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Perspective

The Biomimetic Evolution of Composite Materials: From Straw Bricks to Engineering Structures and Nanocomposites

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Abstract: Advanced polymer-based composite materials have revolutionized the structural material arena since their appearance some 60 years ago. Yet, despite their relatively short existence, they seem to be taken for granted as if they have always been there. One of the reasons for this state of affairs is that composite materials of various types have accompanied human history for thousands years, and their emergence in the modern era could be considered a natural evolutionary process. Nevertheless, the continuous line that leads from early days of composites in human history to current structural materials has exhibited a number of notable steps, each generating an abrupt advance toward the contemporary *new science* of composite materials. In this paper, I review and discuss the history of composites with emphasis on the main steps of their development.

Keywords: composite materials; biomimetics; advanced composites; nanocomposites

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1. Raw Materials

The main raw materials for construction in archaic human history, the Neanderthal Age, were stone, wood and fibers used as such without any processing or modification due to their mechanical properties and availability. Those raw materials were abundant and could easily be collected and assembled in small structures. A makeshift example of a structure made of unprocessed pristine materials could be a stone hut with a log or straw roof tied together with ropes, such as air roots of rainforest plants. Eventually, such raw materials in their pristine state, with no change in their intrinsic compositions, were processed to make building stone, pillars and ropes. Famous examples of the utilization of such basic building materials for construction are King Solomon's Temple with Lebanese cedar and cypress timber shipped from Tyre by King Hiram and "stone prepared at the quarry" (1 Kings 5:1–6:38), and the 150-yearold oak tree wooden-framed spire of Notre-Dame de Paris, consumed by the blaze in April 2019, now to be reconstructed as originally designed by 1000 oaks from the Domaine de Berce forest (https://www.france24.com/en/europe/20210309-france-fells-centuries-old-oaks-to-rebuild-the-notre-dame-cathedral-spire, accessed on 9 March 2021).

A noted change has occurred in the production of construction materials by involving a series of unit operations, such as compounding, heating and molding. As a result, new materials that had not been available earlier were invented. A number of examples can be mentioned, such as terracotta bricks, Phoenician silica or sand glass and clay-based mortar. The involvement of processing also resulted in the manifestation of metallic materials, mostly iron, copper and lead.

If the compounding stage involved the mixing of a least two components, a material of a new composition would be formed. Realizing that the new material is a mixture composed of several constituents, the modern science of structural materials has coined the term *composite* or *composite material* to describe the new entity. A definition of composite can be found in any text book, where, despite minor differences, they all emphasize composites as outstanding in the fact that the compounding of several components does not involve chemical reactions or dissolution, meaning that the original chemical and physical identity of the constituents remains unchanged. Correspondingly, a basic definition of a composite material states that it comprises at least two chemically/physically different materials: a *reinforcement* (which is directionally aligned in *advanced composites*) and a *matrix* that binds the reinforcement and is separated from it by a sharp *interface*. The required presence of an interface indicates that the resulting mixture is not a solution but a combination in which the components retain their respective original entities.

The idea of compounding structural materials by mixing several constituents was based on observations of natural phenomena and structures, such as bird nests, cow dung and beaver dams, which led to the construction of simple fiber-reinforced materials, where natural fibers were used to reinforce mud or clay matrices to form adobe bricks. The most famous example (Figure 1) is straw-reinforced bricks, as mentioned in the book of *Exodus* 5:7 ("Ye shall no more give the people straw to make brick, as heretofore: let them go and gather straw for themselves").

