrication methods have become more advanced (Bhushan, 2017b). Few of the many examples are as follows.

Inspired from lotus leaf, various liquid repellant surfaces have been fabricated by creating multi-level roughness using techniques such as lithography, etching, deformation, deposition, and transfer (Bhushan, 2016). Surface energies of these surfaces are also chemically-modified to repel lower surface-tension liquids, such as oil, shampoo, and detergents. Liquids are also repelled by getting inspired from pitcher plants (Brown and Bhushan, 2017; SLIPS Technologies, Inc.). In this case, a liquid repels from an immiscible liquid trapped in a porous substrate. These surfaces find their many applications including reduction in drag flow, energy conversation and conservation, self-cleaning surfaces, and oil-water separation.

Shark skin has introduced riblets on the surface, which lift the stream-wise vortices built near the surface, and hence reduce drag and biofouling (Bhushan, 2016). Some of the riblet fabrication techniques include using metal shims, machined acrylic, machined aluminum, extruded/coextruded polymer, embossed polymer, soft lithography, photolithography, wet and dry etching, grinding, rolling, and laser etching. Applications of such surfaces are in fluid flow in pipelines, boats, airplanes, and even swimsuits. These suits were worn by Michael Phelps, in 2008 Beijing Olympics, where he broke eight Olympic records, seven world records, and won eight gold medals.
The study of gecko feet has inspired dry-adhesives having the same multi-level hierarchy (Bhushan, 2016; nanoGriptech, Inc.). Some of the fabrication methods are nanoindentation, molding, self-assembly, carbon nanotube arrays, and lithography. It has used in applications including adhesive tapes, fasteners, microelectronic, space applications, and treads of wall-climbing robots.

1.3 Scope of the Thesis

This thesis is divided into two parts — learning lessons from mosquitoes’ painless bite and fabrication of bioinspired water- and oil-repellant artificial leather.

Mosquitoes are reported to be the deadliest animal on the planet with the most kills in a year. They first hunt down their prey using their locomotry appendages—legs and wings—that allow them to stand on water, stick on any surface, and fly in rain. Then they bite their prey by numbing the area and vibrating their fascicle. First, an overview has been presented of the mechanism behind their water-repellent legs, dry-adhesion in foot, water-repellant wings, anti-fogging eyes, and painless biting mechanism. Later, results from nanomechanical characterization of tip of the mosquitoes’ labrum have been presented. The labrum was characterized in static and dynamic loading conditions, since the material was found to be highly viscoelastic and it vibrates in order to pierce the prey. Later, based on the lessons learned, guidelines for manufacturing and functioning of a bioinspired painless microneedle has also been presented.

Leather is an important, strong, and flexible material which has found its applications in many areas including furnishing, automotive, and clothing. For some of the applications characteristics such as liquid repellency, self-cleaning, low adhesion at
high temperature, and anti-smudge are desired. For the first time, leather has been reported to achieve stable water- and oil-repellency. A nanocomposite coating of hydrophobic nanoparticles and binder was used, which was also tested for self-cleaning, low adhesion at high temperatures, and high mechanical durability.
Chapter 2: Lessons Learnt from Painless Mosquitoes’ Bite

2.1 Introduction

From 7–9 million of existing different species of animals (Resh and Carde, 2009; Mora et al., 2011; Barthlott et al., 2016), arthropods form about 70–80% of the total population (Thomas, 1990; McGavin, 1993; Chapman et al., 2013). Physically, arthropods are spineless animals with segmented bodies, paired and jointed legs, exoskeletons, and bilateral symmetry. The word—arthropods—is derived from two Greek words: arthron (joint) + podos (foot), meaning jointed-feet.

As big as the sub-section of animals arthropods is, as worse the medical problems it creates (Manson, 1878; Service, 1978; Mullen and Durden, 2009; Goddard, 2013). They are known to attack on host tissues, cause allergic reactions, release toxins and venoms, and may even cause deaths. A summary of arthropods of medical-veterinary interest has been presented in Fig. 3. The arthropods are classified on the basis of a well-established ranking system—in decreasing order Phylum, Subphylum, Class, Order, and common names of the species (Parker, 1997; Mullen and Durden, 2009; Resh and Carde, 2009; Goddard, 2013). Starting from top, Phylum Arthropoda is divided into four Subphyla Hexapoda, Chelicerata, Myriapoda, and Crustacea. The Subphyla are further divided into six Classes and seventeen Orders and each of the Order lists examples of the medically- and veterinary-important arthropods.
Figure 3: Arthropods of medical-veterinary interest (Adapted from Gurera et al., 2017)
A few medically important arthropods with their feeding mechanism have been summarized in Fig. 4. The arthropods are classified using two criteria—dietary preference and feeding mechanism (Chapman et al., 2013).

Based on dietary preference, the arthropods are classified as herbivores and carnivores, which feed on plants and flesh respectively. Listed herbivore arthropods include caterpillars and plant lice. Listed carnivore arthropods include scorpions, spiders, bees, flies, ticks, and mosquitoes.

Based on their feeding mechanism, arthropods are classified as piercers, and piercers and suckers. Piercers only pierce into their host with their teeth or sharp tail. They, typically, release venom into their host, through openings at tip of the piercing parts, to paralyze it, and/or they chew on it. Listed piercers consist of caterpillar, scorpions, spiders, and bees. Piercers and suckers pierce into their host, and suck on the bodily fluids such as plant nectar, sap, and blood. Listed piercers and suckers consist of plant lice, flies, ticks, and mosquitoes.

Mechanisms used by these arthropods are as follows. In order to pierce, caterpillars use a pair of jaw-like-structures, scorpions use its sharp tail, spiders use a pair of sharp jaw-like-structures, and bees use a pair of barbed stylets that moves back and forth alternatively while being inserted. Plant lice use two pairs of stylets (only a pair is shown) for piercing and use the opening formed by stylets for sucking the fluids in. Flies pierce using their barbed stylets and suck blood using the channel formed by the other pair of mouthparts. Ticks use a pair of barbed stylets in an alternative motion to pierce—
later, the tip of the stylets bends outwards and suck blood through the opening. Mosquitoes use its needle-like mouthpart to pierce into its host and suck blood.

