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Other Biomimetic Surfaces

Abstract The issues of hierarchical organization in biomaterials and surfaces are discussed. Various biomimetic surfaces and effects are reviewed, including the shark skin, darkling beetle, water strider, spider web, and several others.

The concept of bionics or biomimetics emerged in the 1960s, however, it has been developing very dynamically in the past decade due to advancements in nano- and biotechnologies. Many major challenges of modern engineering science are related to miniaturization [286]. Studying natural organisms and biological systems provides insights on how these problems can be solved, while emerging technologies give an opportunity to mimic the biological systems. A successful transition of these ideas into the technical world requires more than just observation, but also detailed analysis and possible modification in view of materials and technologies available to an engineer. In this chapter, we will review biomimetic surfaces with the emphasis on the surfaces with hierarchical structure.

13.1 Hierarchical Organization in Biomaterials

Biomimetics is the application of methods and systems found in living nature to the study and design of engineering systems. In the biomimetic design of materials, a number of ideas have been suggested. This includes the study of biological self-assembly, receptors, protein machines, muscle filaments, and microstructured surfaces. The attention of engineers was driven to such diverse areas as artificial cartilage for shock absorption, the mucus for the solid-fluid transformation, collagen, use of insect cuticle microstructure for advanced composites, biomimetic surfaces to control cell adhesion, and drug delivery [69]. Most technical materials, such as steel, metals, silicon, and plastics, require high temperatures and/or pressures to be manufactured, whereas biological organisms do not have access to these high temperatures or pressures. Nevertheless, nature has developed many materials with remarkable functional properties that are often superior to engineered materials. Although some-times fragile, biological organisms can often deal with extreme mechanical loads. The key is a complex hierarchical structure of the natural materials.

There are several important differences in the ways nature and an engineer use materials. An engineer has a much greater range of available elements, including iron and metals, while nature has to deal mostly with polymers and composites of polymers and ceramic structures built of light elements. Nature builds trees and skeletons by means of growth or biologically controlled self-assembly adapting to the environmental condition and not by the secure design and selection of the materials with required final properties, as engineers do. Biological materials are grown not according to the final "design specification," but using the recipes contained in the genetic code. As a result, biological materials and tissues are created by hierarchical structuring at all levels, adaptation of form and structure to the function, capability of adaptation to changing conditions, and self-healing [114]. The genetic algorithm interacts with the environmental condition, which provides flexibility. For example, a tree branch can grow differently in the direction of the wind and in the opposite direction. The only way to provide this adaptive self-assembly is a hierarchical self-organization of the material. Hierarchical structuring allows the adaptation and optimization of the material at each level.

A remarkable property of biological tissues is their ability for self-healing, which is also related to the hierarchical organization. There are several biological mechanisms of self-repair. At the molecular level, there are dynamically breaking and repairing "sacrificial" bonds, which allow for material to deform in a quasi-plastic manner without fracture. In bones, there is a cyclic replacement of material by specialized cells, which allows for a bone to adapt to changing conditions and to repair damage. Many fractured or critically damaged living tissues can heal themselves by formation of an intermediate tissue (based on the response to inflammation) followed by the scar tissue [114]. While there are almost no self-healing artificial materials available at this point, some interesting biomimetic solutions have been proposed. For example, one system under development contains a reservoir with a hydrophobic polymer that is intended to mimic the wax of the lotus leaf and thus combines superhydrophobic and self-healing properties [57].

We can conclude from this discussion that hierarchical structure is a consequence of the fact that biological materials are not designed in their final form, but self-assembled. This argument applies also to the surfaces, so the biomimetic surfaces are often hierarchical. In the preceding sections we have studied two well-known examples—superhydrophobic surfaces based on the lotus-effect and attachment mechanisms based on the gecko-effect. Here we will discuss several additional examples of biomimetic surfaces that have been suggested as possible engineering solutions.

13.2 Moth-Eye-Effect

The moth-eye-effect is the ability of nanostructured optical surfaces not to reflect light, that is, to remain invisible. The effect was discovered in the 1960s as a re-