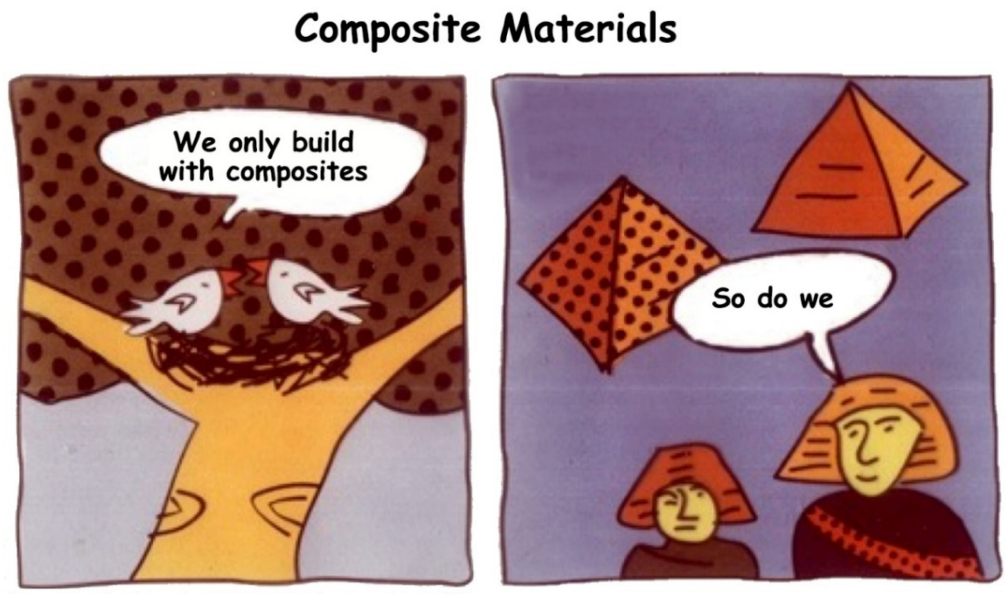

Figure 1. "So the people were scattered throughout all the land of Egypt to gather stubble for straw" (*Exodus* 5:12).

The process of imitating or copying from nature—termed biomimetics—is particularly substantial in the development of composite materials, as described below.

2. Principles of Biomimetic Engineering

The term *biomimetics* or the concept of bio-inspiration is by and large considered to apply to the reverse engineering of natural phenomena into manmade modern technology. It relates to questions regarding what advanced materials science or structural engineering can learn from biological models, processes and systems found in nature [1]. Moreover, in the biomimetic process, the fundamental methods of nature combined with scientific methods and design techniques generate synergistic improvements.

The potential of intimate discovery of nature's hidden mystery gives way to an extensive acknowledgement of nature as a mentor and a measure for the "rightness" of things. It suggests that by drawing inspiration from living entities and by re-creating ideas drawn from nature, humans might get behind the veil of nature's mystery.

The same realization gave birth to biomimetics in the 1960s, a scientific discipline that studies and imitates nature's methods, designs and processes. It is a methodical way of learning from nature and being inspired to recreate its genius ideas. Engineers and scientists faced with the structures and systems of the natural world become aware of the matchless solutions that exist in the optimized systems and extraordinary techniques in nature; thus they are inspired to reverse engineer the biological models for similar engineering problems or produce new technologies [2].

Perhaps the most common example of biomimetic application is the attempt to mimic the mysterious way by which the spider manufactures its silk, which emerges purely from its body that provides all of the raw materials, and the way by which it weaves it into a web while hanging on it (Figure 2). Evidently, biomimetic engineering explores the spider's technique as a potential model for new fiber manufacturing, e.g., nylon fibers, invented in 1935 by Carothers at DuPont, and more recently in the electrospinning of nanofibers to form scaffold webs for tissue-engineering-based implants (Figure 3) [3], or as various carriers of medical drugs, showing promising achievements in nanotechnology [4].

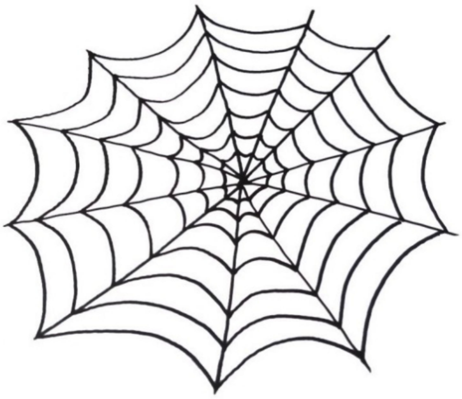

Figure 2. A spider web.