One of the listed arthropod—mosquito—have been reported to cause deaths on the order of 1-3 million every year (Ito et al., 2002; WHO, 2016). In 2015, mosquitoes have been reported to be responsible for about half of the total deaths caused by animals—specifically by malaria alone (Gates III, 2016). A summary on number of deaths caused by various animals is presented in Table 1. The decreasing order of the number of deaths is as follows—mosquitoes, humans, snake, sandflies, dogs, kissing bugs, scorpions, and lions.
Figure 4: Selected medically important arthropods with their feeding mechanisms (Adapted from Gurera et al., 2017). The arthropods are classified using two criteria—dietary preference and feeding mechanism. Based on dietary preference, the arthropods are classified as herbivores and carnivores, which feed on plants and flesh respectively. Based on their feeding mechanism, arthropods are classified as piercers, and piercers and suckers.
Table 1: Summary of number of deaths caused by various animals in 2015 (Adapted from Gurera et al., 2017)

<table>
<thead>
<tr>
<th>Animal</th>
<th>Number of deaths</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mosquito</td>
<td>830,000 (~54%)</td>
</tr>
<tr>
<td>Human</td>
<td>580,000 (~38%)</td>
</tr>
<tr>
<td>Snake</td>
<td>60,000 (~4%)</td>
</tr>
<tr>
<td>Sandfly</td>
<td>24,200 (~1.5%)</td>
</tr>
<tr>
<td>Dog</td>
<td>17,400 (~1%)</td>
</tr>
<tr>
<td>Kissing bug</td>
<td>8,000 (~0.5%)</td>
</tr>
<tr>
<td>Others (scorpion, lion, etc.)</td>
<td>15,370 (~1%)</td>
</tr>
</tbody>
</table>

2.2 Locomotory Attributes of Mosquitoes

Mosquito has a part to feed itself, three parts to sense, and two parts to move (Clements, 1999; Chapman et al., 2013), as shown in Fig. 5 (top). Part to feed itself is known as proboscis. It has length of about 2 mm and diameter of about 80 µm. It is used for piercing into a host and sucking fluids out of it. Three parts to sense are antennas, maxillary palps, and eyes, which helps mosquitoes to hear, taste, and see, respectively. The antennas in mosquitoes are about 1 mm long. They help in hearing by sensing vibrations from the surrounding (Johnston, 1855). Maxillary palps taste components of air, such as carbon dioxide (Kellogg, 1970; Jones et al., 2007). As expected, eyes are used by mosquitoes to see (Gao et al., 2007). The two parts to move are a pair of wings and a three-pairs of legs. The wings are about 3–6 mm long and about 1 mm wide (Christophers, 1960). The legs are about 7–10 mm long. Also, a mosquito weighs about 1–4 milligrams.

Differences in morphology and functioning of mosquitoes’ sexes can be quite significant (Gordon and Lavoipierre, 1962). As shown in Fig. 5 (bottom) have longer maxillary palps, and have more bushy antennas (Mullen and Durden, 2009). Functioning
wise there is a difference in their hearing frequency. Best frequency of female antennas is about 230 Hz and males’ is about 380 Hz. The males’ best frequency happens to be the females flying frequency. This may help the males to find their mates (Clements, 1999). Male and female mosquitoes also have different dietary preferences—male mosquitoes feed on plant nectar instead of blood. Since, the males do not have to pierce skin, the piercing subparts of the proboscis are not used and they atrophied.

Figure 5: (Top) A general visual description of a mosquito and (Bottom) structural differences in a female and a male mosquito (Adapted from Gurera et al., 2017).
To hunt down a prey, mosquitoes use their legs and wings, which have desirable attributes that may serve as an inspiration to bioinspired products. The locomotory attributes—standing on water, sticking to any surface, and flying in rain—are shown in Fig. 4 (Dickerson et al., 2012; Kong et al., 2015).

2.2.1 Standing on Water

Mosquitoes have six legs, which are about 7–10 mm long (Wu et al., 2007). The leg is divided into three parts—femur, tibia, and tarsus—whose diameter ranges from about 200 µm at the base, to about 80 µm at the tip. Femur is attached directly with the body, whereas tarsus is the distal-most part. Lengthwise, femur and tibia are about 2.5 mm long and tarsus is 6 mm long. These parts are joined with each other via joints.

As shown in Fig. 7 (top), the legs are covered in microstructured-scales (Wu et al., 2007). The microstructures consist of longitudinally-running ridges and cross-running ribs. The microstructures along with orientation of the scales, provides, with water-repellent leg with water contact angle >150°, as shown in Fig. 7 (bottom). This water repellency gives them ability to stand on water.

When a mosquito stands on water, only distal part of the leg—tarsus—is in contact with water (Kong et al., 2015). It has been reported that a tarsus can take load up to 20 times the weight of the mosquito, and whole leg can take up to 23 times the weight of a mosquito.
There are two key factors playing role in making tarsus such an efficient weight bearer—flexibility and stepping angle of the foot.

The tarsus is comparatively thinner, hence, it can bend easily under a load. When a mosquito presses its leg against water, due to flexible nature of the tarsus, contact area between tarsus and water keeps on increasing. Hence, pressure remains constant. If the
tarsus had not been this flexible, the contact area would not have increased. In other words, pressure on water would have increased—leading the leg to pierce the water.

Similar theory can be applied to the role played by the stepping angle. Stepping angle is the angle made by the tarsus with the water-level. When the stepping angle is low, contact area between tarsus would be more—leading to low pressure on water. It has been reported that largest force-bearing capacity of the mosquito leg appear in a range of 0°–20° stepping angle (Kong et al., 2015). At stepping angle about 70°, the bearing load appears to diminish, since, now, the leg is almost piercing straight into the water.
Figure 7: (Top) Microanatomy of a mosquitoes’ leg—which is covered in micro- and nano-structures—that gives them ability to stand on water and (bottom) a water contact angle measurement on the leg and a mosquito standing on water (Adapted from Gurera et al., 2017).
2.2.2 Sticking to Any Surface

Mosquitoes foot are a combination of claws and setas that help them attach—
distal part of the tarsus is referred to as the foot (Wu et al., 2007; Chapman et al., 2013).
Figure 8 (top) presents microanatomy of the mosquito foot with claws and setas. The
claws and the setas help attach to rough and smoother surfaces respectively.

Setas—similar to geckos—use van der Waals forces to attach to smooth surface.
The attaching mechanism changes with wettability of the surface. If the surface is
hydrophobic, van der Waals forces are predominant. If the surface is hydrophilic,
capillary forces also played a role to increase the adhesive force.

Setas have a pad area of about 2 µm², which can generate 50–200 nN force per
leg (Pashazanusi et al., 2017). The force magnitude changes with surface roughness.
Higher the roughness, higher is the force.

After attaching to a surface, it uses a gait which is common in most six-legged
arthropods—the tripod gait. As shown in Fig. 8 (bottom), at any given time three of the
six legs maintains contact with the ground and rest of the three are used to move.
Figure 8: (Top) Microanatomy of mosquitoes’ foot showing claws and setas and (bottom) a schematic of mosquitoes walking using the tripod gait (The dotted circles represent foot adhered to the surface) (Adapted from Gurera et al., 2017). The claw and setas help in sticking to any surface using dry-adhesion.
2.2.3 Flying in Air, Rain and Seeing in Fog

Generally, flying species in nature uses leading edge vortex—a mechanism in which a vortex, developed at the front-edge of their wings, decreases air pressure at the top of the wing, gives them a lift (Dudley, 2002). This can be energy consuming. In case of mosquitoes, the flapping happens to be more energy conserving, since, the edge captures the swirling wave from the previous flap. This is due to trailing-edge vortex-formation, which is an exclusive trait to them (Bomphrey et al., 2017). That is why they can flap their wings at a high frequency and low flapping-amplitude of about 700 Hz and 40°, respectively. The flapping amplitude is less than half of the any other flying animal studied.

Structurally, a mosquito-wing has microscales and nanohairs on the wing, as shown in Fig. 9 (top). It beneficial for mosquitoes when they are flying in rain, as it helps the wing to remain hydrophobic, with water contact angle of about 95° (Pal, 1950). The microscales and nanohairs measured about 90 µm and 35 µm in length.

