

Mimicking Nature – Bioinspired Materials and Systems

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ABSTRACT

Nature produces a range of materials attractive for defence applications. Properties including high strength and light weight, adhesion, high strain, hydrophobicity, specificity and sensitivity to chemical compounds and antigens, and self healing capabilities are common in nature. Bone, shell, and spider silk are examples of strong and light weight materials. A gecko can walk up walls and across ceilings. An antibody is specific to a particular antigen, a hormone to a particular receptor, and an enzyme to a particular substrate. The lotus leaf has an extremely hydrophobic surface. Broken bone and cuts will heal. The challenge for scientists and engineers is to understand the structure of these materials and use this knowledge to prepare novel materials. In many instances attempts to produce materials using the bottom up approach common in nature has proven to be difficult if not impossible. However, even if a bottom up approach can not be realized, natural materials have inspired the development of a number of materials including adhesives and adhesive systems, high strain materials, molecularly imprinted polymers, super hydrophobic surfaces and self healing materials.

Nature also produces systems or systems of systems that have properties and/or capabilities that are of interest to Defence scientists and engineers. The range of natural materials discussed above, the way in which these are incorporated into a system, and how systems are organized into systems of systems can act as inspiration for the development of novel defence systems. The application of the knowledge of how these systems are organized and how this might be applied to defence applications may be more productive, at least in the near future, than the ability to directly mimic the way in which nature synthesizes materials. This will be discussed in this paper.

Keywords: Biomimetics, bioinspiration, materials, systems, sensors

1. INTRODUCTION

This paper explores the question - why might one be interested in mimicking materials and systems found in nature? Nature produces a broad range of materials with properties that are interest to Defence forces. A partial list of potential military applications of biotechnology, prepared by the US Army, included:

- Multi-functional, self-healing biosensors
- Biologically derived algorithms and networks
- Flexible body armor for extremities
- Low observables, obscurants and camouflage
- Detection of chem/bio agents and explosives
- Enzymatic decontamination of equipment
- Soldier selection and physiological monitoring
- Human performance enhancement
- Fixed site production of biofuels from waste
- Regenerable power and energy, e.g., biobatteries

Natural materials such as bone and shell (see Figure 1) are strong and lightweight and mimicking them might produce improved body armour for the soldier. Natural materials are often multifunctional. For example the exoskeleton of an animal not only provides protection, but also provides an attachment point for muscle, camouflage, a sensory interface with the environment, and prevents dehydration. Natural materials also have other properties such as hydrophobicity

that if mimicked could be used to produce materials that are resistant to contamination or that can prevent the buildup of ice on a surface such as a helicopter rotor. Nature can also sense a broad range of molecules with specificity, selectivity, and sensitivity. The antibody antigen interaction (see Figure 1) is an example of the specificity found in nature. In addition these molecules are integrated into sensors or sensing systems. This capability has applications in monitoring physiological or metabolic changes in the soldier and monitoring the environment for chemical and biological agents.

In addition to materials or components with desirable properties, nature also produces systems that can act to inspire the development of defence systems. These systems are composed of components that provide mobility (muscle), strength and protection (exoskeleton and bone), stealth (colouring), communication (pheromones and sound) and the ability to sense the environment. The integration of the components produces an organism (see Figure 2) that can sense, exist in and take advantage of environment. There are also many examples of systems of systems in nature. Ant colonies, schools of fish, bee hives, and flocks of birds are examples of systems of systems that operate at a higher level than an individual system.

