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BIOMIMETICS: NANOMECHANICAL DESIGN OF MATERIALS THROUGH BIOLOGY

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ABSTRACT

Biological hard tissues, composites of inorganic materials (such as ceramics) and organic matrices (such as proteins), have unusual engineering mechanical properties compared to those of synthetic materials with similar phase compositions. These biocomposites may serve as guides for the design of technological materials with practical applications. Biomimetics is investigation of biologically synthesized materials to obtain lessons for design of novel engineering systems. Three biological hard tissues are discussed here: (i) A sponge spicule, fibrous, glassy silica with a concentrically-layered structure that has both useful mechanical and optical properties; (ii) Nacre, "mother-of-pearl", of mollusk shells, a segmented layered structure with an excellent combination of strength and toughness; and (iii) Dentin-enamel junction that demonstrates coupling of structurally and functionally different hard tissues in mammalian teeth.

Keywords: Biomimetics, hard tissues, sponge spicule, enamel, teeth, nacre, mother-of-pearl

INTRODUCTION

Biological hard tissues (bone, teeth, spicules, shells, spines, particles) have intricate hierarchical structures and unique combination of physical properties with engineering characteristics (Lowenstam, 1981). These biological materials are composites of minerals and organic macromolecules, a combination of proteins, polysaccharides, and lipids. Normally, hard tissues are mechanical devices (skeletal units, protective armor, and anchoring devices), but they also have other physical functions, such as magnetic, optical, and piezoelectric (Simkiss & Wilbur, 1989). Mechanical properties of biocomposites are often superior to human-made materials with similar phase compositions (Wainwright *et al.*, 1976). They are often made of simple and common materials, e.g., carbonates, oxides, sulfides). Regardless of their simple material components, biological composites have multifunctional properties. For example for a given material, both strength and toughness could be better than a synthetic material with the same phase composition (e.g., calcium carbonate). Furthermore, biomaterials may not only be superior to man-made materials in terms of mechanical properties, but also in other physical

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aspects.

The superiority of biological materials as engineering systems over the synthetic ones has a basis in their structural design and control of its formation by the organism. Furthermore, over the lifetime of organisms, these materials are also monitored and self-repaired leading to durability that is much longer than that is possible in synthetic systems. Biological materials, over millions of years of evolution, were developed into hierarchical structures with intricate architectures at the nm and μm scales that often extend into macro scale resulting in unique, species-specific overall morphology with characteristic functions that provide an advantage for the organism in its environment. Components of bioinorganics can be readily found in water, air, or earth's crust. Therefore, biomaterials are synthesized by the organisms under mild conditions, i.e., in aqueous solutions at pH about 7.0, room temperature and pressure. Biosynthesis processes are environmentally friendly, energy requirements are minimal, and by-products are non-existent.

The synthesis of biological a hard tissue is controlled by an organic matrix that is mostly proteinaceous. Proteins not only act as chemical agents but also as physical ones. They collect inorganic ions into critical concentrations for synthesis, and catalyze them into specific mineral forms. They may provide substrates for nucleation of an inorganic and, as a habit modifier, control its morphology; they also provide compartments within which the inorganic crystals grow into specific sizes or shapes. In addition to being the controlling agent for biomineralization, proteins are present in the hard tissue as an integral part of the composite material. From the materials science and civil engineering points of view, all biological hard tissues are hybrid composites containing a rigid, inorganic filler (biomineral) component and a soft, organic matrix. The size, morphology, crystallography, and distribution of the inorganic filler are the features that affect the overall performance of the biocomposites in its lifelong service to the organism. The organic component is the matrix in the composite that holds the inorganic together and provides the "flexibility" by breaking up the spatial, long-range rigidity of the inorganic. Therefore, similar to the inorganic component, the biopolymer is also an integral component of the hard tissue, thereby, providing mechanical integrity the composite.

Investigation of biomaterial formation and structure-property correlation provides lessons for novel material fabrication through biology (Sarikaya, 1999). Many aspects of materials and systems formation in biological organisms are not fully known, and the details are often missing (Sarikaya & Aksay, 1996). Without a biosynthesis knowledge, it is still worthwhile to learn what a biological hard tissue is composed of including physical and chemical characteristics in its various structural components. Coupled with their behavior under various applied stresses, it may be possible to develop a quantitative knowledge about their structure-function relationships. These are some relationships that are potentially useful in biomimetic design of future, advanced materials and systems with specific applications areas. In this study, we discuss structure and mechanical properties of three hard tissues (a sponge spicule, nacre of a gastropod, and dentin-enamel junction of mammalian tooth) and offer, in each example, biomimetic design criteria.