Mosquitoes also may have to fly in more adverse conditions than raining, such as fog. It can adversely affect its structure. Fog has smaller water drop size on the order of 1–50 µm in diameter (United Nations Environment Programme, 1998) and rain drop has on the order of 1000–5000 µm (NASA, 2016). So when a rain drop is smaller than the distance between the asperities on a surface, it sticks to it. After a while, such small drops coalesce to form a big drop and transversally bends its wing. Surface tension of water is enough to overcome bending stiffness of the wing (Dickerson et al., 2015). Most of the stiffness of wings are provided by its veins, which run in longitudinal direction.
Therefore, the drop gets folded in the transverse direction. It has been reported this is possible when the wing’s thickness and/or width is less than 10 µm and 50 µm, respectively. In practice, mosquitoes attempt to remove the excess water by active flying techniques such as increasing flapping frequency, hard landing, and/or taking off at different angles from the ground.

Figure 9: Microanatomy of mosquitoes wing (top) and eyes (bottom). Mosquitoes wing have a combination of microscales and nanohairs, which makes the wing hydrophobic, and give mosquitoes ability to fly in rain (Adapted from Gurera et al., 2017). Mosquitoes’ hemispherical eyes consist of hexagonally arranged micro- and nanobumps. The hierarchically structured eyes repel water and give mosquitoes ability to see in fog.

Despite having trouble with its wing, mosquitoes are able to take shelter during fog and see using its anti-fogging eyes (Gao et al., 2007). The eyes surface consist for an hierarchical roughness—hexagonally-packed microbumps and loosely-packed nanobumps, as shown in Fig. 9 (bottom) (Gao et al., 2007). Microbumps has diameter of
about 25 µm, and nanobumps have diameter of about 100 nm and inter-spacing of about 50 nm. Since the spacing the micro- and nanobumps is less the fog drop diameter, which is 10–50 µm in diameter, the drops does not stick to the eyes. An air-pocket forms between the drop and the eye, which helps the drop rolls-off easily (Bhushan, 2016). In addition, since the eyes—on a macroscale—are hemispherical, therefore, the rolling of drops may take place in real time.

2.3 Painless Bite

In the previous section, mosquitoes’ locomotory aspects were discussed in detail. In this section, mosquitoes painless bite would be discussed—morphology of its mouth part, piercing mechanism, material properties. The material properties are determined using static and dynamic characterization methods. Later, based on the understanding guidelines for manufacturing a bioinspired microneedle has been presented.

2.3.1 Mouthpart

2.3.1.1 Microanatomy

Mosquitoes use their mouthpart known as proboscis to feed on their prey (Jones, 1978). Figure 10 (left column) presents a detailed-schematic of the proboscis.

Proboscis is a term collectively used for mosquitoes’ fascicle and its retractable-outter-cover, known as labium. The labium being blunt does not pierce and retracts back during the piercing. However, fascicle, being sharper, pierces the host. Fascicle is again a collective term, this time used for the bundle of six further subparts—a labrum, the blood sucker; two mandibles and two maxillae, the piercing initiators; and a hypopharynx, the numbing agent secretor.
All the parts—labium, labrum, mandibles, maxilla, hypopharynx—however, different, work in synergy for a successful piercing. Since labrum is the subpart which does most of the piercing and sucking hence it is term as the microneedle. However, the labrum does not pierce alone. As suggested by the names, it takes helps from other subparts. Thin and serrated nature of the mandibles and maxillae, respectively, help in initiating and maintaining the pierce by anchoring its serrated-design, respectively. Hypopharynx pierces top layer of the skin to release a numbing agent to numb the area (Choumet et al., 2012).

For a successful piercing, there is another part, which does not pierce, but plays a crucial role—labium, the thick outer cover. It is mathematically impossible for a part as thin as the fascicle to pierce without a lateral support from the labrum (Ramasubramanian et al., 2008)

Another useful feature of the labium is its tip—it senses a suitable location to pierce in the host’s body (Mullen and Durden, 2009).

Right column of the Fig. 8 shows scanning electron micrographs of different parts of the proboscis—labium, fascicle, labrum, and maxilla. Labium is covered with scales all around it and has hairs at its end. The hairs help in sensing a suitable spot on host. Fascicle, shows its subparts bundled together. Labrum is a pointed, hollow part. It has an outer diameter of about 30 µm and an inner diameter of about 20 µm. Maxilla, as evident, is a serrated subpart; the teeth will help in easy insertion of the labrum. Having teeth will create more localized high stress areas that will help piercing the skin easily.
Figure 10: A detailed schematic of mosquitoes’ proboscis (left column) and scanning electron micrographs of its subparts (right column) (Adapted from Gurera et al., 2017).
2.3.1.2 Feeding

Mosquitoes use a four-step feeding process, as shown in Fig. 11 (Jones, 1978).

First, mosquitoes search for a suitable spot on surface of its host. They use chemical sensors at end of the proboscis to sense the spot (Clements, 1999). After locating a spot, hypopharynx releases a numbing agent under skin of the host (Choumet et al., 2012). Parasites such as malaria parasite is transferred to the host via this agent.

Second, mosquitoes anchor their proboscis in the host and start the thrusting the fascicle through the outer skin using a vibration motion of frequency about 15 Hz (Kashin, 1966).

There may be a logical reason behind usage of the vibratory motion by mosquitoes. This vibratory motion may help in reducing the pain. It is known from the studies that insertion force is reduced when a needle is vibrated. This supports the fact that insertion force used by mosquitoes, which is 10–20 µN, is three times lower than the lowest reported insertion force by an artificial needle (Kong and Wu, 2010). Lowering of inserting force should also affect the pain—if lower force is used, lesser the tissues will be deformed, lesser the sensation felt by the nerves.

In third step, the labrum constantly searches for a blood vessel inside the host (Choumet et al., 2012). In order to do that, it can bend up to 90° (Gordon and Lumsden, 1939). Finding a suitable blood vessel is a hit-and-trial process, although labrum’s tip reportedly has blood-vessel-locating sensors (Hudson, 1970).
Figure 11: A four step feeding process used by mosquitoes (Adapted from Gurera et al., 2017).
Every part of the fascicle works independently to find a blood vessel, however, only labrum actually pierce it. Again, a vibratory motion was used to do that, but with a lowered frequency of about 5 Hz. There could be multiple reasons for using a lowered inserting frequency. First, blood vessel is a softer material to material to pierce into than the outer skin. Therefore, less vigorous motion is needed to be done. Second, amount of friction the labrum is experiencing when inside the host. Magnitude of friction is directly linked with the contact area only labrum is with the host’s tissues. So, when labrum is fully inserted, it would have experienced highest frictional force. A dynamic distance, which mosquitoes cover during the vibratory motion, is in a range of 40–90 µm (Kong and Wu, 2010).

Continuing with the third step, mosquitoes can suck in blood in two ways (Gordon and Lumsden, 1939; Choumet et al., 2012). First way and which 95% of the mosquitoes have been reported to use, is to pierce a blood vessel at 90° and suck the blood directly from the vessel. This method fills mosquitoes’ appetite. The second method is used 5% of the times. In the method, if the labrum ruptures a blood vessel while looking for one, a blood pool is formed in the tissue. The method is to feed on that pool. However, this does not seem to appear to fill mosquitoes’ appetite.