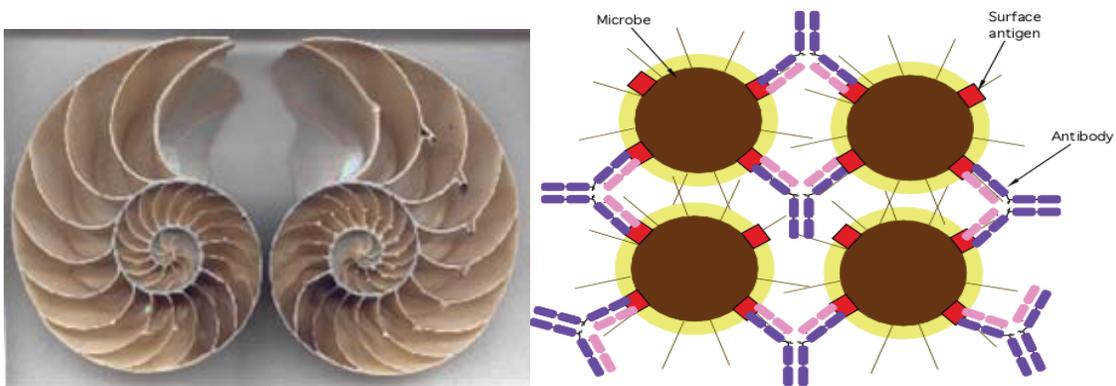


Fig. 1. Left) Sea shell is composed of calcium carbonate, protein and glycoprotein. The organic components create a molecular level template for control of nucleation and crystal growth of the calcium carbonate. The mechanical strength comes from the molecular interfaces between the proteins and calcium carbonate and the complex hierarchal structure consisting of layers of calcium carbonate and proteins. Right) A representation of the interactions responsible for the specificity of an antibody/antigen interaction (www.bact.wisc.edu). The antibody can interact with only one antibody on the basis of their structure, shape and chemistry.



Fig. 2. This bean leaf beetle (www.ent.iastate.edu) is a natural system. The exoskeleton is strong and camouflaged, sensors can find food (or prey) and detect predators, legs and wings provide locomotion, and the bug is self powered.

Although natural materials, sensors, and systems have a number of properties that make them excellent candidates for military applications, attempts to directly mimic how nature constructs materials and systems has met with limited success. This is because nature uses a hierarchical bottom-up approach that results in order at the molecular (nanometer) through the micro (micrometer) and into the macro (millimeter) level. Assembly steps are complex, rate limited and lead to complex and thermodynamically unstable arrangements of atoms and molecules. In addition, natural materials have limitations. These include: pH, temperature, humidity and organic solvent sensitivity, they may be extremely expensive to produce, and for certain sensing applications no natural system exists that can be exploited.

The development of materials and systems using the bottom-up hierarchical approach found in nature has met with limited success to this point. However, there are many materials that have been inspired by the properties of natural materials. These were developed from knowledge of how natural materials work. Several bioinspired materials will be discussed in the next section. These include the development of joining materials, artificial muscle (high strain materials), super hydrophobic materials and surfaces, molecularly imprinted polymers, self healing composites/resins.

2. BIOINSPIRED MATERIALS

2.1. Joining Technology

Figure 3 shows a plot of the strength of various joining techniques against the adaptability of the technique. Adaptability refers to the number of times the joint can be opened and closed without losing its strength. For instance, welded joints have very high strength but are one-time joints while a paper clip and zipper have much lower strength but can be used a number of times. The figure also shows the strength and adaptability of joints found in and inspired by nature. These include the adhesive strength of the Gecko foot pad and Velcro. The study of the gecko foot has been exploited to develop new joining technologies while Velcro is an example of a bioinspired joining system.

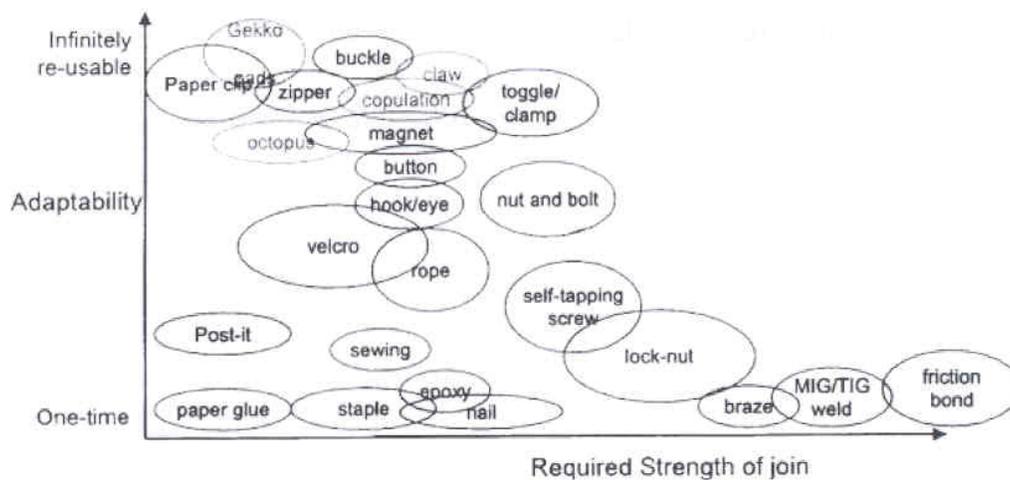


Fig. 3. A plot of the adaptability versus strength of man made, natural, and bioinspired joining technologies (Vincent, unpublished results).