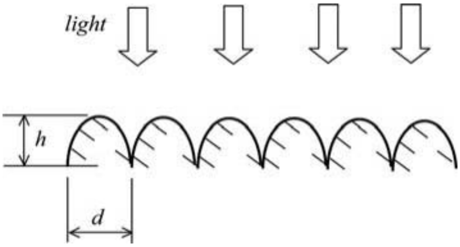

Fig. 13.1. Schematic of the moth-eye-effect

sult of the study of insect eyes. For nocturnal insects, it is important to not reflect the moonlight, since the reflection makes the insect vulnerable to predators. The light reflection is avoided by a continuously increasing refractive index of the optical medium. The little protuberances upon the cornea surface increase the refractive index. These protuberances are very small microtrichia (about 200 nm in diameter). For an increase in transmission and reduced reflection, a continuous matching of the refraction index at the boundary of the adjacent materials (cornea and air) is required. If the periodicity of the surface pattern is smaller than the light wavelength, the light is not reflected [132]. If this condition is satisfied, it may be assumed that at any depth the effective refraction index is the mean of that of air and the bulk material, weighted in proportion to the amount of material present at that depth (Fig. 13.1). For a moth-eye surface with the height of the protuberances of h and the spacing of d, it is expected that the reflectance is very low for wavelengths less than about $2.5h$ and greater than d at normal incidence, and for wavelengths greater than $2d$ for oblique incidence. For protuberances with 220 nm depth and the same spacing (typical values for the moth eye), a very low reflectance is expected for the wavelengths between 440 and 550 nm [340].

This moth-eye-effect should not be confused with reducing of the specular reflectance by roughening of a surface. Roughness merely redistributes the reflected light as diffuse scattering. In the moth eye's case, there is no increase in diffuse scattering, the transmitted wavefront is not degraded, and the reduction in reflection gives rise to a corresponding increase in transmission [340].

In addition to nanostructures that lead to nonreflective surfaces, many insects, such as butterflies, use structural coloration due to the presence of scales and bristles. Scales of scarab beetles bear additional microtrichia responsible for the coloration of their surfaces. This coloration serves for camouflage, mimicry, and species and sex recognition. Some insects use a mechanism called iridescence, using a complex multilayer structure for optical interference. Such structures can produce complicated optical effects including strong polarization, color mixing, and reflection angle broadening [132].

This effect has been suggested for use in the displays of various devices, such as cell phones. Unlike conventional displays that require an internal source of light and become bleak in bright light (e.g., in sunlight), the displays using the biomimetic technology would work from reflected light, they would be seen well in the sunlight and consume little energy. A company in San Jose, CA, is developing such displays, calling the principle the "interference modulation (IMod)." The product is expected to appear on the market in 2008. To display individual pixels, the IMod displays use simple MEMS gap-closing actuators that consist of a plate that can deflect the half-wavelength distance when an electric signal is applied.

A number of attempts have been made to design nanopatterned nonreflective surfaces based on the moth-eye-effect. Hadobás et al. [140] prepared patterned silicon surfaces with 300 nm periodicity and depth up to 190 nm using interference lithography. They found a significant reduction in reflectivity, partially due to the moth-eye-effect. Gao et al. [127] used epoxy and resin to replicate the antireflective surface of cicada's eye. It is also possible to create transparent surfaces using the moth-eye-effect [83]. The moth-eye-effect can be combined with the lotus-effect so that self-cleaning, nonreflective glass can be created.

Due to recent developments in the nanophotonics and plasmonics physics, it became possible to manipulate light at the nanoscale using arrays of nanoparticles [307] and other plasmonic nanodevices [306]. The plasmonic nanodevices are designed for phase, polarization, and feedback control. This allows them to guide light in the nanoscale via nanoparticle arrays. The moth-eye-effect may be viewed as a special case of these devices with the particles forming the moth eye structure to prevent reflection.

13.3 Shark Skin

Shark skin is covered by a special type of scales, called placoid, that form small V-shaped bumps, made from the same material as sharks' teeth. The rough surface reduces friction when the shark glides through water, which makes sharks very quick and efficient swimmers. Shark skin is so rough that it can be used as sanding paper. The "shark-skin-effect" is based on the fact that a body in a stream is provided with small ridges aligned in the local flow direction; a significant drag reduction can be reached in turbulent flow conditions due to the control of the streamwise vortices in the turbulent flow. Wainwright et al. [331] also found that the internal pressure of the shark increases more than ten-fold from slow to fast swimming. This pressure increase causes the shark's skin to deform faster [20, 163, 265]. Several commercial products use the shark-skin-effect. This includes boat and aircraft surfaces, swimming suits, and other applications.

13.4 Darkling Beetle

Some beetles in the Namib Desert in South Africa, such as the darkling beetle, collect drinking water from fog-laden wind on their backs. Droplets form on the top (front) fused "wings" (elytra) and roll down the beetle's surface to its mouthparts. These large droplets form by virtue of the insect's bumpy surface, which consists of alternating hydrophobic, wax-coated regions and hydrophilic, nonwaxy regions [259].

Experiments with artificial fog showed the feasibility of this mechanism, and artificial surfaces consisting of altering hydrophobic and hydrophilic regions have been suggested [130]. While microfluidics with patterned surfaces, as opposed to micro/nanochannels, is a big and promising field, as discussed in the preceding chapters the origin of it may be traced to the "darkling-beetle-effect."