Fourth step, after it is done sucking up the blood, is to use hypopharynx to release an anti-blood-clotting agent.

Most annoying part of the mosquito bite is post-bite localized, inflammatory response. It is generally caused by dilating of blood vessels and leaking of blood out of the vessel, which stops after of eight hours of the bite (Choumet et al., 2012). Average
amount of sucked blood by mosquitoes is on the order of few milligrams, which is comparable to their bodyweight (Nayar and Sauerman, 1975). Depending on age of a mosquito, finding a suitable location on host can take on the order of 5–30 seconds (Choumet et al., 2012). Once inside the host, finding a blood vessel can take on the order of 150–400 seconds. The blood feeding can take on the order of 250–350 seconds. Plasmodium-infected mosquitoes, which means malaria-infected mosquitoes, takes longer to fill their appetite.

2.3.2 Nanomechanical characterization of mosquitoes’ labrum

It is well known that biological materials are viscoelastic materials, which change their properties in dynamic conditions. It is exactly what a mosquito does—vibrate its labrum to pierce into the host. Therefore, it creates a need to study their properties in dynamic condition, in addition to the static properties. Labrum’s tip was chosen because it is the widest part of the fascicle—thirty-five times wider than maxilla and mandibles.

2.3.2.1 Characterization technique

To measure the nanomechanical properties of the labrum’s tip, a depth-sensing characterization technique, known as nanoindentation, was used (Bhushan et al., 1996; Fischer-Cripps, 2011; Bhushan, 2017a). In the technique, a load applied to the sample using a nanoprobe. As the load is being applied, the load and the probe’s penetration are being continuously measured. The load vs penetration depth data is used to calculate elastic modulus and nanohardness.
Across the labrum’s tip, nine uniformly-distributed locations were characterized, as shown in Fig. 12. The nine locations are defined by intersection of three non-parallel longitudinal lines, L1–L3, with three parallel transverse lines T1–T3. A nomenclature of the locations has also been chosen—for example, the location formed by intersection of L2 and T1 will be called as L1, T1. However, due to close proximity of the three points along T3, the characterized values were considered same.

Figure 12: The labrum’s tip was characterized at presented seven locations (Adapted from Gurera et al., 2017). The locations were formed by intersection of three longitudinal lines, L1-L3, with three transverse lines, T1-T3. Due to close proximity, points on T3 are considered as one.

To study the static and dynamic properties, two types of load functions were used, as shown in Fig. 13. For static characterization, the load function is a trapezoidal shaped function, in which the sample is loaded to 10 μN in six seconds, the load is hold for two seconds, and then it is unloaded to zero-load in last six seconds. For dynamic characterization, a small dynamic load of 0.2 μN amplitude and frequency sweeping from 5 Hz to 200 Hz was super-imposed on a static load of 10 μN; the frequencies that were used are 5, 10, 15, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 Hz.
For the characterization, a TI 950 TriboIndenter® (Hysitron, Inc., Minneapolis, MN, USA), with the Berkovich tip (tip radius is on the order of 100 nm), calibrated with fused silica was used.

Figure 13: Labrum’s tip was characterized using two loading functions: static (top) and dynamic (bottom) (Adapted from Gurera et al., 2017). The static load function has a peak load of 10 µN. The dynamic load function has quasistatic load of 10 µN and dynamic load of 0.3 µN. The tested frequencies were 5, 10, 15, 20, 40, 60, 80, 100, 120, 140, 160, 180, and 200 Hz.

2.3.2.2 Experimental Data

Figure 14 summarize results for the static characterization of the labrum’s tip.
The figure (top) shows representative load-displacement data on two extreme locations, L2, T1 and L2, T3. Note that the material creeps when the load is held for two seconds. Also, under the same load, the location, L2, T3, displaces more as compare to the location, L2, T1 that implies inhomogeneity in the tip. It does not come as a surprise, because biological materials are known to be inhomogeneous (Oyen, 2010). To further investigate the inhomogeneity, the tip was tested at greater penetration depths and found material properties to be decreasing with the depth. It suggests labrum’s outer layers are stiffer and harder, than the insides.

**Figure 14** (middle) shows trends observed in the mechanical properties of the labrum’s tip. The trends observed in the longitudinal directions, L1–L3 (left column), and the transverse directions T1–T3 (right column). The elastic modulus and nanohardness was obtained from the load-displacement curves. The values presented are average of values obtained from give different labrums. Error bars are one standard deviation from the average.

First trend observed is the decreasing elastic modulus along the longitudinal directions, L1–L3. Elastic modulus is measure of resistance to deformation; it can also be qualitatively termed as stiffness. In the figure, it is seen that end of the tip has lesser value of elastic modulus. This implies end of the tip is compliant. Another trend observed is, the property, along the middle longitudinal line, L2, is lower than the along the adjacent longitudinal lines, L1 and L3. This implies the tip is stiffer on sides, as compare to its middle.
The trend can be confirmed from the trend presented in the transverse direction, T1–T3. There is a dip in the elastic modulus in middle, along L2. The curve is shifting down and flattening as one move towards end of the tip, T1 to T3. Having more stiffness on the sides may help labrum to resist bending/buckling during piercing.

Similar trends were observed in the case of nanohardness. Hardness is a measure of resistance to plastic deformation. Nanohardness decreased along L1–L3, and it has a dip along T1–T3. This implies that the tip is softer at locations on L2 and T3, as compare to locations on L1 and L3, and T1 and T2, respectively. Having hardness will help the labrum to pierce host easily. Softer the labrum, more force will be required to pierce host. Globally, the labrum tip is one order less hard than another piercing part, human tooth (Oyen, 2010).

**Figure 14** (Bottom) present, elastic modulus and nanohardness maps. It is clear from the maps that the labrum tip is compliant and softer at its end. End of the tip may be compliant and soft because of the fact that it is used for sensing blood vessels inside host (Hudson, 1970; Mullen and Durden, 2009). The tip gets stiffer and harder if one moves away from the end. The change is stiffness and harness is higher on sides as compare to its middle.

The tip is viscoelastic and it is vibrated to pierce into host. During the vibration, oscillatory deformations may induce stress and strains in it. The compliant and softer tip in middle may help in accommodating those oscillatory deformations and reduce overall induced stress. The stiffer and hardness sides of the tip may help in successful piercing.
Figure 14: Representative load-displacement curves at two locations (top) (Adapted from Gurera et al., 2017). Inhomogeneity is observed in the labrum’s tip. Mechanical property trends (middle) and maps (bottom). The tip has a gradient of mechanical properties, which decrease along L1-L3, and has a dip along T1-T3. The end of the tip is compliant and soft, whereas the sides are stiffer and harder.
Figure 15 summarize results for the dynamic characterization of the labrum’s tip. Figure 15 (top) presents mechanical properties as a function of loading/unloading frequency in the longitudinal direction, L1, and in the transverse direction, T1. The mechanical properties are storage modulus, and tan δ. The solid-lines shown are fitted-lines. The error bars are deviation of the average values from the fitted lines. Negative errors have been equated to positive errors, and vice-versa.