2.1.1. Velcro

Velcro (1) is one of the best known examples of a bioinspired joining system. It was developed and patented by Georges de Mestral. He came up with the idea in 1941 after investigating how burdocks adhered to clothing and animal fur. He observed that the burdock had a number of hooks that would catch in loops in fabrics or tangles in animal fur. He spent a number of years perfecting the technique to produce a joining technology based on the burdock and patented the idea in 1951. He named the material Velcro after the French words *velours*, meaning 'velvet', and *crochet*, or 'hook'.



Fig. 4. From left to right, the hook structure on the surface of a burdock (*Arctium lappa*), the hook structure of Velcro, and the loop structure of Velcro.

2.1.2. Gecko adhesion

How do insects and geckos walk up walls and across ceilings? Research has shown that the bottoms of their feet have a large number of hairs called seta and the setae are further subdivided into structures called spatulae. The setae of a beetle, a fly, a spider and a gecko are shown in Figure 5. All are shown at the same magnification. It is obvious from these photographs that the spatulae become smaller in going from the beetle to the fly to the spider and finally to the gecko. Research has shown that the strength of adhesion increases as the size of the spatulae decrease. This is due to the shape and size optimization of the individual spatula and the basis of adhesion which is Van der Waals (2) and capillary forces.

The hierarchal structure of the foot pad of a gecko is shown in Figure 6. The foot pad has a number of parallel ridges called lamellae. These are visible to the human eye and are 400 to 600 μm in width. The lamellae are made up of a large number of setae that are typically 100 μm long and 6 μm wide. In turn the setae are composed of a large number of spatulae that are 0.2 μm in diameter. A calculation of the adhesive strength of a single seta indicates that it can lift (hold) 20 μN or 20 mg. The four feet of a gecko have approximately two million setae and are capable of lifting approximately 41 kg (3).

H Gao and H. Yao (4) at the Max Planck Institute for Metals Research have investigated the size and shape for the contact surface of the tip of the spatulae that results in optimum adhesion. The critical contact size was found to be $\sim 100\text{nm}$ (0.1 μm) and below. This size minimizes the effect that surface roughness (irregularity) has on adhesion and results in uniform stress distribution. This is shown in Figure 7. A synthetic adhesive system has been developed by Gottlieb Binder GmbH, Holzgerlingen, Germany based on the foot soles of beetles (5). This bioinspired adhesive is shown in Figure 7. It is made using a metal mold. The required surface is embossed as a negative image on a metal surface to prepare the mold. Polymer is poured into the mold, cured and removed. The construction of the mold is reported to have been difficult and is a trade secret.



Fig. 5. The spatulae on beetle, fly, spider and gecko feet. As the size of the spatulae decrease the strength of the bond formed by the spatulae increases.

