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## Composites, Multifunctional

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### Glossary

**Biocomposite** Biological composite materials made through biological processes usually in living organisms. Biocomposites formed through biomineralization processes are referred to as biomineral composites

**Biomimetics** Also known as biomimicry, is the study of biological systems with the aim of applying the methods and processes in these systems to the design of engineering materials and systems to produce engineering devices and structures with superior or comparable functionalities.

**Biomineralization** Mineralization carried out through biological processes to convert organic materials to inorganic materials to form biominerals. Biomineral composites are composed of inorganic minerals formed through biomineralization processes by living organisms in organic matrices of proteins and polysaccharides.

**Composite** A combination of two or more monophase materials arranged into a material (or “material structure”) to produce one or more particular properties that are superior to the same properties exhibited by the individual component materials.

**Multifunctionality** This is the ability of a material or device to perform two or more functions simultaneously or consecutively.

**Self healing** The ability of a structure to repair damage without external intervention. For example, a small cut on a human skin will be repaired automatically by the body. Man-made structures with such ability are under early development.

### Definition of the Subject

A composite material is a combination of two or more monophase materials arranged into a single entity material (or “material structure”) to produce one or more particular properties that are superior to the same properties exhibited by the individual component materials. Until recently, most composites were designed with a single

function in mind, most commonly focusing on improving strength or durability of the material. Many high performance composites have been developed and are performing excellently in this respect. For example, carbon fiber reinforced epoxy is now commonly used in many engineering applications. Carbon fibers have high theoretical strength and high stiffness, but are brittle and therefore readily break if a very small flaw is initiated. By embedding the fiber in epoxy, which is relatively ductile (less flaw sensitive) compared to the carbon fiber, the composite structure combines the strength and stiffness of the carbon fibers with the ductility of the epoxy. A natural extension of this concept is to develop materials that are optimized for engineering applications in conditions that demand more than one function being performed by a single material. For example, a material acting as a structural support may as well function as a thermal sensor at the same time.

A multifunctional composite, therefore, is a composite material that is capable of performing two or more functions simultaneously or consecutively. The need for improved performance in current engineering application and in entirely new areas of application has been the major driving force behind the design and development of multifunctional composites. Multifunctionality is achieved in a composite by deliberately and purposefully engineering the microstructures of the component materials and the composite as a whole usually at the micro- and nano-range levels (that is at the length scales of  $\mu\text{m}$  and  $\text{nm}$ ). When the reinforcement scale is in the nano-region the resulting composites are commonly referred to as *nanocomposites*, which is a new frontier in materials science and engineering. Today, much effort is being geared towards research and development of multifunctional composites at various materials research departments and institutions across the world.

## Introduction

Multifunctional composites are designed, through microstructural modification, to enhance or introduce new material properties in order to improve or increase the functionalities of a structure, with respect to a broad range of properties. This can include various combinations of magnetic, electronic, electrical, optical, chemical, thermal and mechanical properties. In other words, a multifunctional composite provides two or more functionalities simultaneously or sequentially with improved performance, with less complexity, cost and weight compared to a structure where these functions are provided by individual components. In many cases, a multifunctional composite

is the only means by which the combination of the desired functions can be achieved.

Requirements for high performance, durability, conservation of natural resources, low cost, and in many applications miniaturization have led to research and development of multifunctional composites with high specific properties, e. g., high strength per unit weight. These have especially been the driving forces for applications in space exploration, aerospace, information technology and energy production and transmission. Thus, materials science is a critical tool to bring together different materials as composites that can perform more than one function. Such composites are designed and engineered at various scales, ranging from the atomic level and up. For example, load-bearing composites have been developed to simultaneously act as thermal sensors by utilizing carbon nanotube reinforced polymers [109].

A very important multifunctional composite group that has been researched over the past two decades is the group of carbon nanotube composites because of the remarkable mechanical, electrical, thermal and structural properties exhibited by the fiber-like carbon nanotubes reinforcing component of the composites [35]. Carbon nanotubes are added to polymeric matrices to form carbon nanotube polymer composites with excellent mechanical and electrical properties [105]. With the nanotubes the scale of reinforcement is now in the nano region hence these composites are termed nanocomposites, and will be discussed in Sect. “[Functionalized Carbon Reinforced Polymer Matrix Composites](#)”.

Living organisms are made up of multifunctional materials. An example is the human skin that functions as a container and protector for all internal organs and the human structure. It also serves as a heat sensor, touch sensor, and an outlet for sweat and oil. The human skin, made up of various cells and layers of cells consisting of blood vessels, sensory receptors, glands, and hair follicles, is therefore a natural multifunctional composite. Moreover, human skin has the amazing ability of self healing. Consequently, nature serves as an inspiration for the development of multifunctional materials. A second class of multifunctional natural composites is the biomineralized materials found in living organisms. Biomineral composites are natural materials, a group of bioceramic-biopolymer composites, produced through cell-mediated processes [40]. They are composed of inorganic nano- or micro-scale amorphous or crystalline minerals formed through biologically induced or biologically controlled mineralization processes by living organisms in organic matrices of proteins and polysaccharides [42,116]. Their functions include structural support, mechanical protection, move-

ment, grinding, and gravity or magnetic field sensing. This class of multifunctional composites is of importance in biomimetics and is of interest to both biologists and materials scientists. They are tough materials combining high hardness with high fracture resistance. Examples are bone, dentine, enamel, shells, scales, eggshells and sponge silica skeletons. There are many other biocomposites that are not organic-inorganic such as skin, wood and leaf – these are organic and are also multifunctional.

Many other types of composite materials are now being developed aiming towards multifunctional composites as demands are increasing for smaller, lightweight but smarter products. Reinforcing components could be particles (0-dimensional), fibers (1-dimensional) or plates (2-dimensional). The orientation of these reinforcing components in a matrix could be random, unidirectional or bidirectional, and could be laminar. They are in the form of distinct phases in the matrix with sizes varying from macrophases to nanophases. When the size of the reinforcement is in the nano-range, the composite is referred to as a nanocomposite. When the nanoreinforcements are composed of a functional nanophase the composite is then a multifunctional nanocomposite in which the nanophase provides an advanced functional behavior through enhanced properties such as mechanical, chemical, biological, electrical, magnetic, optical properties.

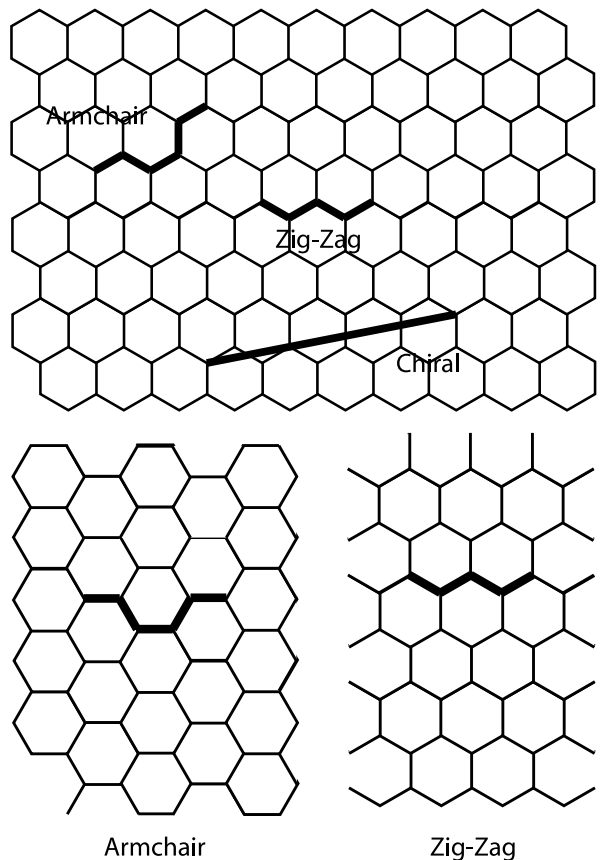
### A Short Note on Carbon

Carbon is a critical, enabling material and consequently an important component of many multifunctional composites. We will, therefore, outline some of the key properties for this element.

Carbon is one of the most common elements found on earth. It appears in three major forms: diamond, graphite, and as various forms of “fullerenes” and “carbon nanotubes.” The two former versions occur naturally, whereas the latter is typically artificially produced. Diamond, with a cubic crystal structure where the atoms are arranged in a tetrahedral configuration, is the hardest material found in nature. It is an electric insulator. In graphite, the atoms are arranged in hexagonal planes that are stacked parallel to each other. This layered nature of the structure makes graphite anisotropic and relatively soft, since fracture easily occurs along these layers. In this form, carbon is electrically conductive.