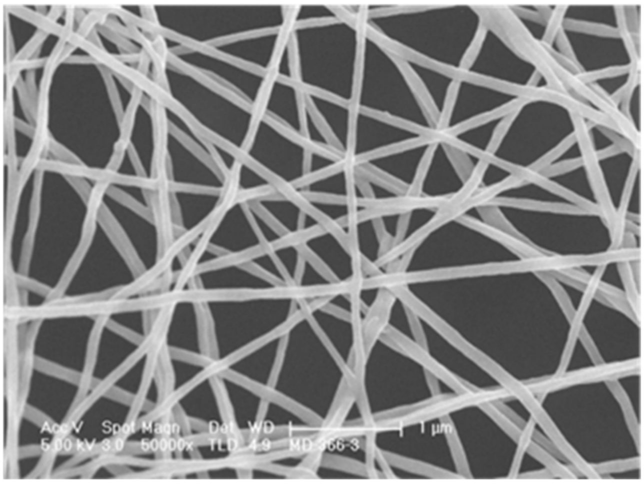

Figure 3. A scanning electron micrograph of a water-soluble electrospun fiber tissue for drug-carrying applications: the composition is based on poly (ethylene oxide) nanofibers that contain 15 wt.% propylparaben nanocapsules.

Another example that corresponds to advanced composite materials pertains to the field of biomedical engineering in which prosthetic implants are designed to imitate nature, as in our study of a filament wound composite vascular graft (Figure 4), whose structure mimics the anisotropic elastic compliance of the natural collagen/elastin artery [5–8].

Figure 4. An arterial prosthesis made of filament wound Lycra fibers in a biocompatible, biodegradable segmented copolymer matrix of polylactic acid and polyethylene oxide.

Currently, with the availability of refined techniques for the analysis of microscopic structures, the concept of biomimetics has been adopted and utilized in micron and sub-micron phenomena, e.g., adhesion (based on the adhesive system of the gecko's toe pads, as reviewed in [9]) and dewetting (based on the superhydrophobicity of lotus leaves, as reviewed in [10]). In the context of this article, a biomimetic approach was applied to invent layered nanocomposites, such as graphene paper [11], based on the hierarchical structure of nacre (Figure 5) [12].

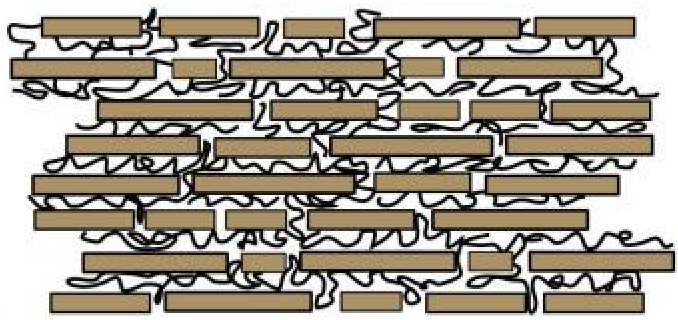

Figure 5. A scheme of the hierarchical structure of the aragonite tiles in nacre separated by interfacial layers composed of biopolymers such as chitin.

An extensive review of the field of biomimetics can be found in [13].

3. Polymeric Matrices

The appearance of modern synthetically manufactured composite materials is marked by the development of thermosetting synthetic resins reinforced by glass fibers in the mid-1930s. It was linked to the earlier invention of continuous glass fibers and glass fiber strands and by the successive invention of a suitable resin for combining the fibers with a plastic to produce a composite material. Thus, the first revolution in the field of structural composite materials occurred when peroxide-curing polyester resins were developed (Figure 6), which allowed for the fast curing of high mechanical property hard panels.