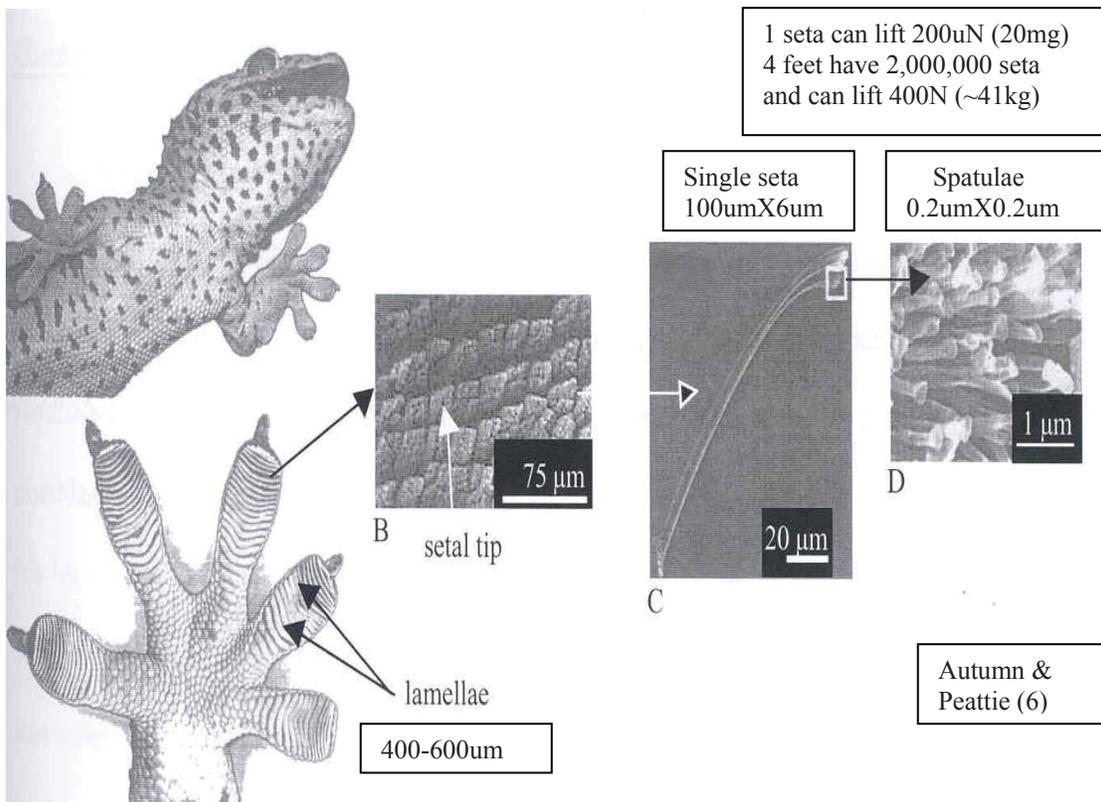


Fig. 6. The structure of the pads on a gecko foot (6).

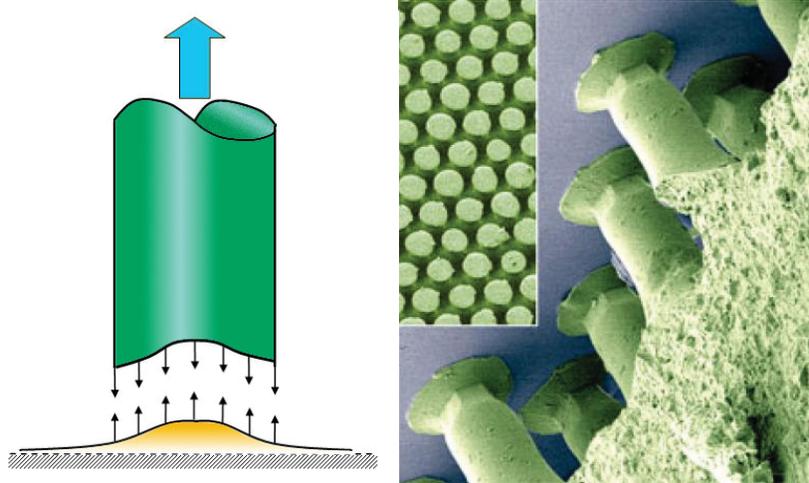


Fig. 7. Left) Schematic showing how the size and shape of a spatula affect adhesion. As the contact size of the spatulae decreases the effect of surface irregularities become less important. Right) Adhesive system based on spatulae adhesion.

2.2. High Strain Materials

Natural muscle is an example of a high strain material. It is composed of sarcomeres (7). A sarcomere and a schematic of a sarcomere are shown in Figure 8 (8). Sarcomeres are anisotropic, hierarchic, liquid crystalline structures composed of proteins including actin and myosin. These proteins are responsible for both the elasticity of muscle and its ability to do work. The ratio of actin to myosin filaments vary from 2:1 for vertebrates to 3:1 for insect flight muscles to 5-6:1 for arthropod leg and trunk muscles. In addition the length and arrangement of individual sarcomeres varies. For vertebrate species, sarcomeres are typically between 2 and 3 micrometers long but for invertebrates they can range from 0.9 micrometers to 20 micrometers. They can be arranged in a series or parallel which affects the movement (strain) or force that the muscle can exert.