A third form of carbon was categorized in 1985 [54] (even though earlier work indicated their existence) and will play a key role in functionalizing composite materials. This third form is a variant of graphite, where one layer of graphite is wrapped to form a sphere or cylinder. The ini-

tial form described was a 60-carbon atom sphere, where the carbon atoms are arranged in 20 hexagons and 12 pentagons on the surface of the sphere. Soon after this discovery, variants of the 60-atom sphere were found, where, in particular, the tubular form, carbon nanotube (CNT) have provided an exciting new research field [50]. There are endless variants of how CNTs can be assembled, but the major categories can be summarized as single- and multi-wall tubes along with their major division by the atomic structure (armchair or zigzag; if arbitrary direction “chiral” see Fig. 1). CNTs are one of the most promising materials for functionalizing composites, due to their unique properties. For example, the armchair styled CNT are metallic, but the other versions are semiconductors. In particular, single CNTs are excellent conductor, and can therefore serve as nano-sized electrical wires. CNTs also have excellent mechanical properties, for example as high as 1 TPa elastic modulus has been reported [48,60]. Multi-walled CNTs consist of either single walled tubes layered



**Composites, Multifunctional, Figure 1**

Illustration of the various atomic configurations a carbon nanotube can assume. A carbon atom is located in each of the corners of the hexagons

over each other (“Russian doll-style”), or as a continuous, rolled sheet forming a wrapped layered sheet (parchment-style). There are several interesting review papers discussing CNT tubes, for example by Thostenson et al. [106] focusing on mechanical properties, by Gooding [43] focusing on electrochemistry and by Bandaru [5], discussing electrical properties of CNTs. Two recent review papers on theoretical aspects of the thermomechanical properties of carbon nanotubes can be found in [20,21].

### Functionalized Carbon Reinforced Polymer Matrix Composites

Carbon reinforced, polymer matrix composite are now commonly used in engineering applications, due to their relatively high strength and low weight. The carbon fibers give the composite their strength and stiffness, for which the structures traditionally have been optimized. However, recent developments make it possible to utilize the ability of carbon fibers to be electrically conductive. This opens up a broad range of opportunities for functionalizing carbon reinforced polymer matrix composites.

#### Electromagnetic Shielding

Electromagnetic interference (EMI) is caused by electromagnetic radiations emitted from sources that carry electrical current. A common source for EMI is an electronic device, but natural sources such as the Northern Lights and the Sun can also cause EMI. EMI results in anything from annoying “sound sparkles” on the television or cell phone to a malfunction of a device or a system (e. g., an aircraft). In warfare, EMI can be used to disrupt communications by the hostile side. Thus, it is important to shield aircrafts and communication devices from EMI. Carbon reinforced polymer matrix composites can readily be designed to shield EMI. Since carbon is electrically conducting, the carbon fibers can be used to reflect the radiations. By adding conductive fillers into the polymer matrix, the composite material can work efficiently as an EMI shield. It is now commonly used in many consumer products to shield them from EMI, both for protecting the machine and from spreading EMI the machine is generating. For example Bagwell et al. [4] added short copper fibers to increase EMI. A review of EMI shielding can be found in reference [27] and a review of conducting polymer composites that are primarily optimized for EMI shield is found in [101].

#### Electrified Carbon Fiber Polymer Matrix Composites

Interestingly, research from the groups of Sierakowski and Zhupanska have shown that the material properties

in a carbon fiber polymer matrix composite may change when subjected to an electromechanical field [97,98,121]. Early work [98] indicated that the strength, in particular the resistance to fracture and delamination, increases when the composite is subjected to an electric current. Several factors contribute to this, including that (i) the mechanical and electromagnetic fields are coupled when mechanical and electromagnetic loads are imposed simultaneously; (ii) the heat generated in the conducting carbon fibers are transferred to the polymer matrix; and possibly that (iii) the failure mechanisms change when the structure is subjected to an electromagnetic field. Recent work [97,121] where the impact resistance was investigated, show that the gains are short-term. The impact resistance initially can increase as much as 30%, but for a structure subjected to long-term exposure to an electromagnetic field, the gain is reduced back to the initial properties. The losses appear to be caused by the increasing temperature of the polymer due to the heating of the carbon fibers. Nevertheless, a structure can temporarily be strengthened by imposing an electromagnetic field. Moreover, the heat generated in the carbon fibers could potentially be used to activate self healing mechanisms (self healing mechanisms are discussed in Sect. “Self-healing Composites”)

#### Functionalized Composites with Carbon Nanotubes

As discussed in the introductory section of carbon, carbon nanotubes are probably one of the single most promising materials to functionalize composites. The possibilities appear to be endless and a few limited examples will be discussed here.

Single-walled carbon nanotubes (SWNTs) have great promise for functionalizing composite materials. They are light weight and have high mechanical strength, high thermal and electric conductivity and unique optoelectronic properties. They are also light weight, with a small diameter and high aspect ratio. However, these properties may be compromised when incorporated into a polymer matrix. This is primarily caused by the SWNT not being compatible with the polymer matrixes. This results in the SWNTs tending to agglomerate into clusters. When the SWNT are not bonded properly to the polymer matrix and/or appear in clusters, their unique properties may not be transferred to the composite materials. Therefore, significant efforts are being aimed towards improving the dispersion and bonding.

Chen et al. [19] suggest that molecular engineering is a viable approach to achieve good mechanical strength and retain the electric conductivity of CNT. They pointed out

that the problem with dispersion and bonding is due to the smooth surface of the SWNT. In a mix of SWNT and a polymer matrix, the mechanical load can be transferred through mechanical interactions between the SWNT and the polymer matrix, via van der Waals' interactions or covalent bonds, or via special non-covalent bonds, such as hydrogen bonding. The covalent bonding is in general the strongest type of bonding. However, when this is implemented, the electrical and thermal properties are often seriously challenged since these bonds tend to interfere with the SWNT structure [19].

CNTs can be used for energy absorption, which have been shown by Chen and co-workers [22,45,86]. In their work, they developed a solid-liquid composite which combines a non-wetting liquid with a hydrophobic nanoporous solid. The basic premise is that a liquid is absorbed into nanopores (such as the inside of a CNT) when a pressure is applied on the system. They showed that this infiltration absorbs and converts mechanical work into solid-liquid interface energy, with high energy absorption (10–100 J/g). Due to the ultra-high specific surface area of the nanopores, this is several orders of magnitude higher than conventional energy absorption materials. Moreover, by varying the interface energy, the energy absorption performance may be adjusted in a wide range, suitable for damping protections, vibration proof, or blast resistance. The interfacial energy can be changed by using chemical admixtures, or using viscous liquid. If the load rate can be controlled, this can also change the interfacial energy. In addition, by using functional liquids (such as electrolytes), the ion density at the nanopore-liquid interface may be perturbed by external mechanical or thermal fields. Thus, the multifunctional solid-liquid nanocomposite may harvest thermal and mechanical energies into electricity [46,87].

Polyaniline (PANI) is formed by polymerizing aniline (phenylamine, aminobenzene) which is an aromatic amine with the formula  $C_6H_5NH_2$ . PANi is a conductive polymer, and consequently has great potential to be a useful material component in multifunctional composites. When aniline is polymerized with the presence of multi-walled carbon nanotubes (MWNT), to form a polyaniline-carbon nanotube composite, the MWNT are coated with PANi and form a three-dimensional network within a matrix of PANi. This results in a composite with excellent electro-optical properties [90]. Preliminary work has shown that PANi can also work as a biological sensor [61]. Here the SWNT was wrapped with a single-stranded DNA and mixed with a self-doped polyaniline, poly(anilineboronic acid). The composite is able to detect nanomolar concentration of dopamine (a naturally occur-

ring hormone). The sensitivity for detecting dopamine was increased with a factor of four by adding the SWNT compared to the self-doped polyaniline [61].

Polypyrrole (PPy) is formed from synthesized (connected) pyrrole, where pyrrole is a heterocyclic aromatic organic compound,  $C_4H_4NH$ . PPy have been used for corrosion protection of metals, discussed in Sect. "Multifunctional Coatings". In a similar manner as PANi, PPy is conducting. An interesting application is to use PPy with MWNT, where supercapacitive properties have been measured [49]. To achieve this, the MWNTs must be aligned and then coated by an appropriate layer of PPy. Alignment of the MWNTs can be obtained by growing them on a quartz glass under appropriate conditions, described for example by Hughes et al. [49]. Measurement of the charge storage capacity of the aligned-MWNT-PPy composite film show several times charge storage than either PPy or MWNT alone (e. g.,  $2.55 F/cm^2$  for the composite film compared to  $0.62 F/cm^2$  for pure PPy film) [49]. Thus, aligned MWNTs coated with PPy have potential applications for supercapacitors and batteries, as well as sensors.