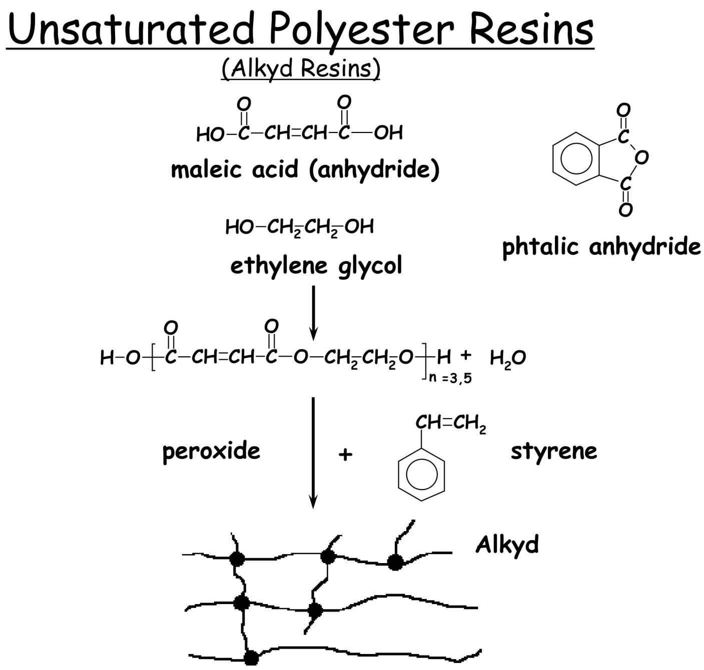

Figure 6. A scheme of the common alkyd resin utilized in Fiberglas [14].

It is interesting to note that the new science of composite materials for structural applications was triggered by the invention of high-property resins, which enabled the utilization of reinforcements such as glass fibers and asbestos whiskers—suitable for reinforcement due to their relatively high-aspect ratios—that were already available in the market. Thus, initially, the emphasis was set on developing new high-property resins, e.g., epoxy (Figure 7), with relatively high thermal stability expressed by the glass transition temperature. Only thereafter was materials science harnessed to the development of advanced fibers, whose emergence resulted in tremendous upgrading of the mechanical properties of composite materials.

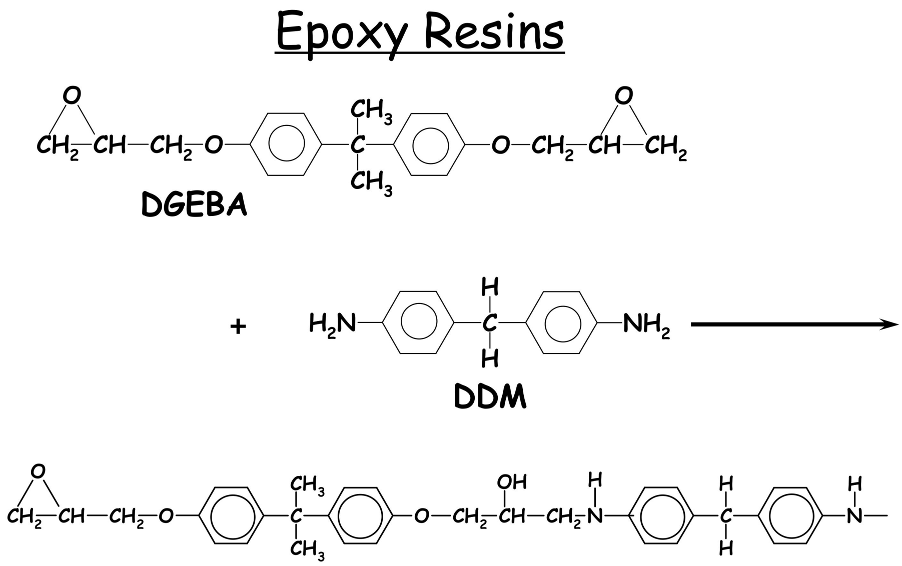

Figure 7. A scheme of the common epoxy resin based on diglycidyl ether of bisphenol A hardened by diaminodiphenylmethane [15].

4. Reinforcement Fiber

Simultaneously with the push to develop new thermosetting polymer matrices for composite materials, it has been identified that high properties combined with low weights call for the development of new fibers that exhibit highly specific mechanical properties, namely, high strength and modulus combined with low specific gravity [16]. As a result, polyacrylonitrile-based carbon and graphite fibers were invented, which exhibited specific modulus and strength of 162 and 3.0 MN*m/kg (carbon fibers) and 256 and 2.0 MN*m/kg (graphite fibers), respectively. Such fibers combined with aviation-grade epoxies, e.g., tetraglycidyl diaminodiphenylmethane and diaminodiphenylsulfone (TGDDM/DDS), have become the main structural materials for the airplane and sports goods industries.

For other applications, where high fracture toughness combined with weight saving, e.g., ballistic protection, organic fibers were invented, such as poly (p-phenylene terephthalamide) aramid and extended chain, ultrahigh molecular weight polyethylene, whose typical specific mechanical properties of modulus and strength are 80 and 1.9 MN*m/kg (Kevlar 49) and 110 and 3.5 MN*m/kg (Dyneema SK60), respectively.