The figure (top), first, shows trends in storage modulus vs frequency. Storage modulus is a measure of elastic properties of the material. It is a measure of degree of resistance to displacement in dynamic conditions. The data shows that the values are decreasing along the longitudinal lines, L1–L3. The presented data is for L1. Second trend is the values have a dip along the transverse lines T1–T3. The presented data is along T1. The change in the values is irrespective of the frequency. Another trend that can be observed is increase in storage modulus values with increase in frequency. This may help labrum during the piercing.

Figure 15 (top), secondly, present trends in tan δ vs frequency. Tan δ is a ratio of viscous properties to elastic properties. It is a measure of amount of viscosity in a material to its elasticity. It is parameter for comparing dynamic nature of different materials. None of the previous trends were observed in tan δ. However, the data is on the same order as of dragonflies’ wing (Sun and Bhushan, 2012) and beetles’ cuticle (Sun et al., 2016).
Figure 15: Storage modulus and tan δ plots as a function of frequency (top) and maps (bottom) (Adapted from Gurera et al., 2017). Storage modulus is increasing with increase in the frequency. However, the tan δ does not change. Similar to the static properties, irrespective of the frequency, the modulus decrease along L1, and has a dip along T1. Similar to the static properties, irrespective of the frequency, the end of the tip is compliant, and sides of the tip are stiffer.
Figure 15 (bottom) presents data from the dynamic mechanical properties for all the locations in form of mechanical property maps. The mechanical properties presented are storage modulus and tan δ as a function of frequency. The frequencies presented are 0, 10, 20, 60, 100, and 200 Hz. 0 Hz in the storage modulus section is the elastic modulus map, which was presented in Fig. 14. It was included for comparison; however, elastic modulus should not be quantitatively compared with storage modulus. The three trends discussed earlier can be observed here for the entire labrum’s tip. Storage modulus is higher at the sides. They decrease as one moves towards the middle or towards end of the tip. The same goes for the loss modulus.

As discussed earlier, mosquitoes use vibratory motion to pierce into host. Vibratory motion induces oscillatory deformations to the vibrating body, and that induces stress and strains in the body. Having lower stiffness and lower damping in the middle will take care of the stresses caused by the oscillatory deformations. Higher stiffness and damping in the sides will help keeping the labrum’s tip intact and to pierce into host. Also, the vibration frequency increase stiffness and damping of the entire tip. It may also help because higher frequency means more deformation and higher induced stresses. The increase in the properties may compensate the stresses.

Measures were taken to obtain the scientific data. First, data was taken in a temperature-controlled environment. The temperature was maintained between 21°–23°C. It is known of temperature to affect viscoelastic properties (Ferry, 1980). Second, all the labrums were tested for all the seven locations in one study, and right after the mosquitoes were sacrificed. It is known that desiccation affects mechanical properties of
the labrum. Third, penetration depth of all the tests were less than 10% of the labrum’s thickness, 10 µm, except for the location, L2, T3, at end of the tip. This implies there was no effect of the substrate on which the labrums were mounted on.

2.3.3 Biting Mechanism

As discussed earlier, to pierce into host, first they secrete a numbing agent. Second, using the serrated subpart, they start piercing into host. Thin subparts pave a way for the wide-labrum to pierce in host, and the serration helps labrum to be anchored inside the host. Third, the piercing is actuated by a vibratory motion. For mosquitoes’ mouthpart to be considered pierced, its widest subpart, labrum, is to be pierced. Based on nanomechanical property measurements, the tip of the labrum has a gradient in its mechanical properties. End of the tip has lower stiffness, hardness, and damping. The properties increase if one moves upwards from the end.

This combination of the material-gradient, serrated-design, numbing agent secreting, and vibratory actuation is believed to be the secret to the painless piercing. Compliant and soft tip of the labrum will deform the skin less. The less deformation will not be sensed by the nerve endings in the skin, which implies less pain. The pain will also be further reduced by the numbing agent secreting. However, compliant and soft end of the tip will increase the insertion force. To compensate for that increase, serrated design and vibratory actuation are useful. Serrated design increases number of high-stressed points on the skin. It means easy insertion. Vibratory actuation has been known to lower the insertion force. Vibratory motion has also been known to increase stiffness and damping of the labrum.
2.3.4 Proposed schematic of microneedle

In market, there are conical-shaped microneedles available made up of a medical grade polymer, of length on the order of 1500 µm (Anonymous, 2015a). However, they lack the functionalities found in the mosquitoes’ microneedle. Therefore, a mosquito-inspired microneedle has been proposed in Fig. 16 (top). In the proposed design, the needle is accompanied by numbing agent secretor, which together are enclosed within a thick covering. The thick covering, primarily, is to prevent microneedle from buckling and to hold both the parts together. The outer covering functions similar to the covering observed for the case of mosquitoes, as seen in Fig. 7. The microneedle shown in the cross-sectional, exploded view is based on the combination of properties discussed earlier. The microneedle is made up of viscoelastic material having a material gradient similar to as of the labrum. The material also gets stiffer, harder, and more damped with increase in frequency. The material and numbing agent secreting is to reduce pain. Second, it has serrated design and vibratory actuation, as shown in Fig. 16 (bottom), for easy insertion. Hence, to pierce into body, first a numbing agent will be secreted. Second, the microneedle will be inserted using a vibratory actuation. After successful insertion based on need, either blood can be sucked or a therapeutic agent can be secreted.
2.4 Conclusion

It has been reported that there are about 7 to 9 million identified animals on planet earth, out of which 70–80% are arthropods. Being highest in number, they cause various medical problems to their living hosts. Out of all the arthropods and in fact out of all the animals, mosquito trumps the number of deaths caused by them in a year. On positive side, mosquitoes can painlessly pierce, stand on water, stick to any surface, and fly in
rain. To painlessly pierce, mosquitoes secrete a numbing agent and use vibratory motion to pierce its serrated-designed fascicle. Mosquitoes are able to stand on water because of their hydrophobic legs, which are covered in hierarchically structured scales. They are able to stick to any surface due to dry adhesion in their foot, which is due to a combination of claws and setas. The foot can apply adhesive force of one to two order of nanonewton on a rough surface. Lastly, mosquitoes are able to fly in rain because of its hydrophobic wings, which are covered in microscales and nanohairs, and antifogging eyes, which are covered with micro- and nanobumps on their eyes.

In this study, mechanical properties of tip of mosquitoes’ labrum were characterized to elucidate the painless piercing process. The tip was characterized in static and dynamic conditions. Since it is viscoelastic material and properties change with vibration frequency. In static conditions, it was found that end of the tip is more compliant and soft as compared to rest of tip. The stiffness and hardness increase as one from end of the tip, towards its mouth. The sides of the tip are stiffest and hardest. In dynamic conditions, same trend was followed for the stiffness and dampness of the tip. Sides of the tip are comparatively highly stiffen and damped, whereas end of the tip having low stiffness and damped. Degree of the stiffness and damping increase with increasing the vibrating frequency.