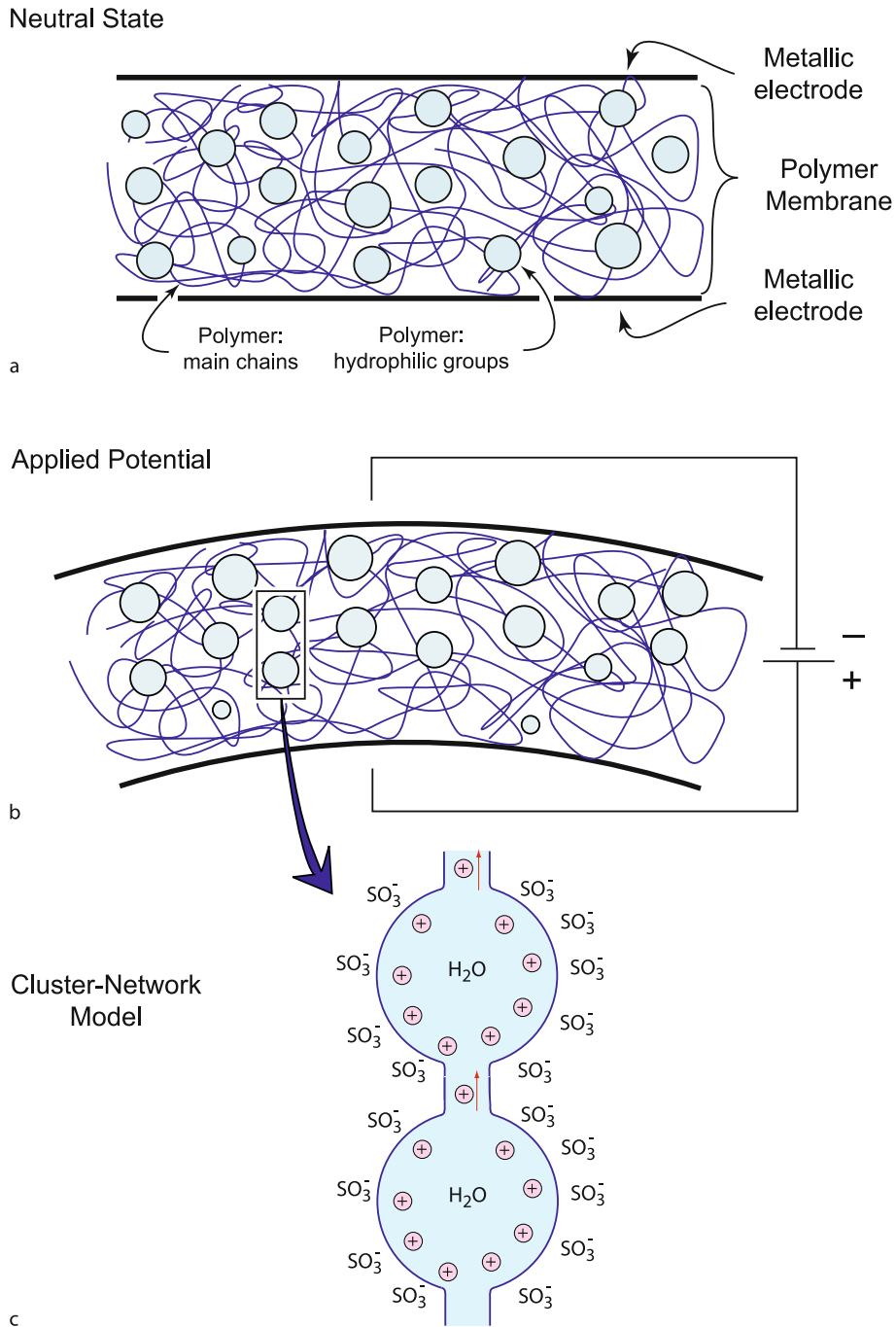
## Composites as Actuators and Sensors

**Ionic polymers** have received significant attention during the last decade, based on their ability to work as electromechanical transducer and potentials to work as sensors and/or actuators, and also as electrolytes in polymer fuel cells. Today, the preferred polymer materials are perfluorosulfonic acid (PFSA) polymers, a class of fluoropolymers consisting of a hydrophobic polytetrafluoroethylene (PTFE) backbone attached to hydrophilic sulfonic acid groups ( $SO_3^-$ ) or carboxylate groups via the fluorocarbon polymer side chains. Upon water uptake, the hydrophobic groups ionize and attach to the hydronium ions ( $H_3O^+$ ) to provide a conductive path for proton transport, while the polymer network maintains the overall structure of the membrane. Commercial material products include Nafion<sup>®1</sup> membranes and Flemion<sup>®2</sup> membranes. These membranes are also used as the proton exchange membranes (PEM) for fuel cell applications. A PEM functions as a "filter" (an electrolyte), letting protons through the polymer membrane, whereas the electrons are forced to take a path outside the PEM. From the path of the electrons, electric energy can be harvested.

Actuators and sensors can be made by an ionic polymer metal composite (IPMC) [3,8,9,56,57,74,75,76,89],

<sup>1</sup>Nafion<sup>®</sup> is a registered trademark of E.I. DuPont De Nemours & Co.

<sup>2</sup>Flemion<sup>®</sup> is a registered trademark of Asahi Glass Group in Japan.



**Composites, Multifunctional, Figure 2**

A schematic of the principle of an IPMC actuator. **a** Geometry before a voltage is applied highlighting the morphology of the polymer chains (hydrophobic) and the hydrophilic groups forming a cluster. **b** The structure deforms when an external voltage is applied. **c** The cluster-network model for Nafion® membranes, illustrating the cation migration. Adapted from [47,67,76,95]

with a potential application as artificial muscles [3,8,9,10, 56,57,67,76,94,95,112,114]. In this case, the ionic polymer is sandwiched between two metallic electrodes. The ionic polymer is hydrated, typically with water or ionic liquids

such as salts [3], to achieve its functionality. The metal electrodes are flexible layers, resulting in a soft and flexible actuator which can perform large dynamic deformation if placed in an alternating electric field, see Fig. 2.

Currently, platinum (Pt) and gold (Au) are the preferred electrode materials, which diffuses into the ionic polymer membrane, resulting in a material gradient over the thickness of the IPMC. The actuation is governed by the mobile cations (positively charged) moving towards the fixed cathode (negatively charged), resulting in a biased morphology and consequently a bending of the membrane as indicated in Fig. 2. When the current is switched, the location of the cathode is reversed and the cations will consequently move towards the other side, causing the actuator to move in the reverse. Alternatively, the IPMC can work as a sensor, where it generates a voltage if it is suddenly bent.

Nafion® polymer based IPMCs relaxes (reduces its deflection), whereas Flemion® polymer based IPMCs slowly increases its deflection under constant voltage. This is attributed to the mobile cations initially repelling the sulfonic acid groups in Nafion® polymer (which gives a fast actuation), but when the polarization is held constant, the cations relocate slowly, relaxing the IPMC. The carboxylate in Flemion® polymers are weaker in polarizing the structure, and therefore the relaxation is not observed [75,76].

These actuators can strain up to 3% for voltages less than 7 V [67]. This induces a significant bending, where stresses up to 30 MPa are reported [67]. Future research efforts are focused on reducing the negative effect of dehydration (an ionizing liquid is needed for the function), as well as addressing the reduced efficiency over time. Current applications range from fins to robotic fish to artificial eyes [67].

## Biomaterial Composites

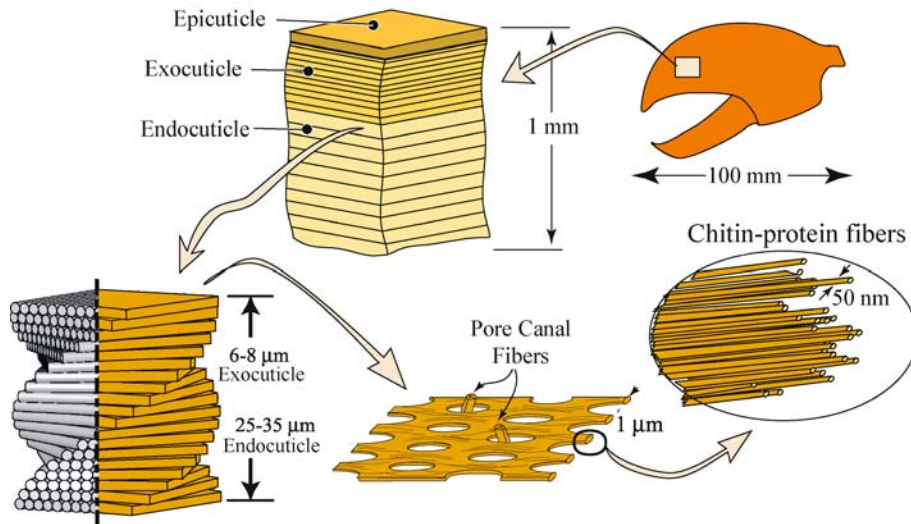
Nature has presented us with a variety of biological composites (biocomposites) such as skin, bone, shell, leaf and wood, which are all multifunctional in living organisms. Some are organic in nature, e.g. leaf and wood, whereas some are organic-inorganic, e.g. bone. Attempting to mimic nature, the design of these biocomposites are now intensely studied, including the structure and microstructure and the physical, chemical, electrical, magnetic and even optical properties. For example, using a biomimetics process M. C. Chang and co-workers have been able to develop a synthetic bone [17,18].