There is great interest in the development of materials that can perform like muscle, that is, provide high strains and exert reasonable force. Artificial muscle based on dielectric polymer actuators has been developed. Dielectric actuators consist of a dielectric polymer between two compliant electrodes. When a voltage is applied to the electrodes they are attracted to each other and cause deformation (strain) of the dielectric layer due to Maxwell's stress. Preliminary comparisons of mechanical properties such as stress, strain, and power capabilities of polymer actuator materials indicate that they are similar to or exceed those of natural muscle. However, dielectric polymer actuators do not mimic the structure of natural muscle and are examples of bioinspired materials. One can envision that with time that artificial muscle that more closely resembles natural muscle in both form and function will be developed.

2.3. Superhydrophobic Materials

The development of super hydrophobic surfaces is another example of a bioinspired materials development. The surface of a lotus leaf is naturally hydrophobic and self cleaning. Scanning electron microscopy reveals that the lotus leaf surface is composed of a pattern of cones (10um) covered with tiny wax crystals (submicron size) (9). The cones and microcrystalline wax crystals are shown in Figure 9. The microstructure on the cones plays a significant role in the hydrophobicity of the leaf. When the leaf was heated the tiny wax crystal melted (see Figure 9), and the hydrophobicity of the surface was decreased (10).

Researchers at the University of Twente (11) have produced a water-repellent surface that mimics the complex surface of a naturally hydrophobic and self-cleaning lotus leaf. The researchers created laser-machined structures in injection molds that are then used to mold polymer surfaces, which, due to their structure, are highly water-repellent. The laser-

texturing process must mimic the overall macroscopic background (cone structure), as well as the microstructures on the cone surfaces. In addition to the cone structure with feature sizes in the 10 μm range, a submicron superimposed structure is essential to the hydrophobic nature of the surface.

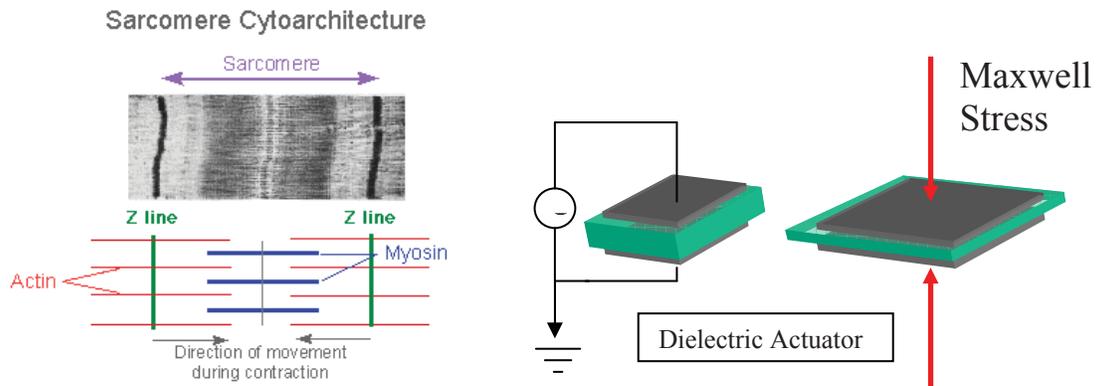


Fig. 8. Left) Scanning electron micrograph (top) and representation (bottom) of a sarcomere (8). Right) A dielectric polymer actuator.