Based on the findings and available literature, a hypothesis on the painless piercing process was formulated. The mechanical properties have a frequency-dependent gradient, the design has serrated sides, and working mechanism is to numb the area first and use vibratory motion to piece in. Vibratory motion is believed to reduce pain in hosts.
Based on combination of morphology and properties, a mosquito-inspired, vibrating, viscoelastic microneedle with serrated design and material gradient has been proposed.
Chapter 3: Fabrication of Bioinspired Superliquiphobic Leather

3.1 Introduction

Leather has been an important material since beginning of the human race (Kite and Thomson, 2006; Simply Leather (Wales) Ltd., 2006; Leather Resource LLC., 2008; Harris and Veldmeijer, 2014). Before the development of woven textiles, leather was the only available material, harvested in large sheets of sizes of about 0.1 m$^2$–5 m$^2$. Leather has some unique physical properties including high tensile strength, impact resistance, flexibility, resistance to tearing, puncturing, and abrasion, low bulk density, thermal resistance, and permeability to air and water. Due to these desirable traits, leather has applications in footwear, furnishing, automotive, clothing, book binders, gloves, sports, bags, and cases (Grand View Research, 2017). For some applications, leather should have liquid-repellency, self-cleaning, low adhesion, and anti-smudge properties. The leather manufacturing industry poses a threat to the environment (People for the Ethical Treatment of Animals, 2017). The amount and type of chemicals used in the leather treatment, including arsenic, formaldehyde and coal-tar derivatives, are dangerous and potentially cancerous. Therefore, there has been a growing demand for artificial leather (Grand View Research, 2017). Artificial leather is more economical, since it is produced from polymers. It can be mechanically durable with more consistent material composition. It is easier to work with and its color, design, and composition can be
changed at will. It also has no ethical issues associated with it (Mitchell Faux Leather Upholstery Fabrics, 2014).

Commercially, two types of artificial leather are primarily used based on polyurethane (PU) and polyvinyl chloride (PVC) (Design Life-Cycle, Unknown; Grand View Research, 2017). A general manufacturing process of artificial leather is presented in Fig. 17(a) (Anonymous, 2008, 2015b). It is typically a four-step process. In the first step, a leather solution is laid on a paper layer and pressed between heated rollers, creating a thin layer of artificial leather. A leather solution is a mixture of about 55% PU/PVC polymer, about 40% plasticizer, about 1% stabilizers, and the balance fillers (Design Life-Cycle, Unknown). In the second step, the leather solution mixed with a riser is laid on the previous layer. This is passed through an oven, which forms second, thick, foamy leather layer. The third step includes simultaneous addition of a cotton-polyester layer and peeling of paper layer, while the structure is being cured in an oven. Fourth step is laying of a resin layer and the setup being passed through textured rollers. This step is optional, as to give artificial leather a shine and a real leather like look. All the layers formed through the process are in Fig. 17(b). Table 2 summarizes a list of plasticizers and fillers used in making the leather solution (BYK Additives and Instruments, Unknown; Elementis Specialties, Unknown; Sheftel, 1995; Mitchell Faux Leather Upholstery Fabrics, 2014; United States Environmental Protection Agency, 2014). The list includes surfactants that make the surface chemically active (Kim and Hsieh, 2001; Martin et al., 2017).
Figure 17: (a) Artificial leather manufacturing process can be divided into four steps: first, pouring of thin leather layer; second, pouring of thick, foamy leather layer; third, pasting of strengthening cotton-polyester layer; fourth, adding of leather-like grooves and shine (Adapted from Gurera and Bhushan, 2017). (b) Cross sectional view of manufactured artificial leather.
Table 2: Typical composition of leather solution (Adapted from Gurera and Bhushan, 2017)

<table>
<thead>
<tr>
<th>Components (% composition by volume)</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymer (~55%)</td>
<td>PU, PVC</td>
</tr>
<tr>
<td>Plasticizer (~40%)</td>
<td>Non-ionic surfactants, butyl benzyl phthalate, dialkyl phthalate, triethyl phosphate</td>
</tr>
<tr>
<td>Stabilizer (~1%)</td>
<td></td>
</tr>
<tr>
<td>Filler (~5%)</td>
<td></td>
</tr>
<tr>
<td>Riser</td>
<td>Dialkyl phthalate</td>
</tr>
<tr>
<td>Releasing agent</td>
<td>Polysiloxane</td>
</tr>
<tr>
<td>Surface modifier</td>
<td>Polysiloxane</td>
</tr>
<tr>
<td>Coloring dye dispenser</td>
<td>Anionic surfactant, amine organic compound, phosphoric ester</td>
</tr>
</tbody>
</table>

For some applications, leather should have liquid-repellency, self-cleaning, low adhesion, and anti-smudge properties. Bioinspired superliquiphobic surfaces have been fabricated inspired from superhydrophobic lotus leaf (Neinhuis and Barthlott, 1997; Bhushan, 2016). Lotus leaf surface consist of hierarchical roughness which is coated with hydrophobic wax. In order to repel oil, which has much lower surface tension than water, surface structure needs to be coated with low surface energy fluorinated material. Various multilayered nanocomposite coatings have been used to achieve superoleophobicity (Wang and Bhushan, 2015; Bhushan, 2016; Martin et al., 2017). A common approach involves deposition of nanoparticle composite coating with a fluorinated top layer, to provide hierarchical structure and low surface energy respectively.

In one study, real leather was made superhydrophobic by using spray coating of silica nanoparticles and an epoxy binder (Ma et al., 2015). However, the coating lost its superhydrophobicity in just one hour. In this study, artificial polyurethane (PU) and
polyvinyl chloride (PVC) leather surfaces were made superliquiphobic by using a multilayered nanoparticle composite structure. To demonstrate superliquiphobicity, distilled water and hexadecane droplet were used for contact angle and tilt angle measurements. Further, experiments were conducted for self-cleaning, low adhesion at high temperature conditions, and mechanical durability of the coating.

3.2 Experimental Details

A multilayer coating structure was used to achieve superliquiphobicity, as shown in Fig. 18 (Wang and Bhushan, 2015; Bhushan, 2016; Bhushan and Martin, 2017). A nanocomposite layer of hydrophobic silica nanoparticles and methylphenyl silicone resin was used to achieve hierarchical structure. The nanocomposite layer was deposited using spray coating technique because it provides a desired surface as compared to other techniques. The nanocomposite layer was coated with a layer of low energy fluorosilane, which provides repellency to oils. Since fluorosilane does not get attached easily to a surface, the undercoat has to be chemically activated first.

Fluorinated materials are commonly used because fluorine is very electronegative and has a low polarizability. The chemical activation was achieved through ultraviolet-ozone (UVO) treatment. The light excites and/or dissociate molecules at the substrate’s surface that react with dissociated atomic oxygen to form desorbing, volatile molecules. The desorbing molecules create adsorption sites for oxygen to form highly active and polar surface groups. That leads to a chemically active, hydrophilic surface.
The leather surface consists of grooves and requires a thick undercoat layer to fill these grooves before nanoparticle composite and fluorosilane layer is deposited. When only spray coat is used, the sides of the leather grooves remain uncoated, hence the surface remains liquiphilic, as shown in Fig. 19 (top). When a droplet of liquid is placed on such a surface, the uncoated sides of the leather grooves pulls the droplet across the surface. A thick undercoat helps in filling up the grooves, as shown in Fig. 19 (bottom), and thereafter contact angle was found to be stable, as reported later. To get a uniform undercoat, spin coating was used. Dip coating can also provide a thick uniform coating, but it damaged the leather.