Biocomposites formed through a biomineralization process are referred to as biomineral composites. Examples of biomineral composites include bone, dentine, enamel, mollusk shells, crustacean exoskeletons, eggshells, sponge silica skeletons, and a variety of transition metal minerals produced by different bacteria (see references in

references [42] and [33]). The functions of the biomineral composites include structural support, mechanical protection and movement, anchoring (to another body or to ocean floor) grinding, filtering, gravity or magnetic field sensing, optical and piezoelectric [33]. Biomineral composites are composed of an organic matrix of proteins, lipids and polysaccharides. The structure consist of a nano- or micro-scale amorphous or crystalline minerals formed by a biologically induced or controlled mineralization processes, through complex chemical interactions between organic and inorganic matrices [2,42,91,116]. The structure is usually complex with the organic and the mineral components tightly interwoven at the nanoscale level, highly ordered and hierarchical to give high strength, rigidity along with mechanical and chemical stability, that are superior to synthetic materials made from the same materials. Biomineral composites are normally designed to function under a narrow range of environmental conditions, such as narrow temperature regimes and restricted mechanical loads. However, the compositions of biocomposites can be altered over time when a gradual change in environmental conditions occurs, to achieve necessary properties for the survival of the organisms [63]. Mollusks and sponges are known to make use of sophisticated biomineralization mechanisms to obtain structures that exhibit attractive combinations of strength, stiffness, resilience, and energy absorbing capabilities [63]. Even though the mechanisms of biomineralization are yet to be fully understood [69], biomineral composites are of much interest to warrant in-depth studies by biologists and chemists as well as material scientists. The structures of a few biomineral composites that are multifunctional are briefly described below.

The crustacean exoskeleton is a layered structure made up of the epicuticle layer, which is the topmost layer, the exocuticle layer and the endocuticle layer, which is the innermost [25]. The epicuticle is a relatively thin layer of about 2–4 µm. It is waxy, acting as a diffusion barrier [77]. The exocuticle is about 150–180 µm in *Homarus americanus* (American lobster) claw with the endocuticle 3–4 times this thickness. As a comparison, for the *Callinectes sapidus* (Atlantic blue crab) claw, the exocuticle is about 40–50 µm and the endocuticle 6–8 times thicker [25]. The exocuticle and the endocuticle are the major load bearing structures of the exoskeleton and are made up of multiple fibrous layers arranged parallel to the surface. The fibrous layer consists of chitin-protein (chitin is a biological polysaccharide with the generic formula  $(C_8H_{13}O_5N)_n$ ) fibrils bonded by a matrix of minerals and other proteins. Each of these fibrous layers is rotated by a small angle relative to the next layer in parallel, building up to a band of





**Composites, Multifunctional, Figure 3**

The cross-section (top) of the exoskeleton of a *Homarus americanus* (American lobster) taken from the claw (top right). The outer layer (epicuticle) acts as a diffusion barrier while the exocuticle and endocuticle layers are load bearing structures built of mineralized fibrous chitin protein. The helicoidal nature of the arrangement of the fibrous layers of the exocuticle and the endocuticle layers is shown on the left. The pore canals and the pore canal fibers in a layer are shown (bottom). Each layer is composed of chitin protein fibers (bottom right). Note that the exocuticle layer is denser than the endocuticle layer

layers that is twisted by  $180^\circ$  to form a helicoidal architecture (Fig. 3). The exoskeleton has through-the-thickness holes, *pore canals*, through which chitin-protein macrofibrils fibers, *pore canal fibers* run perpendicularly to the layers. Even though some disagreement exists in the literature, the pore canal fibers appear to run from the bottom of the endocuticle to the top of the exocuticle [25,28]. The pore canals and the pore canal fibers fill important functions in building the exoskeleton after molting. Moreover, Cheng et al. [25] showed that the pore canal fibers are important for strength of the exoskeleton. In all, the multiscaled structure of the exoskeleton, a biomineral composite, provide the crustacean with a strong structural support, an impervious defense covering for the body of the crustacean, and also serve as a carrying, holding and tearing tool in case of attack or feeding.

Nacre is another natural biomineral nanocomposite; it is also known as mother-of-pearl. It is the iridescent lining on the inside of the shells of many sea-going bivalves and gastropods such as oysters, mussels and abalones. Like many other biomineral composites, nacre has a hierarchical structure. It is composed of about 95% inorganic hexagonal platelets of aragonite (a crystallographic form of  $\text{CaCO}_3$ ) 5 to 8  $\mu\text{m}$  wide and 0.2 to 0.5  $\mu\text{m}$  thick [6], arranged in a continuous parallel lamina in 5% organic matrix composed of elastic biopolymers (such as chitin, lustrin and silk-like proteins and polysaccharides). The or-

ganic biopolymer is typically 5 to 20 nm thick. Nacre has received significant attention in recent years due to its high ductility, enhanced toughness and fracture strength, along with its low weight, resulting in excellent specific properties. Its fracture resistance is about 1000 to 3000 times greater than that of its component aragonite crystals [30,31]. Its high toughness is as a result of the ductility of the organic matrix in connection with the repeated unfolding of the protein molecules. The nanostructure resembles a brickwork arrangement with a significant overlap of the platelets and the organic matrix serving as the mortar [15]. This architecture is a critical factor that is responsible for the high fracture strength observed in nacre [6,41]. In addition, Li et al. [59] showed that the rotation of the nano-sized grain during loading is a key contributor to the high ductility. Many studies have been carried out on nacre using various experimental and modeling techniques to study its formation, its structure and morphology, and its deformation and properties, especially the mechanical properties [6,16,52,55,62,63,65,73,85].

Mimicking this material is of interest in the design of high performance materials such as impact resistance armor [7,55,92]. Using layer by layer assembly technique, Podsiadlo et al. [84] have been able to prepare a nanostructured analogue of nacre from nanometer sized sheets of montmorillonite clay and a polyelectrolyte. Artificial nacre

has also been synthesized [103]. Mimicking nacre in creating one nano-layer of material at a time, Nicholas Kotov and his team have evolved a process that allows the creation of materials one nano-layer at a time. They use this process to produce a new material from clay nanosheets and a water-soluble polymer that shares chemistry with white glue. The material is transparent, very strong, yet lighter in weight [64].