13.5 Water Strider

A water strider (*Gerris remigis*) has the ability to walk upon a water surface without getting wet. Even the impact of rain droplets with a size greater than the strider's size does not make it immerse into water. Gao and Jiang [123] showed that the special hierarchical structure of strider legs, which are covered by large numbers of oriented tiny hairs (microsetae) with fine nanogrooves, may be responsible for the water resistance. According to their measurements, a leg does not pierce the water surface until a dimple of 4.38 mm depth is formed. They found that the maximal supporting force of a single leg is 1.52 mN, or about 15 times the total body weight of the insect. The corresponding volume of water ejected is roughly 300 times that of the leg itself. Gao and Jiang [123] suggested that superhydrophobicity of the water strider leg is responsible for these abilities. They measured the contact angle of the insect's legs with water and found it equal to 167.6°. Scanning electronic micrographs revealed numerous oriented setae on the legs. The setae are needle-shaped hairs, with diameters ranging from three micrometers down to several hundred nanometers. Most setae are roughly 50 μm in length and arranged at an inclined angle of about 20° from the surface of leg. Many elaborate nanoscale grooves were found on each microseta, and these form a unique hierarchical structure. This hierarchical micro- and nanostructuring on the leg's surface seems to be responsible for its water resistance and the strong supporting force.

13.6 Spider Web

Spider web gives an interesting example of a structure built of a one-dimensional fiber. Spiders fabricate a very strong, continuous, insoluble fiber. The web can hold a significant amount of water droplets, and it is resistant to rain, wind, and sunlight. Spider silk is three times stronger than steel, having the tensile strength of 1.2 GPa. The spider generates the silk fiber and at the same time it is hanging on it. It has a sufficient supply of raw material for its silk to span great distances [25]. Some spider silks have high stiffness with a tensile modulus of about 10 GPa, while others are elastomeric with a stiffness of about 1 GPa and extension to rupture of 200%. The spider web fibers are produced by spinning concentrated aqueous protein solutions. Research in genetic engineering suggests that the synthesis of structural proteins in microbial culture to produce polymers for fibers may become commercially useful in the future [134]. Dzenis [103] suggested an electrospinning technique to produce

$2\,\mu$m diameter continuous fibers from polymer solutions that are somewhat similar to spider silk fibers.

While mechanical properties of the web fiber are remarkable, it is also quite interesting how a spider creates a two-dimensional web out of its silk fiber. Krink and Vollrath [193] analyzed spider web-building behavior using a computer model that constructed artificial webs with a rule-based simulation. They found that web characteristics like spiral distances, eccentricities, and vertical hub location could to a large degree be accurately simulated with the model. They later proposed a "virtual spider robot" that builds virtual webs which mimic perfectly the visual architecture of real webs of the garden cross spider *Araneus diadematus*. They suggested that the garden spider uses web-building decision rules which are strictly local and based on the interactions with previously placed threads to generate global architecture [194]. This may be interesting for modeling biological self-assembly of complex material using local rules for the overall structure that is still adaptive to external conditions.

13.7 Other Biomimetic Examples

Biomimetic surfaces are not limited to the above-mentioned examples. Many other ideas in this area have been suggested. For example, the impact sensitive paint mimicking bruised skin [25]. Our skin is sensitive to impact, leading to the purple color in areas that are hit. This idea inspired researchers in mid-1980s to develop a coating that indicates impact damage. Such a coating, on the basis of a paint mixed with micro-capsules (sized 1 to $10\,\mu$m) with a certain chemical reagent, was used in the air industry to indicate possible damage to components made of impact-sensitive composite materials. An impact may lead to a significant strength loss in such a material without visible structural damage, so the change of color indicates the damage that may be potentially dangerous for the aircraft [25].

The desert sand fish skink (*Scincus scincus*) is a lizard that has adapted to an underground existence. The skink can virtually dive and "swim" beneath the surface of loose sand due to special properties of its scales—they have very low friction and abrasion. This skink specie's scales are covered by "nanothresholds," long ridges with submicron height and distance of $10\,\mu$m or less. Rechenberg and El Khyeri [279], who brought attention to this lizard and to what they called the "sandfish-effect," suggested that electrostatic charge created by submicron sized thresholds on the scale plays a role in friction reduction by creating a repulsive force between the scale and sand grains.

Other examples of functional biomimetic surfaces include surfaces with periodic roughness for sound generation mimicking certain spiders and insects, thermoregulation and prevention of drying, grooming, sampling, filtrating, and grinding [132]. Recent studies of the artificial skin design principles should also be mentioned, due to the importance of these studies for medicine [347].