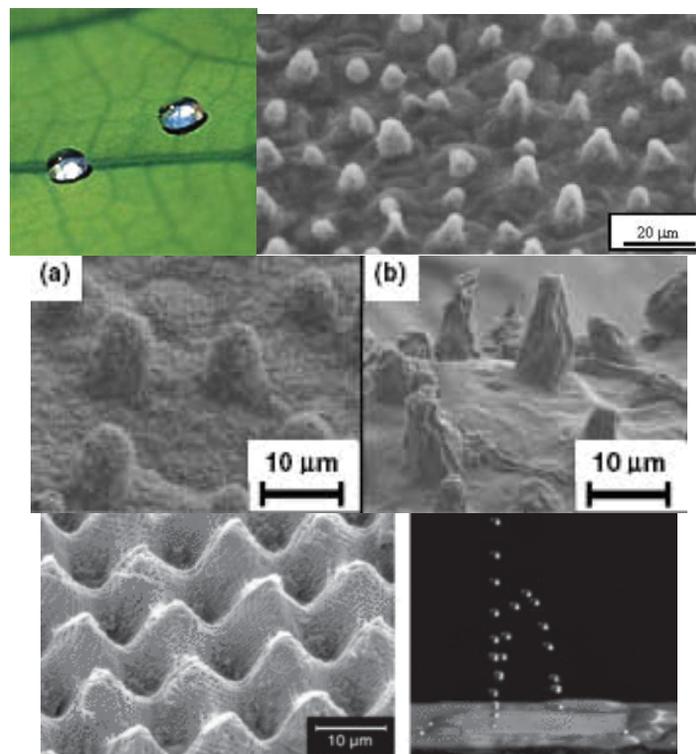


Fig. 9. Top left) Water beading on the hydrophobic surface a lotus leaf. Top right) Scanning electron micrograph (SEM) of the cone structure of the surface of the lotus leaf (9). Middle left) Higher magnification SEM of the surface of the lotus leaf showing the microcrystalline wax on the cone structures. Middle right) Cone structure after heating; the microcrystalline wax structure has been destroyed (10). Bottom left) SEM of bioinspired cone and submicron fine structure on a hydrophobic polypropylene surface. Bottom right) Water droplets are repelled from the hydrophobic polypropylene surface (11).

2.4. Molecularly Imprinted Polymers (MIPs)

Biological sensing systems or biosensors have several characteristics that make them attractive for use in or as models for sensing systems. The first of these is specificity. Biological sensing systems are based on enzyme/substrate, antibody/antigen or hormone receptor interactions. The specificity of antibody/antigen reactions are based on binding interactions, such as hydrophobic, van der Waals and electrostatic interactions and hydrogen bonding. The surfaces of the antibody and antigen have complimentary shapes with respect to their surface structures and this maximizes affinity and enhances specificity. The second is that biological systems produce very complex molecules and structures in a reproducible way. The third is biological systems/sensors can detect a wide range of analytes. Biomolecules are nanoscale in size, can be integrated into nanoscaled structures and are available, that is, they can be produced at any time from natural sources. However, they do have limitations. They can be sensitive to extremes of temperature, pressure, pH, many are incompatible with organic solvents, and in some instances there is no biological source for specific detection of some analytes.

The synthesis of imprinted polymers can overcome some of the limitations of natural sensing materials (12). Molecularly imprinted polymers are prepared in one of two ways. In the first the analyte is mixed with a polymerizable monomer that interacts with the analyte through weak interactions such as hydrogen bonds. The complex is then polymerized and the analyte washed from the polymer leaving voids that are specific for the analyte. This process is shown schematically in Figure 10. In the second the analyte is reacted with the polymerizable monomer, polymerized, and the analyte chemically removed from the polymer. The MIPs will then selectively absorb the analyte from a mixture of chemicals.