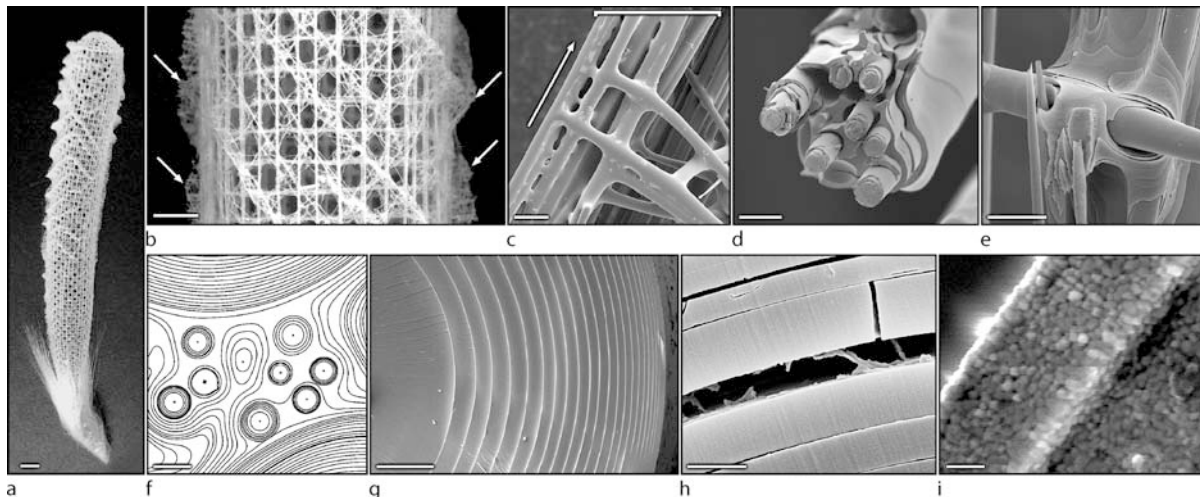
Animal skeletons are made up of bones which are hard and rigid tissues. Bone is self-healing and can continuously regenerate itself. Moreover, bone is relatively stiff and tough, and can withstand and adapt over time to local stresses. These properties make bone a reliable biological structural material. Bone is considered as a nanocomposite of minerals and proteins [18,26]: It is composed of a matrix impregnated with calcium carbonate, calcium sulphate and small amounts of sodium and magnesium. The matrix, consist of collagen fibers impregnated with crystals of hydroxyapatite,  $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ , and water. Among the functions of the bone is support, locomotion, protection for soft and delicate organs (like the skull protecting the brain), manufacturing of blood cells and homeostasis. An example of bone is the femur; it has a covering of a tough, strong membrane, called periosteum which is richly supplied with blood vessels. Next to the periosteum is a layer of compact bone and bone forming cells (osteoblasts), arranged in concentric layers (lamellae) with round small interconnecting canals (the Haversian canals) that contain blood vessels, nerves and lymph vessels. Embedded in this hard bone matrix are osteocytes, which are associated with bone deposition and bone remodeling. Inside the compact bone is a thin soft membrane known as the endosteum that encloses the marrow cavity that contains soft tissues, the yellow marrow [88,108]. The growth and strengthening of bone is stimulated by mechanical stresses through strain detection. This function is carried out by specialized cells within the bone that are sensitive to and respond to strains. In the absence of mechanical stresses bone becomes weak and less developed. Thus, the more the bone performs its intended functions the stronger it becomes. Mimicking this ability will produce excellent synthetic engineering materials for structural or load-bearing applications.

In a study of the sponge *Euplectella sp.*, Aizenberg et al. [2] described the structure of its skeleton as being hierarchical in nature. It has a layered arrangement that gives it a high resistance to crack propagation. The skeleton is thus composed of a layered biocomposite material. The structure is described in Fig. 4, after Aizenberg et al. [2]. The microstructure is made up of consolidated hydrated silica nanoparticles forming sets of concentric rings glued

together by an organic matrix to form spicules. This layer approach provides toughness and resistance to crack propagation. These spicules are then assembled in parallel into bundles within a silica matrix to form struts. The struts are arranged to make the cylindrical cage with the ability to resist tensile and shearing stresses and a significant capacity for recovery after deformation of the skeleton.

Aizenberg et al. [1] showed that the tunic spicules of the ascidian *P. pachydermatina* are a biocomposite material with well-defined domains of both amorphous and crystalline calcium carbonates, separated by an insoluble organic layer. The crystalline calcium carbonate is polycrystalline calcite, and it forms around the amorphous calcium carbonate which serves as the core. The calcium carbonate layers contain magnesium and proteins with a higher content in the amorphous than in the crystalline. The amino acid compositions of macromolecules associated with the two mineral phases are also quite different.

Wood is a natural biocomposite material with a multifunctional capability. It differs from the above mentioned bicomposites in that it is *not* a biomineral composite. Wood is a naturally hard and tough biocomposite material that forms the trunk or stem of trees. The material consists essentially of elongated hollow cells that carry nutrients from the roots to the leaves. The cells make up the cellulose fibers that are arranged generally in the grain direction, parallel to the surface of the trunk. Cellulose, with a generic chemical formula  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , is one of the major chemical constituents of wood, others are hemicellulose and lignin. It is a linear polymer with thousands of mers in a single molecule and it constitutes about 40 to 50% of wood. The cross section of wood is composed of several layers: the outer bark, the inner bark, the cambium, the sapwood, the heartwood, and the pitch. The thickness of each layer depends on the age of the tree, the species to which it belongs, and on the particular tree. The cambium layer is microscopically thin and it grows by cell division to increase the diameter of the trunk. The tree trunk increases in diameter by addition of new peripheral growth layers that constitute the growth rings. The sapwood layer conducts moisture, minerals, oxygen, and nitrogen. As the stem (or trunk) grows in diameter, the sapwood progressively forms the heartwood. The heartwood is the thickest of the layers and it is the one that provides the structural strength. It is usually darker in color because of the mineral deposits, gums and resins that are present in it. Cutting across these layers horizontally are tissues called wood rays radiating out from the center outward. They help in storing and transferring nutrients. Botanically, woods are classified as softwoods and hardwoods depending on their basic cellular structure and on how moisture moves within



#### Composites, Multifunctional, Figure 4

Structural analysis of the mineralized skeletal system of *Euplectella* sp. **a** Photograph of the entire skeleton, showing cylindrical glass cage. Scale bar: 1 cm. **b** Fragment of the cage structure showing the square-grid lattice of vertical and horizontal struts with diagonal elements arranged in a chessboard manner. Orthogonal ridges on the cylinder surface are indicated by *arrows*. Scale bar: 5 mm. **c** Scanning electron micrograph (SEM) showing that each strut (enclosed by a *bracket*) is composed of bundled multiple spicules (the *arrow* indicates the long axis of the skeletal lattice). Scale bar: 100  $\mu\text{m}$ . **d** SEM of a fractured and partially HF-etched single beam revealing its ceramic fiber-composite structure. Scale bar: 20  $\mu\text{m}$ . **e** SEM of the HF-etched junction area showing that the lattice is cemented with laminated silica layers. Scale bar: 25  $\mu\text{m}$ . **f** Contrast-enhanced SEM image of a cross section through one of the spicular struts, revealing that they are composed of a wide range of different-sized spicules surrounded by a laminated silica matrix. Scale bar: 10  $\mu\text{m}$ . **g** SEM of a cross section through a typical spicule in a strut, showing its characteristic laminated architecture. Scale bar: 5  $\mu\text{m}$ . **h** SEM of a fractured spicule, revealing an organic interlayer. Scale bar: 1  $\mu\text{m}$ . **i** Bleaching of biosilica surface revealing its consolidated nanoparticulate nature. Scale bar: 500 nm. (Taken from reference [2] with permission from AAAS)

the living tree. Softwoods are mainly made up of long cells of between 3 and 5 mm called tracheids. Hardwoods, on the other hand, are mainly made up of two kinds of cells, wood fibers (0.7 to 3 mm long) and vessel elements (with wide ranging lengths).

The important physical properties of wood are moisture content, permeability, shrinkage, density. These give it the multifunctional capability such as serving as a super-structure, acting as a nutrient storage and transport medium, the ability to withstand harsh weather, and self-healing. The properties, however, vary greatly across species and also depend on factors such as the age of the tree, stem form, type of soil and climate. Wood is anisotropic with the mechanical properties varying across the growth rings and along the height up the tree. The mechanical, electrical and thermal characteristics of wood make it a popular excellent engineering material over ages.

Leaf is an organic biocomposite that is flat, broad and thin. It is a plant organ in which photosynthesis is carried out. The upper surface of the leaf is waxy for the purpose of water-proofing. It performs functions such as converting sunlight to chemical energy in the mesophyll, transporting glucose, water and minerals through out the plant by

the vascular bundle; it is water-proof and provides shade for the tree. The cross-section is made up of different layers in this order from the top: upper cuticle, upper epidermis, palisade mesophyll, spongy mesophyll, lower epidermis and lower cuticle. Embedded in the mesophyll layers is the vascular bundle (phloem and xylem) and air spaces for the supply of air (carbon dioxide) and moisture that comes in through the stomata that dotted the lower epidermis through the lower cuticle. The broadness of leaf allows it to gather as much sunlight as possible as a supply of the energy needed for photosynthesis. Leaf provides a system that could be mimicked in designing materials for energy conversion and at the same time distributes the product.

Biocomposites materials produced by nature have properties that could be beneficial when reproduced in synthetic materials. The design, manufacture from simple raw materials, economical use of raw materials and energy, multifunctionality and degradability of biocomposites are inspirational to biomimetics or biomimicry in the design and manufacture of synthetic engineering materials. Another inspiration from nature is the building from bottom up, from atomic or molecular level to the macro structural level. This provides for efficient use of raw ma-

terials. A thorough study of nature's biocomposite materials could, therefore, yield viable procedures and techniques for the design and manufacture of synthetic engineering materials with excellent combination of properties that will provide for multifunctionality in them.

## Self-healing Composites

Biological systems have an outstanding ability in self-healing; that is, automatically detecting and repairing damaged tissue. The repair is made by a material similar to the original (causing a scar tissue), or identical tissue (leaving the damage area undetectable after repair). For humans, the latter can for example be observed in bone, whereas the former on skin. Moreover, biological systems can adapt to new conditions. Humans build more muscles and bones if we increase our daily exercise regime and a tree grows branches to find the most sunlight.