Another interesting object of biomimetic research is diatoms and marine sponges. Diatoms are a common type of sea phytoplankton. Most diatoms are unicellular, and their characteristic feature is that they are encased within a unique cell wall made of silica (hydrated silicon dioxide) called a frustule. These frustules show a wide diversity in form, some quite beautiful and ornate, but usually consist of two asymmetrical sides with a split between them. The biogenic silica of the cell walls is synthesized intracellularly and then extruded to the cell exterior and added to the wall.

Hildebrand et al. [153] examined silica cell wall synthesis in the diatom *Thalassiosira pseudonana*. The innate capabilities of diatoms to form complex three-dimensional silica structures on the nano- to microscale exceed current synthetic approaches because they use a fundamentally different formation process. Understanding the molecular details of the process requires identifying structural intermediates and correlating their formation with the genes and proteins involved. They observed distinct silica morphologies during the formation of different cell wall substructures, and identified three different scales of structural organization. At all levels, structure formation correlated with optimal design properties for the final product.

Since silicon-based materials are widely used in nanotechnology, researchers are looking for ways to mimic how these materials are synthesized in diatoms. This requires understanding the corresponding parts of the diatom's DNA code and the involved biochemical mechanisms. Thamatrakoln et al. [315] studied silicon transport mechanisms in diatoms and involved proteins and amino acids. They also identified genes involved in the silicon transporters. Poulsen et al. [270] shows that the biomineral-forming machinery of diatoms can be genetically tailored to incorporate functional proteins into diatom silica in vivo.

Another interesting and promising field involves the application of an array of sensors that analyze chemical structure and can lead to an "artificial nose" or an "artificial tongue." Various techniques, such as the AFM cantilever arrays, have been suggested for this purpose. Single-cantilever sensors can determine quantities below the detection limits of equivalent "classical" methods, thus catalytic processes can be observed with picojoule sensitivity in nanocalorimetry [131]. Baller et al. [21] used a microfabricated array of silicon cantilevers for the detection of vapors. Each of the cantilevers was coated with a specific sensor layer to transduce a physical process or a chemical reaction into a nanomechanical response. The response pattern of eight cantilevers was analyzed with principal component analysis and artificial neural network techniques, which facilitates the application of the device as an artificial chemical nose. Interestingly, they reported that natural flavors, such as bitter almond, cherry, orange, artificial rum, vanilla, and lemon, could be recognized with high reliability [21]. Attempts have also been made to design an "artificial tongue" in a similar manner [328].

13.8 Summary

We have reviewed several characteristics of micro- and nanopatterns found on biological surfaces. Hierarchical organization of biological tissues and surfaces is a consequence of the way these objects are built: not according to a final "blueprint," but using a genetic algorithm. Therefore, biological surfaces can use the advantages of the hierarchical structure, such as the ability to control processes at several scale levels. The most interesting examples of this are the lotus-effect and the gecko-effect. Other effects associated with micron and submicron scale patterns, such as the moth-eye-, shark-skin-, darkling-beetle-, and sandfish-effects, are also, at least to a certain extent, based on this hierarchical design.

Interestingly, the evolutionary study of these functional surfaces shows that similar solutions have multiple origins, rather than emerge from the same lineage of living organisms. For example, attachment systems consisting of a pair of surfaces with microscopic hairs appeared independently in different organisms. Similar optical systems are found in insect, birds, and plants and have an independent origin [132]. Instead of evolutionary divergence, we deal here with convergence. In a similar way, convergence is found in the mechanical design of lamnid sharks and tunas, which irrespective to the evolutionary lineage provide similar solutions to similar mechanical problems [100]. This is especially interesting from the biomimetic point of view because they correspond to optimum solutions for a particular problem.

Historically, the technology on the scale size comparable with the human body, that is, the macroscale, was first developed. To obtain technologically important materials such as iron and other metals, people used heat and pressure, and details and devices built of these materials were comparable with the size of human body. In the twentieth century, with the development of microelectronics, it became clear that miniaturization is possible and advantageous. Richard Feynman stated in his famous lecture some 50 years ago that there are no physical laws that prohibit the creation of very small machines. However, it was not clear then how to build such machines in practice and whether it was possible to build them using existing tools. Consequent discoveries in molecular biology and biochemistry demonstrated that organic molecules provide “building blocks” that allow us to create very sophisticated systems and materials with properties that are not attainable at the macroscale. This attracted attention to the biological systems as a source of inspiration for engineers and to the hierarchical organization of these systems. As nanotechnology matures, more sophisticated and complex ways to organize multiscale hierarchical structures will be found.