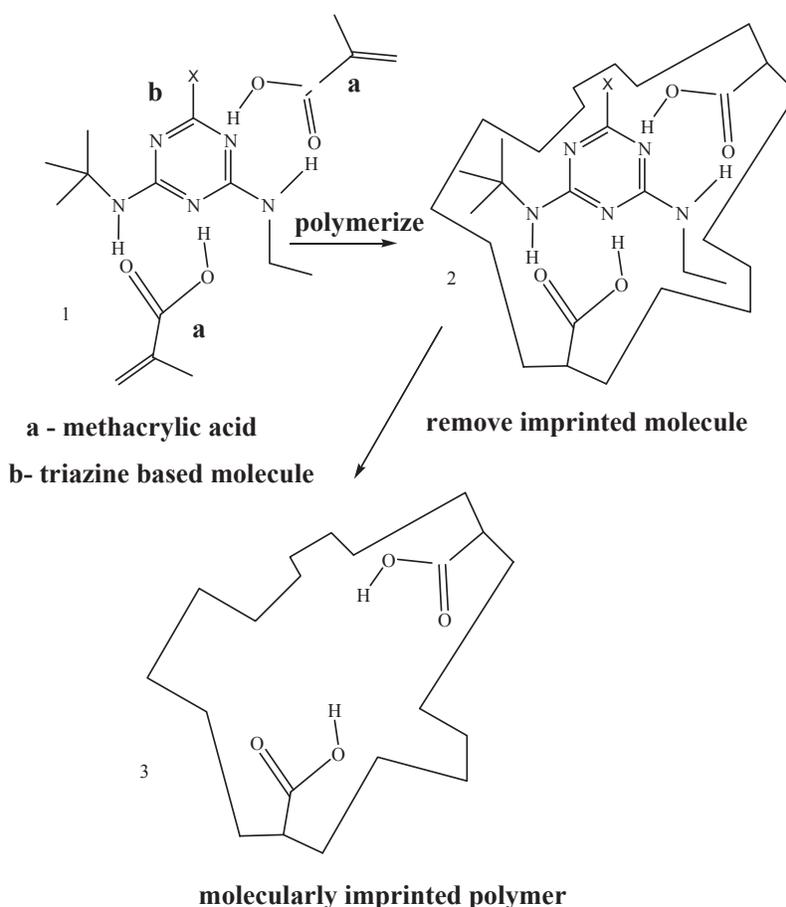


Fig. 10. Schematic showing the preparation of a polymer imprinted for the detection of a triazine based molecule.

2.5. Self healing Materials

Providing that damage is not too significant, animal species are self healing. For instance, if one is cut a complex series of actions that lead to clotting of the blood and ultimately to the healing of the wound are triggered.

Self healing polymers are an example of bioinspired approach to materials development. Resins containing capsules of uncured resin and a catalyst to promote cure of the resin have been developed (13). As a crack grows in the polymer the capsules of resin are broken. The resin cures when it comes in contact with the transition metal (Grubbs) catalyst incorporated into the polymer. This is shown in Figure 11. The load displacement curves for virgin and healed epoxy resin samples are also shown in Figure 11. The healed polymer retains considerable percentage of the load to failure measured for the polymer prior to cracking. More recently, polymers containing a three dimensional system of channels, inspired by the circulatory system in living organisms, have been developed. The polymer contains a catalyst and when a crack occurs uncured resin can be moved via the channels to the crack site where it cures (14).

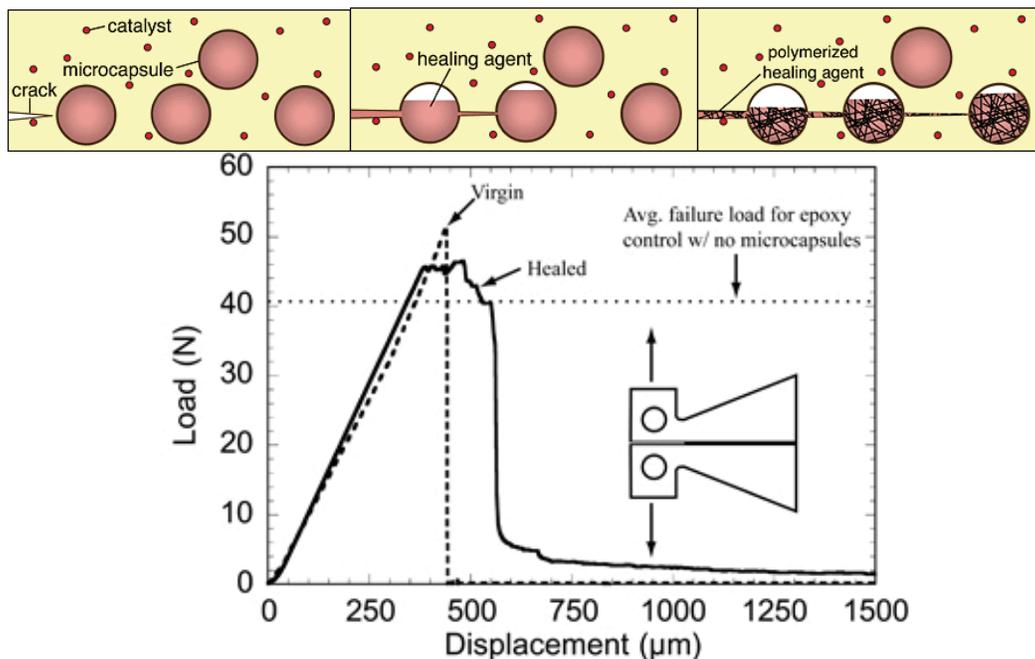


Fig. 11. Top) Graphic representation of how a self healing resin works (13). Bottom) Load displacement curves for a self healing resin prior to and after cracking and self healing.

3. SYSTEMS AND SYSTEMS OF SYSTEMS

3.1. From Components to Systems

In the previous section examples of bioinspired materials were discussed. However, when we consider nature we usually think of what might be referred to as systems and these are composed of a number of components. These components are composed of materials that provide mobility, the ability to sense, protection from the environment and predators and are integrated into functioning organisms.