Man-made structures traditionally do not have these features. If damage occurs, damage will continue to accumulate until it is detected via human intervention or until the structures fails. Today, there are many sophisticated means of detecting failures. Even though tremendous advances have been made towards detecting and repairing damage in structures, *self-healing materials* would significantly improve the reliability of structures. During the last decade, significant advances have been made towards developing self-healing composites. The current approaches results in a "scar tissue" in the sense that the original material is not exactly reproduced, but that the structure will function satisfactory. Two materials systems will be discussed here; (i) ceramic matrix composites and (ii) polymer matrix composites.

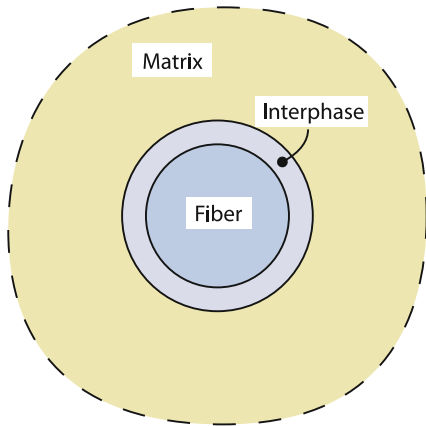
**Ceramic materials** typically have high strength and stiffness, and retain their strength even at high temperatures. Since they are brittle and therefore are considered unreliable (tend to break without warning signs that metals exhibit, such as plastic deformations, especially under tensile stresses) their uses have been limited. To negotiate the brittle response, ceramics can be reinforced. Most commonly, ceramics are reinforced with a second ceramic, forming a ceramic matrix composite (CMC). The bonding between the reinforcement and the matrix is a key parameter that governs the toughness of the CMC. By controlling the interface material, referred to as "interphase", the interfacial bonding can be optimized, allowing for the load transfer between the matrix and the fibers, deflects matrix cracking and serve as a barrier towards diffusion. When considering the strength of the interface material, it must be optimized to be "just right," not too strong and not too weak.

Self-healing of CMCs can be achieved through high temperature oxidation in silicon carbide based CMCs. Silicon carbide (SiC) reinforced with SiC fiber (SiC/SiC composites) or carbon fibers (SiC/C composites) is mechanically durable up to 1500°C and is therefore considered a promising composite for high temperature applications such as engines and gas turbines [70]. Even though the fibers are brittle in a similar manner as the matrix, the fibers and matrix work synergistically to create a ductile material. Micro-cracks develop during loading, but these micro-cracks are stopped by the microstructural features, simulating a non-linear response paralleling yielding in metals. When silicon is subjected to elevated temperatures, it quickly forms a protective coating of silica (SiO<sub>2</sub>). Unfortunately, the micro-cracks that are associated with the CMC become pathways for oxygen to penetrate into the structure, causing internal oxidation. This can weaken the structure. By coating the fibers with carefully selected materials, the oxidation can be controlled and result in self-healing of the micro-cracks. Graphitic carbons ("pyrocarbons," "PyC") and boron nitride (BN) have emerged as the most prominent interphase [39,44,70,71,72]. When oxygen diffuses through the micro-cracks, a fluid oxide is formed due to the oxidation, filling the cracks, Fig. 5. These glassy oxides that form can be optimized through the interphase. For example, when a borosilica glass is used as an additional coating on the fibers, no loss in composite strength was observed after 200 h at elevated temperatures [39]. Thus, a self-healing mechanism in silicon carbide (SiC) matrix composite reinforced with SiC or carbon fibers has been observed, which is caused by oxidation at high temperatures. The oxidation occurs at temperatures above 800°C. The self-healing can continue until the reducing material has been consumed.

**Polymer composites** might be the most promising systems where self-healing mechanisms can be developed. There are several reasons for this. Polymer based systems are in general less expensive than ceramic based systems, and tends to be easier to work with. All self-healing ceramic systems are based on activating the healing process through subjecting the material structure to heat. Even though some self-healing polymer systems are based on heating, the temperature regime for healing polymer is significantly lower than for ceramics, thus simplifying the process. Furthermore, many self-healing approaches to polymer systems are not dependent on heating. Lastly, several different approaches for self-healing of polymer have been developed so far, thus inviting alternative approaches for self-healing.

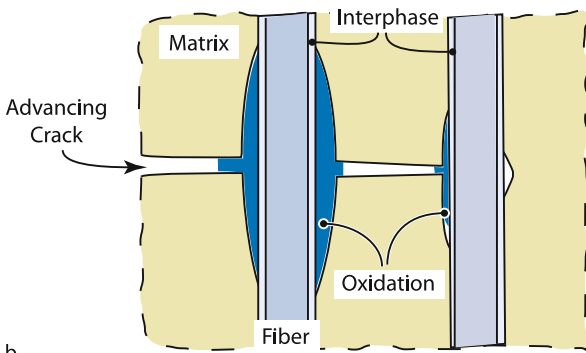
One simple concept of healing a damaged structure is to subject the material to elevated temperatures as was

Top view of a coated fiber in a matrix



a

Side view, propagating crack and oxidation



b

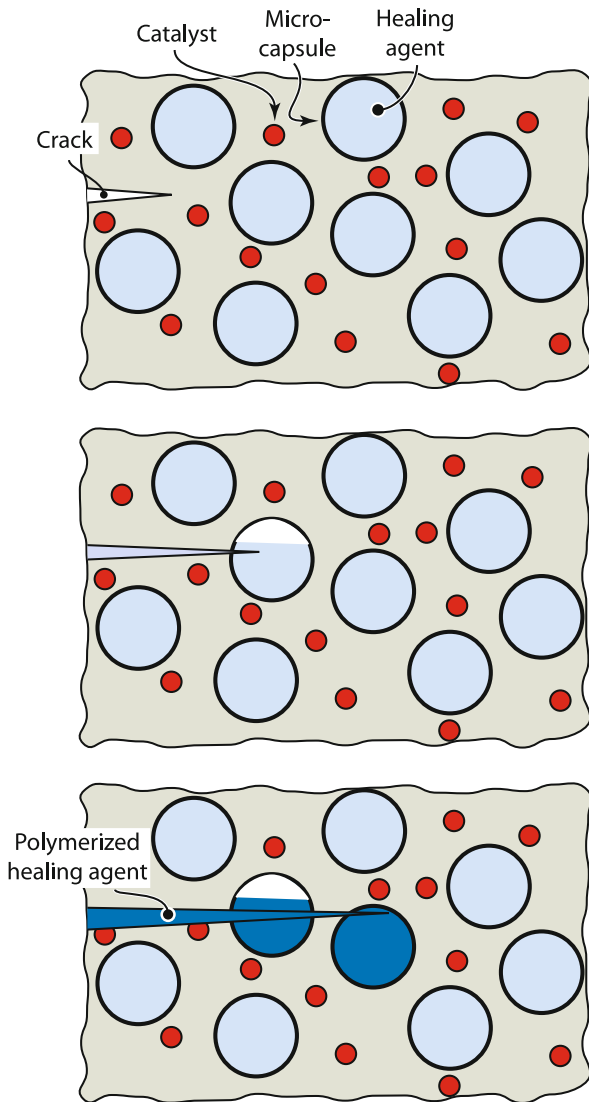
**Composites, Multifunctional, Figure 5**

Examples of interphases used in SiC matrix composites a schematic top view of a fiber with a coating (interphase) in a matrix b schematic side view of an advancing crack exposing the interphase that oxidizes, resulting in self-healing

seen for ceramics. This idea is based on that the elevated temperature activates a chemical process that results in healing. For example, by utilizing a particular thermally reversible reaction (e.g., a selected Diels–Alder reaction) for cross linking linear polymer chains, a fractured material can be healed, as demonstrated by Chen and co-workers [23,24]. For one material system investigated, after fracture and subsequent heat treatment, the original strength was regained. In this case, the polymer (a furan-based monomer synthesized with 1.8-bis(maleimido)-3.6-dioxaoctane) was subjected to mechanical testing leading to fracture followed by heat treatment at 130°C for 30 min. In this case, there was no loss in the original strength when the structure was re-tested [24]. This approach to self-healing has the clear advantage that no additional material is needed to be added: the material is in-

trinsically self-healing. However, only a very limited set of materials that can self-heal by cross-linking the polymer chains upon reheating. An alternative approach for healing via heating utilizes an additional material phase incorporated into the original material. When subjected to sufficient heating, this additional material is activated, and can mend the damage structure. For example, a composite made of glass fiber reinforced epoxy retained its stiffness after the heated repair [120]. By adding a heat-activated material to the composite structure, a design engineer would not be strictly limited to a narrow set of materials. However, a major disadvantage with both of these heat activated healing methods is that the healing is not automatic; rather, the structure needs to be treated in a separate process. (This may be differentiated from the ceramic self-healing that was discussed above. The ceramic is operating at the temperature at which oxidation occurs, but this polymer operates at temperature lower than where self-healing appears.) Nevertheless, depending on the application, this approach can be quite useful.