The coatings were characterized for liquid repellency, self-cleaning, low adhesion at high temperature conditions, and mechanical durability.
3.2.1 Materials

Artificial PU and PVC leather were obtained from FurFabric, China, and SyFabrics, Los Angeles, CA, respectively.

To prepare the nanocomposite coating, methylphenyl silicone resin (SR355S, Momentive Performance Materials) and hydrophobic silica nanoparticles (NP, 10 nm diameter, Aerosil RX300) were mixed in a solvent and spray coated. Methylphenyl silicone resin was chosen because it has been reported to be durable and to provide strong adhesion between nanoparticles and substrate (Ebert and Bhushan, 2012). Silica nanoparticles were chosen because of their high hardness and high wear resistance. Solvent used in this study was isopropyl alcohol (IPA, Fisher Scientific). In some studies,
40% tetrahydrofuran (THF) and 60% IPA has been used (Ebert and Bhushan, 2012; Wang and Bhushan, 2015), however, THF reacts with the leather substrates and is not desirable.

To get the chemical activation, the UVO exposure was generated from a U-shaped, ultraviolet lamp (18.4 W, Model G18T5VH-U, Atlantic Ultraviolet Co.). The lamp was placed in an enclosure with width, height, and length dimensions of 17, 15, and 45 cm, respectively.

Fluorosilane used in this study was trichloro(1H, 1H,2H,2H-perfluorooctyl)silane (448931, Sigma Aldrich), because it can form thin, self-assembled layers that would not conceal the small topographical features (Bhushan, 2016).

### 3.2.2 Coating Procedure

Samples of size 10 mm by 10 mm were cut out and wiped with IPA to remove the surface contamination. To prepare the coating solution 375 mg of nanoparticles were dispersed in 30 mL of solvent. This mixture was sonicated using an ultrasonic homogenizer (20 kHz frequency at 35% amplitude, Branson Sonifer 450A) for 15 min. Then, 150 mg of resin was added. The mixture was then sonicated for an additional 15 min to form the final coating solution. The coating solution was either spray coated over the substrate via spray gun (Paasche®) from 10 cm away with compressed air at 210 kPa or spin coated at 3000 rpm.

As shown in Fig. 18, first, an undercoat was applied using spin coating 1 mL of the coating mixture. It was later dried in oven at 50°C for 5 min. Second, 1 mL of the coating mixture was spray coated and dried in oven at 50°C for 5 min. Next, the sample
was chemically activated using the UVO treatment for 60 min. The samples were placed 2 cm underneath the light source. Lastly, one droplet of the fluorosilane was vapor deposited on the sample using a closed container. The sample was attached to the top of the container via double-sided sticky tape with the surface facing down. The droplet was placed on the bottom of the container. Sample was placed 2 cm above the droplet and vapor deposited occurred for 30 min.

3.2.3 Characterization of the coating

Liquid repellency was measured using a goniometer. Goniometer processes image of the droplet to measure contact and tilt angle. Contact angle refers to the angle at which a liquid contacts a surface and tilt angle refers to the angle when the droplet just began to roll off the sample surface (Bhushan and Jung, 2011). The self-cleaning characteristics were examined by contaminating the sample with silicon carbide particles and comparing the removal of particles by water droplet before and after the experiment (Bhushan and Jung, 2011). Low adhesion was measured by measuring tilt angle of water after keeping the sample into an oven. Tilt angle is a characteristic of adhesion and low tilt angle indicates low adhesion. Surface tension of liquids decrease with increase in temperature (Jasper, 1972; Haynes, 2014) and given the variety of applications of leather, including clothing, footwear, purses and gloves, low adhesion is desired during a warm day in hot and wet conditions. The mechanical durability of the surface was examined using a ball-on-flat tribometer (Bhushan, 2013).
3.2.3.1 Contact angle and tilt angle

Contact angles and tilt angles were measured using a standard automated goniometer (Model 290, Ramé-Hart Inc.) using 5 µL distilled water and hexadecane droplet deposited onto the samples using a microsyringe. Contact angles were measured by taking a static profile image of the liquid-air interface, which was analyzed using DROPimage software. All angles were averaged over at least five measurements on different areas of the sample and reported as ±σ.

3.2.3.2 Self-cleaning experiment

Silicon carbide (SiC, Sigma Aldrich) particles of size 10–15 μm were dispersed in a glass chamber (0.3 m diameter and 0.6 m high) by blowing 1 g of SiC powder for 10 s at 300 kPa. After dispersion, the particles were allowed to settle on the sample mounted on a 45° tilted stage for 30 min. The contaminated sample was then secured to a 10° tilted stage and water droplet (total volume of 5 mL) were dropped onto the surface from 1 cm in height. The removal of particles by the water droplet was compared before and after tests. The ability for the water droplet to remove particles was quantified using image analysis software (SPIP 5.1.11, Image Metrology A/S, Horshølm, Denmark).

3.2.3.3 High-temperature Experiment

Coated leather sample were put in an oven for 5 min at various temperatures. Immediately, after it was taken out, contact angle and tilt angle measurements were measured.
3.2.3.4 Wear Experiment

A 3 mm diameter sapphire ball was fixed in a stationary holder. A load of 10 mN was applied normal to the surface, and the tribometer was run in a reciprocating motion for 100 cycles. Stroke length was 6 mm with an average linear speed of 1 mm/s. The surface was imaged before and after the experiment using an optical microscope with camera (Nikon Optihot-2).

In order to check for any loss in wettability after the wear, TA was measured using water droplets on the worn surface. First, water droplet was dragged over the wear track to check for obvious pinning. Next, a water droplet was placed away from the track and was rolled over it, and TA was measured. Next, a droplet was kept over the track and rolled along it and TA was measured.

3.3 Results and Discussion

3.3.1 Wettability of Surfaces

The measured contact angle (CA) and tilt angle (TA) values for various coatings on PU and PVC leather are shown in Fig. 20a. Both the leathers are liquiphilic to start with. Untreated PU leather has water CA of 76°±5° and hexadecane completely wets it. PVC leather has water CA of 62°±6° and hexadecane CA of 19°±2°. TA for untreated substrates were greater than 90°, hence are not mentioned.
Figure 20: (a) Contact angle images for water and hexadecane droplet on PU and PVC leather, with nanoparticle-binder coating and nanoparticle-binder/fluorinated nanoparticle/binder coating (Adapted from Gurera and Bhushan, 2017). (b) Photographs demonstrating repellency of water and oil by comparing untreated, nanoparticle-binder, and nanoparticle-binder/fluorosilane coated leather.
After depositing the nanoparticle-binder coating, both the leathers become superhydrophobic, with TA about 2°. As expected, the coatings were superoleophilic. After the application of fluorosilane coating, surfaces became superoleophobic. Hexadecane TA for the coating were about 3°. Figure 20b presents movie stills of liquid droplet on various coatings of leather. Water is dyed blue and hexadecane is dyed red. The sample was angled at 10°. For untreated leather, water just sticks on the surface, and hexadecane completely wets the surface. For nanoparticle-binder coating water rolls-off the surface. Same happens to water (not shown) and hexadecane in case of nanoparticle-binder/fluorosilane coating.

The superhydrophobicity was lost after seven days and the superoleophobicity was non-uniform. It is believed that the surfactants, shown in Table 2, mixed with the spraying solution leach out through the coating via capillary action, as shown in Fig. 21. That make leather chemically active with its affinity for liquids.