It is interesting to note that with the availability of high-performance resin matrices, a retro derivative movement has recently emerged, which is imitative of the historical past in terms of the utilization of natural fibers. Obviously, its main drive is based on environmental protection considerations, such as recycling and biodegradability of agro by-products. The main natural fibers used for modern composite materials are wood, sisal, hemp, coconut, cotton, kenaf, flax, jute, abaca, banana leaf fibers, bamboo and wheat straw. The composites made with those fibers are of relatively low mechanical properties, attempting to at least match those of Fiberglas.

5. Nanocomposites

The appearance of nanocomposites revolutionized once again the young area of modern composite materials [17]. The term *nano* refers to the size range of the reinforcement, which has become highly relevant to composite materials in the last two decades mostly due to the introduction of carbon nanotubes (CNTs). Obviously, the rapid development of various nanoparticles of unique mechanical and physical properties that followed the invention of CNTs enabled the generation of a new family of composite materials classified as *nanocomposites*, where nanoparticles perform as reinforcement. Potentially, due to their extremely high properties, even a small amount of nano-dimensional reinforcements may show high improvements across the range of mechanical, optical, electrical and thermal properties [18]. These properties depend on the type of nanoparticles, their shape and area-to-volume ratio and the interfacial interactions with the matrix.

Generally, nanoreinforcements are classified according to their shape: nanoparticle, nanoplatelet and nanofiber, as shown schematically in Figure 8 [19].

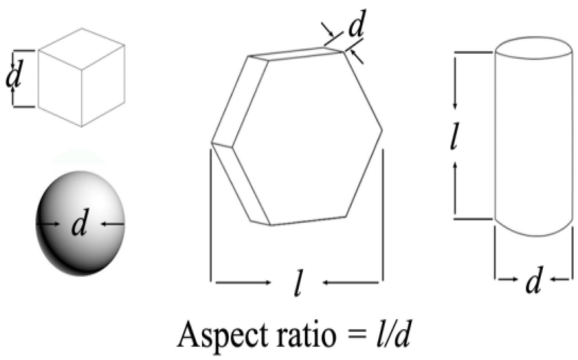

Figure 8. Classification of nanoparticles based on the number of their nano-dimensions and aspect ratio.

Of the various properties that determine the contribution of nanoparticles to the properties of the nanocomposite, their nanometric size is of utmost significance. Small changes in particle size present a significant difference in the surface area–volume ratio. Therefore, nanosized dimensions significantly increase the surface area–volume ratio of the reinforcement, which is critical since the chemical and physical interactions occur at the interfacial region between the polymer matrix and the particle. In order to provide a sufficient surface area for an interaction to obtain the desired improvement of the matrix properties, only minor quantities of nanoreinforcement are needed to generate massive surface interactions, as opposed to the addition of micro- or macro-reinforcement. Such interactions can totally modify the properties of the matrix and the micromechanics of reinforcement; hence, nanocomposites are nicknamed "interface materials", and they strongly depend on the type and nanometric size of the reinforcement.

Finally, in a recent viewpoint article entitled "A perspective on the structure and properties of nanocomposites", we took the area of nanocomposites yet another step forward, suggesting that they behave as solid solutions, and if the perception of nanocomposites as solid solutions is proven and accepted, a new science of nanocomposites can be anticipated, where the focus will be shifted from structural performance to physical properties, which draw on a wealth of material combinations with unique properties for a wide range of applications, such as electronic, optical and toughness properties [20]. Moreover, biomimetics will continue to play a significant role in the next generations of composites, particularly in nanocomposites for biomedical applications.

6. Concluding Remarks

For generations, mankind used natural material-based composites as structural materials. Then, two factors appeared almost simultaneously, resulting in a fast-forward change that revolutionized the development of new materials by introducing *advanced composite materials*. The first factor was the realization of biomimetics in the 1960s as a methodical scientific discipline of learning from nature and imitating nature's methods, designs and processes by reverse engineering of natural phenomena into manmade modern technology. The second factor was the scientific effort in the 1930s to develop new synthetic thermosetting polymers for matrices, which was followed by successive efforts to invent synthetic fiber and, later, nanoparticle reinforcements.

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