A more convenient approach to self-healing of a structure compared to the heat activated systems described above is a system that heals itself without active interference. Most approaches aiming to achieve this are based on introducing one or more phases into the composite material. These additional material phases are automatically activated when damage occurs. A successful approach have been developed by White, Sottos and co-workers, where spherical microcapsules containing a “healing agent” and a second phase containing a catalyst are embedded in a polymer matrix composite [12,13,14,53,115]. When a crack propagates, the micro capsules in the crack path burst and release their healing agent into the crack, Fig. 6. As the healing agent fills the crack, it will eventually contact the catalysts. When this occurs, the healing agent will polymerize, filling the crack and effectively healing the crack. In the work by White, Sottos and co-workers, the agent was a dicyclopentadiene (DCPD) monomer and the catalyst a bis(tricyclohexylphosphine)benzylidene rhenium (IV) dichloride (a Grubbs’ catalyst) [12,13,14,53,115]. This results in a ring-opening metathesis polymerization (ROMP) of the DCPD, resulting in a highly cross-linked polymer. When stabilized with 100–200 ppm p-tert-butylcatechol, the DCPD has a long life and healing can be achieved even for aging structures. The micro capsules containing the DCPD ranged from 40–240 μm and were made with poly-ureaformaldehyde. In early work, curing for 48 h was required to retain 45% of the initial strength (if the curing occurred at 80°C, up to 80% of initial strength was achieved) [12,115]. Subsequent studies showed that 10 h were sufficient to achieve full polymer-



**Composites, Multifunctional, Figure 6**  
 Schematic of a propagating crack in a polymer with micro-capsules filled with a healing agent

ization (full healing or full strength), and that the fatigue life can be increased with over 200% if the structure is allowed to rest sufficiently for the healing agent to polymerize [13,14]. Most engineering structures are allowed to “rest” between operations. For example, cars are normally used for commuting to work and get sufficient time to “rest,” both day and night, whereas airplanes are scheduled for regular maintenance that keeps them grounded for many hours that may be sufficient for the polymerization to take place. Thus, this system is a promising approach towards extending the lifetime of polymer matrix composites.

The micro-sphere approach has the clear advantage of being possible to be incorporated into a range of materials, and that no particular treatment is needed to activate the healing processes. There are, however, some drawbacks. These include that the shell of the micro-capsules have to be designed so that it breaks when a crack has developed in the bulk material, and that the healing agent comes across the catalyst. Moreover, the up to 200  $\mu\text{m}$  diameter spheres can possibly interfere with the reinforcement of the polymer, including introducing an unwanted waviness of the fiber reinforcement. The latter drawback can be addressed by replacing the micro-spheres with hollow micro-cylinders [11,36,68,82,83]. The current state-of-the-art for hollow micro-cylinders focuses on using commercial hollow glass fibers embedded in composite materials [11,82,83]. In a similar manner as to the case of micro-spheres, the hollow cylinders are filled with a “healing agent” that is activated once the fiber breaks. A two-phase epoxy system is used, where the epoxy resin is stored in one set of cylinders and the hardening agent is stored in a second set of cylinders. In a layered composite material, the hollow glass fibers are aligned with the reinforcement fibers, for example the fibers with the epoxy resin are aligned with the 0°-ply and the fibers with the hardening agent with the 90°-ply. When cracks develop and propagate, the glass tubes break, allowing the epoxy and the hardening-agent to fill the damaged zone. The materials are selected so that the epoxy cures at ambient conditions. The major challenge with this approach relates to the difficulty of finding suitable glass tubes. Ideally, the properties of the hollow glass tubes should match that of the original reinforcement, so they can replace or enhance the composite structure. To address this, Pang and Bond [83] purchased commercial borosilicate glass tubing and using in-house facilities drew the fibers to external diameter of 60  $\mu\text{m}$  and inner diameter of approximately 42  $\mu\text{m}$ . The fibers were filled with a commercial epoxy repair agent (MY750 Ciba-Geigy) and the corresponding hardening agent respectively [83]. In this case, about 90% of the strength of the original strength is retained after repair, but the strength degrades with time.

With the exception of the reversible cross linking polymers, the repair schemes discussed so far for polymer composites are all based on one-time repairs; once a micro-capsule or micro-fiber breaks the healing agent is consumed, and no further healing will occur if another crack should develop again at the same point. In contrast, self-healing in biological systems can occur multiple times for repeated injuries, assuming a reasonable frequency of injuries. In animals, this is possible by the continuous flow of an intelligent mixture of biochemicals in the vascular network, which is related to the circulatory system. Some at-

tempts are made to mimic vascular network for self-healing [104,107], where a constant supply of healing agent could potentially be provided. There are several manufacturing issues involved here, and opens up many potential research avenues.

## Multifunctional Coatings

Applying coating on a structure is many times a cost effective way of obtaining a multifunctional composite material. There are many examples that illustrate this, for example environmental barrier coatings, coatings for increased wear resistance, and thermal barrier coatings. Most coatings combine several functions by having multiple layers where each layer contributes a particular function.

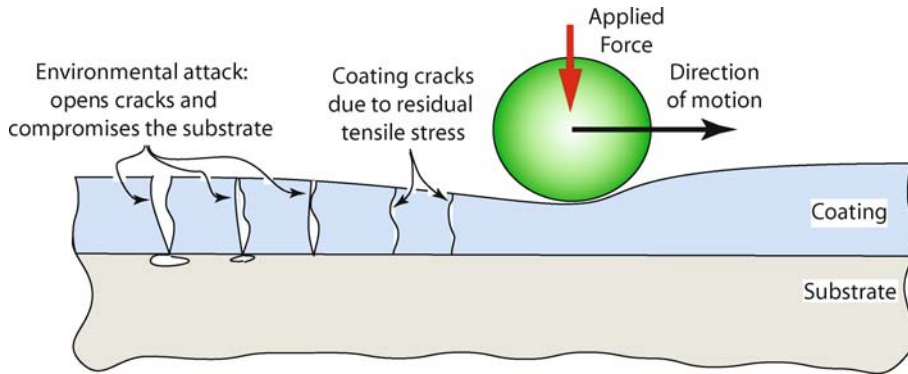
Coatings for corrosion resistance (sometimes referred to as environmental coatings) are probably one of the most common classes of coatings, for example covering steel with zinc to obtain a galvanic protection, (the zinc is sacrificed to protect the underlying steel). Even though functional, these cannot be categorized as multifunctional and will not be discussed here. More advanced coatings are now being developed to protect steel and other metals. Some of these coatings have multifunctional capacities. Some particular interesting coating materials are electropolymerized polymer composites including polyaniline (PANi) [51,78,93,102] and polypyrrole (PPy) [51,102]. Polyaniline (PANi) is formed by polymerizing aniline (phenylamine, aminobenzene),  $C_6H_5NH_2$  and polypyrrole (PPy) is synthesized pyrrole,  $C_4H_4NH$ . The polymers are typically deposited through an electrochemical synthesis in which the thickness can be controlled. The corrosion resistance depends on the deposition parameters including applied potential and the feeding rate of the monomers. By producing a composite of PPy and PANi, the corrosion rate can be reduced with more than two orders of magnitude compared to unprotected materials [51]. To achieve this improved rate, it is crucial to ensure a proper bonding of the structure of the polymer composites deposited on the metal, which must be controlled through the processing parameters [102]. This class of coatings protects in sulfuric acid ( $H_2SO_4$ ), not so well in hydrochloric acid (HCl), and not at all in a Sodium chloride (NaCl) solution [93]. Thus, care must be taken when using this type of coating for corrosion protection, but evidently, it can be quite useful for a range of applications.