Figure 21: Schematic of potential reason for unstable superliquiphobicity (Adapted from Gurera and Bhushan, 2017).
3.3.2 Self-cleaning Experiment

**Figure 22** (top) shows black particles on the nanoparticle-binder coating before and after the self-cleaning test. It is clear that after the test most of the particles were removed. **Figure 22** (bottom) shows a quantitative comparison of self-cleaning abilities of untreated and nanoparticle-binder coating. Untreated leather removed about 10% of the particles, and the nanoparticle-binder coating removed about 90% of the particles. The untreated is less efficient because it is liquiphilic, hence a droplet will slide on it instead of rolling.

Figure 22: (Top) Optical micrographs of coated leather before and after self-cleaning test (Adapted from Gurera and Bhushan, 2017). (Bottom) Quantitative comparison of self-cleaning abilities of untreated and nanoparticle-binder coating; error bars represent first standard deviation from the mean values of three measurements.
3.3.3 High-temperature Experiment

Figure 23 shows water CA and TA on the nanoparticle-binder coating at 22°C (room temperature), 70°C, and 80°C. The CA of about 160° and TA about 2° were maintained from the room temperature up to 70°C. Around 80°C, leather starts to lose its superhydrophobicity. It is believed that the polymer in the leather reaches its glass transition temperature, which is about 80°C for PVC (Drobny, 2007). In addition, 80°C also happens to be a typical temperature inside an automobile on a hot day (Manning and Ewing, 2009). That may be a reason why one feels leather being sticky on a hot day.

Figure 23: Effect of temperature on repellency of water on coated leather (Adapted from Gurera and Bhushan, 2017).

3.3.4 Wear Experiment

Figure 24 (top) shows optical micrographs of untreated and nanoparticle-binder coating after the wear experiment. The dotted lines show boundary for the wear track. For
the untreated leather, there was no visible track marks, because the polymer is compliant. For nanoparticle-binder coating, some burnishing was observed.

To check any loss of wettability after the wear, TA measurements were made, and droplet images are shown in Fig. 24 (bottom). When the droplet was dragged, the droplet was pinned somewhat over the track. When a water droplet was allowed to roll across the wear track, TA increased from 2° to 7°. A TA of 7° still maintains self-cleaning properties. When a water droplet was placed and allowed to roll along the wear track, TA increased to 44°, suggesting some loss of the coating performance.
3.4 Conclusion

For the first time, superliquiphobic artificial leather was fabricated.

Superhydrophobicity was achieved by applying nanoparticle-binder coating, with a contact angle of about 160° and tilt angle of about 3°. Superoleophobicity was achieved
with contact angle of about 155° and tilt angle of about 4°. However, the superoleophobicity was non-uniform. A possible explanation is that active surfactants, used in manufacturing of the leather, leach out of it and make the surface chemically active. About 90% of the contaminations were removed in self-cleaning tests, the coating withstood about 70°C, and was found to be wear-resistant using a ball-on-flat wear experiment. These surfaces could find its use in wide variety of applications of leather.
Chapter 4: Closure

Nature has gone through evolution over the 3.8 billion years since life is estimated to have appeared on the Earth. Since then biological material, surfaces, and objects have evolved into highly organized structures with nano-, micro-, and macroscales, often in a hierarchical manner. Properties of materials and surfaces result from a complex interplay between surface structure and morphology and physical and chemical properties. Many materials, in general provide multi-functionality.

In the second chapter multi-functionality of mosquitoes were investigated and lessons learned in the case of mosquitoes were as follows. They are able to stand on water because they have multi-level hierarchy involving macro-scales, micro-ridges, and nano-ribs, which provide superhydrophobicity. They were able to stick to any surface because their foot has claws and setas which adhere to the surface using van der Waals forces or capillary force depending on wettability of the surface. They are able to fly in rain because their wings are hydrophobic—due to micro-scales and nano-hairs, and anti-fogging eyes—due to hexagonally-packed micro-bumps having loosely-packed nano-bumps on top of it. They are able to painlessly pierce due to a combination of pre-bite numbing, the frequency-dependent-gradient in its labrum’s mechanical properties, its serrated-design, and vibratory actuation.
The frequency-dependent-gradient mechanical properties were nanomechanically investigated. End of the labrum’s tip has lower stiffness, hardness, and damping. The properties increase if one moves upwards from the end. Compliant and soft tip of the labrum will deform the skin less. The less deformation will not be sensed by the nerve endings in the skin, which implies less pain. The pain will also be further reduced by the numbing agent that is secreted. However, compliant and soft end of the tip will increase the insertion force. To compensate for that increase, serrated design and vibratory actuation are useful. Serrated design increases number of high-stressed points on the skin. It means easy insertion. Vibratory actuation has been known to lower the insertion force. Vibratory motion has also been known to increase stiffness and damping of the labrum.

Based on the lessons learned, a set of design-guidelines and working-mechanism for mosquito- and bioinspired microneedle were proposed. In the proposed design, the needle is accompanied by numbing agent secretor, which together are enclosed within a thick covering. Primarily, the thick covering—similar, to mosquitoes—is to prevent the microneedle from buckling and to hold both the parts together. The microneedle is made up of viscoelastic material having a material gradient similar to that of the labrum’s tip. The material properties and numbing agent secreting is to reduce pain. Second, it has serrated design and vibratory actuation for easy insertion. The material also gets stiffer, harder, and more damped with increase in frequency. From working-mechanism perspective—to pierce into body, first a numbing agent will be secreted; second, the microneedle will be inserted using a vibratory actuation. After successful insertion based on need, either blood can be sucked or a therapeutic agent can be secreted.
In the third chapter, after having another look at nature, one of the heavily studied source-of-inspiration is lotus leaf. The lotus leaf structure consists of hierarchical structure with micropapillae superimposed with nanotubules that are formed by self-assembly of long-chain hydrocarbon wax. The wax makes the surface hydrophobic with water contact angle of $95^\circ-110^\circ$. The hierarchical structures make it superhydrophobic with water contact angle of about $164^\circ$ and self-cleaning with contact angle hysteresis of about $3^\circ$.

Inspired from this property, a bioinspired superliquiphobic coating on leather was prepared. Leather is an important material which has found applications including footwear, furnishing, automotive, clothing, gloves, sports, and bags. For many applications, the leather should have properties such as liquid-repellency, self-cleaning, low adhesion at high temperature, and anti-smudge. Superhydrophobicity was achieved by applying nanocomposite coating of nanoparticles and a binder. It had a contact angle of about $160^\circ$ and tilt angle of about $3^\circ$. Superoleophobicity was achieved by coating a fluorinated material over the top of it to achieve a hexadecane contact angle of about $155^\circ$ and tilt angle of about $4^\circ$. The coating was found to be self-cleaning, since it removed about 90% of the contaminations, having low adhesion at high temperature, since it withstood about 70°C, and was found to be mechanically durable, since less loss of wettability properties were observed using a ball-on-flat wear experiment.

This thesis provides a guidance in understanding role of material properties, along with design and functioning, of mosquitoes’ labrum, in its painless bite. The thesis also provides successful bioinspired fabrication method for superliquiphobic leather.
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