The concepts of an intelligent remote autonomous sensing (IRAS) system (UK) or a distributed autonomous sensing (DAS) system (USA) are bioinspired in so much that many examples of these exist in nature. The IRAS concept is shown in Figure 12.

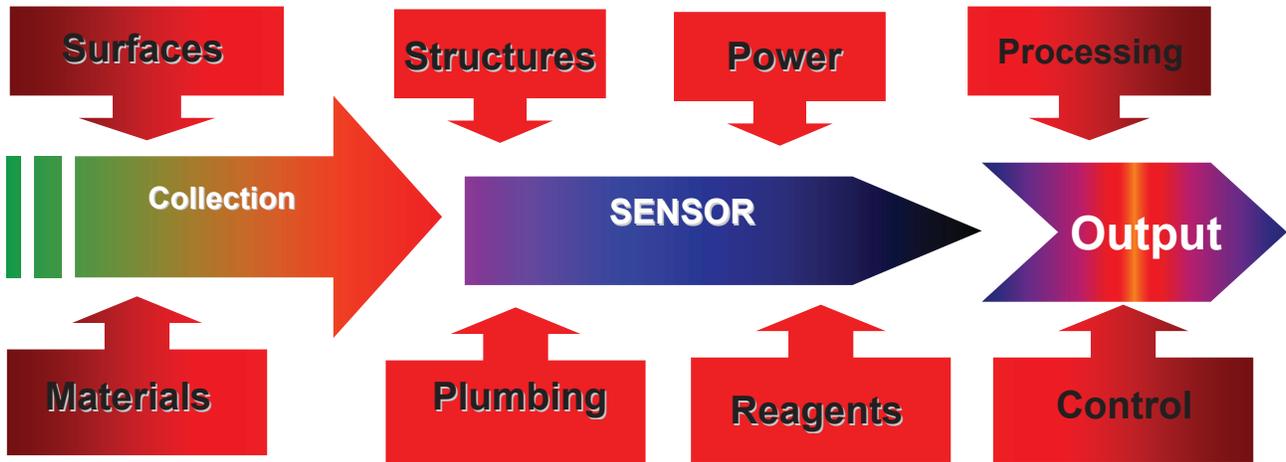


Fig. 11. The components of an IRAS system.

This is a sensing system and includes the ability to collect the input of interest (for instance chemicals, vibration or electromagnetic radiation in the visible, infrared, or ultraviolet regions), sense the input and produce an output. Natural sensing systems (insects, birds, dogs and humans) could be thought of as bioinspiration for the IRAS concept. The incorporation/integration of materials, surfaces, structures, and power into the sensor allow it to be used in a wide range of environments, and can provide protection, stealth, and mobility.

The IRAS can be used for a broad range of applications. Some of these are described by the graphic in Figure 12. The applications vary from covert to overt, can monitor a broad range of inputs, and may or may not require power which depends on both mobility and whether or not the sensor can be monitored remotely. The final form of the IRAS system will depend on the environment in which it will be used, what is being sensed, what level of detection is needed, mobility requirements, the requirement for properties such as camouflage, stealth, and biodegradable, and whether it can exploit or use the natural environment (power generation).

It is interesting that a hardware system, such as an unmanned aerial vehicle or drone which one might suggest was inspired by a bird, can be used as the model for developing bioware (Figure 13). The bioware could be a rapidly employable, disposable bio-based unattended ground sensor (BUGS). The BUGS represent a “system” capability which adapts to the environment and provides refined situational awareness, rather than raw data. It could be deployed to detect humans, vehicles, ammunition, explosives, and chemical, biological, radiological and nuclear threats (CBRN). The goal of such a system would be to provide inexpensive, rapid, and disposable sensor suites.

4. CONCLUSIONS

Biotechnology and bioinspiration provide novel methods and approaches for developing new materials and systems. There are a large number of material developments that employ or are inspired by the methods used by natural systems. These have tremendous potential for defence applications if they can be integrated into systems. However, the greatest developments may come from an understanding of how natural systems are organized. The IRAS concept may provide an excellent framework (focus) for future studies of the application of biotechnology and bioinspiration to the development of defence systems. The exploitation of the IRAS concept will require an interdisciplinary approach to realize its potential. That is, biologists, chemists, physicists, material scientists and engineers must be involved in R&D program if it is to be successful.

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