A second class of important coatings is coatings used to ensure low friction and increased wear resistance of the underlying structure, tribological coatings. These coatings are critical for a range of applications, including moving contacts (e.g., bearings), materials processing (e.g.,

drilling), and applications where addition of lubricants or materials debris from wearing is unacceptable (e.g., food processing, medical implants). Also, by reducing friction in moving parts in vehicles, the fuel efficiency of the vehicle can be significantly increased. When optimizing a coating for wear resistance, the goal is to reach as high hardness as possible [110]. When combining wear resistance with low friction, many other aspects must be considered. There are now several systems used as solid lubricants which allow for both low friction and wear resistance. These include diamond and diamond-like carbon, graphite, molybdenum disulfide, hexagonal boron nitride, boric acid as well as soft metals [37]. An interesting example of a low friction wear-resistant coating consists of a composite coating made from a titanium nitride matrix, TiN, with molybdenum sulphides,  $MoS_x$ , dispersed as a second phase. Up to 8% (by weight) addition of  $MoS_x$  does not affect the hardness of the coating (thus promoting wear resistance), but decreased the coefficient of friction with more than a factor of two, and consequently increasing the life up to 500 times compared to the TiN coating alone [29].

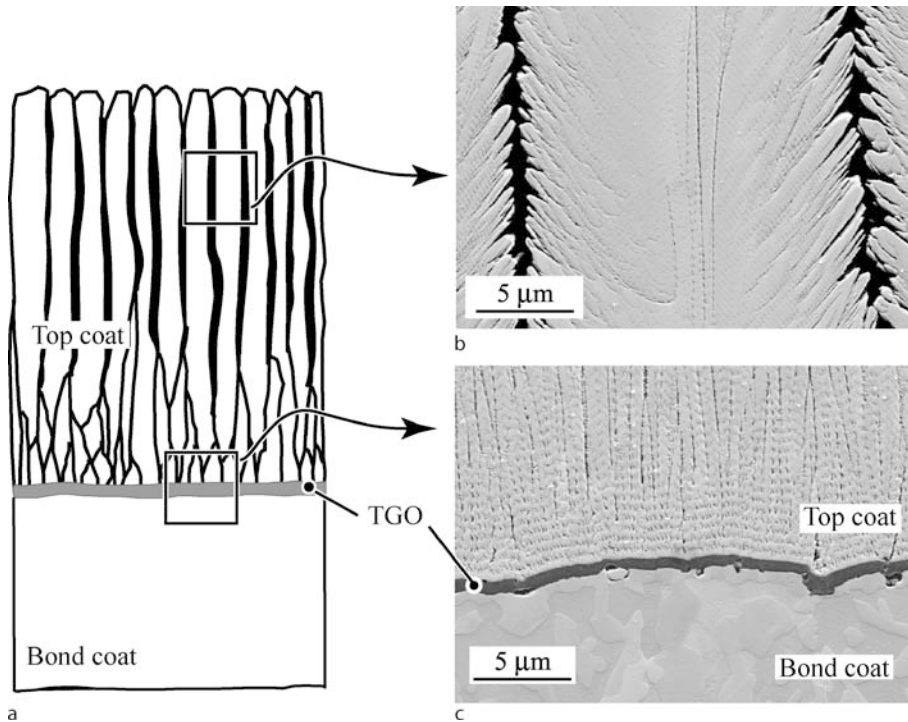
Of high interest is to combine the corrosion resistance coating with the tribological coatings. This multifunctional coating would then resist both corrosion, wear and provide a low coefficient of friction [113,117]. This would increase the lifetime of many engineering applications, and for example, increase the fuel efficiency of vehicles since it reduces energy losses due to friction. Tribological coatings under stress and at the same time in aggressive environments degrade at a significantly faster rate compared to if they were subjected to wear alone or to the aggressive environments alone, since the two conditions aid each other to aggravate the deterioration of the coatings, as illustrated in Fig. 7. In a recent review by Wood [117] it is clear that this is a research area that requires significant attention in the future.

The last class of coatings we will discuss is coatings used for high temperature protection: thermal barrier coatings (TBCs), used to protect the underlying metallic substrate. TBCs are commonly used for protecting superalloys in gas turbines (both stationary for energy production and mobile for propulsion of airplanes). These systems are a material system with multiple layers, in which each layer is optimized for a particular function. It is made up of a *bond coat* being deposited on a metallic base, after which a ceramic *top coat* is deposited, see Fig. 8. In gas turbine engines, a thermal gradient over the top coat of up to  $150^\circ C$  is achieved from active cooling of the superalloy and by selecting top coat materials with relatively low thermal conductivities [38,66,79,99,100,118]. The metal-



**Composites, Multifunctional, Figure 7**

Illustration of a degradation caused by combined wear and corrosion of a coated structure. Wear (illustrated by a sphere moving on the surface with an applied normal force) causes cracks in the coating. As the cracks develop, the environment can reach the substrate and deteriorate the substrate quickly



**Composites, Multifunctional, Figure 8**

An example of a thermal barrier coating produced by electron-beam physical vapor deposition (EB-PVD). **a** Sketch of the system; **b** scanning electron microscopy (SEM) image of the cross-section of the top coat, close to the surface; **c** SEM image of the interface between the top coat, thermally grown oxide (TGO) and the bond coat. Note that **b** and **c** are of the same scale. The top coat (yttria stabilized zirconia) is intentionally made porous to allow for strain tolerance during thermal cycling

lic bond coat provides oxidation protection to the superalloy by sacrificing itself by supplying aluminum to form an alpha-alumina scale ( $\alpha\text{-Al}_2\text{O}_3$ ) between the bond coat and the top coat (Fig. 8). As the alumina scale grows, the aluminum content decreases in the bond coat, ultimately

changing the bond coat properties [32,96]. Thus, it is important to control the chemical content of the materials since even small amounts of critical trace elements can enhance or reduce the interfacial fracture toughness of the structure. Even though TBCs have been used for more



than a decade, improvements of these multifunctional materials are still critical. By improving their reliability and durability, gas turbine powerplants and aircraft engines can become significantly more efficient, reducing their fuel consumption and reducing the pollution associated with energy production and propulsion.

### Other Multifunctional Composites

Polyaniline (PANi) as discussed earlier has also been used as nanoparticles (rather than the matrix) to achieve multifunctional composites. For example Dispenza et al. [34] used PANi particles in a hydrogel matrix obtaining a biocompatible nanocomposite with properties suitable for the development of optoelectronic devices. The composite was obtained by a multistep process, starting with water dispersion polymerization of aniline, followed by  $\gamma$ -irradiation. The  $\gamma$ -irradiation cross links the PANi to the steric stabilizers (either poly-vinyl-pyrrolidone, PVP or poly-vinyl-alcohol, PVA). Depending on the processing conditions, various properties can be obtained, but the PANi particles remain spherical [34]. The composites can undergo two optical transitions and the fluorescence signals can vary in wave-length as a function of pH-value.

Composites with 3-dimensional reinforcements have been developed in order to eliminate a number of shortcomings like low shear and transverse stiffness and strength exhibited by laminated composites, with application in areas such as the aerospace industry. 3-dimensional braided reinforcements give reinforcing support in all the three directions thereby suppressing delamination in the composite and giving a higher damage tolerance [80,81,119].

Another group of composites that are multifunctional are the hybrid composite materials. A hybrid composite is made by combing two or more types of fibers in a single matrix material or in two or more types of matrix materials. This gives a greater possibility of achieving multifunctions by changing the combinations of fibers and/or matrix materials [111]. However, the interactions of the constituent components of a hybrid composite and large number of design variables involved make the design of such a composite complex. Examples are carbon-aramid reinforced epoxy, glass-carbon reinforced epoxy, and carbon-Kevlar reinforced epoxy. Lee [58] classified hybrid composites as (1) interply or tow-by-tow, in which tows of the two or more constituent types of fiber are mixed in a regular or random manner; (2) sandwich hybrids, also known as core-shell, in which one material is sandwiched between two layers of another; (3) interply or laminated, where alternate layers of two (or more) materials

are stacked in a regular manner; (4) intimately mixed hybrids, where the constituent fibers are made to mix as randomly as possible so that no over-concentration of any one type is present in the material; (5) other kinds, such as those reinforced with ribs, pultruded wires, thin veils of fiber or combinations of the above [58].

### Future Directions

Biomimetics is seeking to mimic nature to design and produce materials comparable or better than the ones nature has produced. The goal is to be able to synthesize organs for replacement in the body. Such organs should be able to perform and grow just like the natural one being replaced. This will eliminate looking for or waiting for donors wanting to donate such a needed organ which, in some cases, the body of the patient may reject in the end.

For non-biological applications, mimicking multifunctional biocomposites should be directed at designing synthetic composite materials that can simultaneously perform more than one function. Self-healing is another aspect being targeted to be achieved in material design. The future goal is not only to achieve multifunctionality in composite materials but also such materials should be self-healing. One great lesson from nature is that nature does not waste materials in building its structures yet with incredible relevant properties. This is because nature builds from bottom up, from molecular level to macro level. Ability to control the design and structure of the material on the molecular level will allow production and fabrication of components, devices and structures with incredible properties and functionalities without excessive use of material or energy inputs. This is a great advantage in conservation of material and energy.

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