SPONGE SPICULE: A BIOMIMETIC OPTICAL FIBER

The transmission of light through glass fiber typically brings the mind applications in the telecommunications industry (Blyler & DiMarcello, 1987). Glass is usually considered to be fragile based on our experiences with broken windows, glass cups and bottles. In fact, the use of glass fiber in technological applications is only possible with polymeric coating that significantly improves the mechanical durability of fibers by sealing the surface cracks and by providing a barrier to water and other contaminants. As we demonstrate, even more impressive are mechanical properties of a sponge spicule (Simpson, 1984), a hydrated siliceous glass, used as a wave-guide that is biosynthesized under seemingly rudimentary synthesis conditions from seawater. The demosponge species used in this work, *Rosella racovitzea* (Rosella) lives 120 m under water in Ross Sea near Antarctica (Sarikaya *et al*, 2001). The Rosella's pentactinal spicules are 10 cm long, have a diameter 200-600 µm, and a cross-shaped apexes (a lens) that collect light from all directions. The presence of a filamentous green algae inside the sponge, adapted to dim light conditions, suggests that light may reach the inside of the sponge body via these siliceous spicules acting as optical wave-guides. In this scenario, sponge/algae form a symbiotic system where the spicules are optical lenses and fibers, gathering and transferring the dim light present at these depths to the algae, which provide the nutrients to the sponge (Sarikaya *et al*., 2001).

We measured optical properties of the Rosella spicule and found that the index of refraction, constant throughout the thickness, is similar to that of commercial silica fiber. We established structure-property relations of sponge spicules and compared them with those of synthetic glass optical fibers to assess durability and mechanical integrity. The microstructure of the spicules were studied by examining the fractured surfaces of the samples using an SEM (Fig. 1(a) and (b)). Instead of a fairly smooth fracture surface that would be expected to appear from a solid bar (as it could be seen in a silica bar studied in this work), all the fractured spicules displayed a rough surface with a layered structure (layer thickness of 2–15 µm) across the diameter surrounding a proteinaceous central filament. The total number of layers varies 50 to 200 for the spicules studied. The layered nature of the structure clearly plays a role in the mechanical properties of the spicule. A relatively weak interface (interlayer) deflects the crack, stopping the crack from propagating directly in to the next layer during fracture.

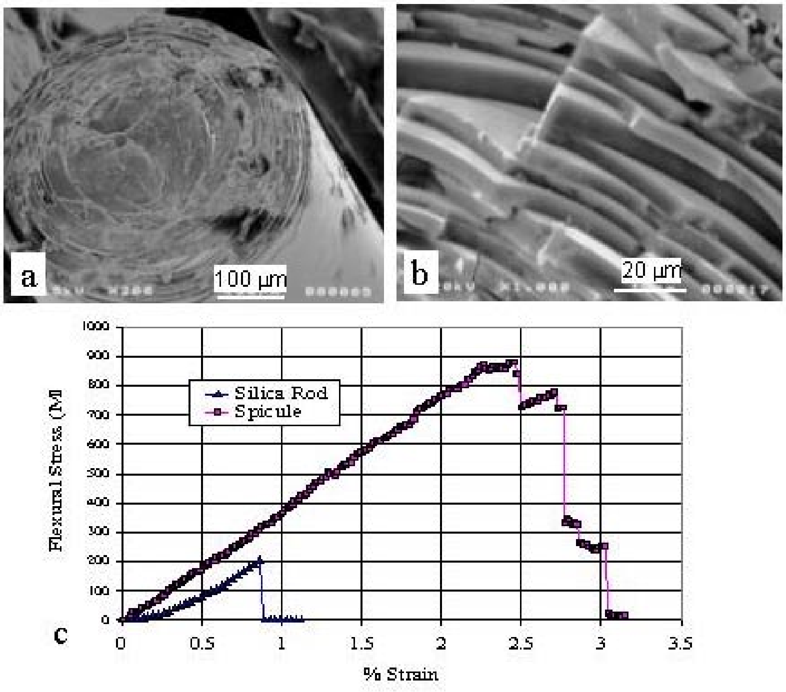

Figure 1 – (a) and (b) are SEM images of a fractured surface of sponge spicule showing concentric layering. (c) Three-point bend test profiles of silica rod and sponge spicule.

Bulk mechanical properties of sponge spicules were determined using three-point bend tests (Fig. 1(c)). The results of these tests (Table-I) indicated that fracture strength, strain-to-failure, and fracture energy are several times greater than those for silica glass rods with similar diameter. The bulk tests also revealed that, under bending stress, the sponge spicule undergoes "soft-failure," unlike glass rods that fail catastrophically and at significantly lower stresses. The bulk mechanical properties and soft failure of these spicules could partially be explained based on their layered structure revealed in this work.

For more detailed understanding of the mechanical properties, nanoindentation tests were carried out on the individual layers of the throughout the diameter of the spicules. Indentation and atomic force microscopy (AFM) imaging were performed with a Hysitron Picoindentor® (a nano-mechanical testing apparatus) attached to a Park CP® scanning probe microscope (SPM) using a Berkovich diamond tip. Both elastic modulus (E) and hardness (H) of the spicules (Table-I), obtained via standard nanoindentation procedures (Oliver & Pharr, 1992), are half those of commercial glass rods. These values were fairly constant across the diameter, regardless of the layered nature of the spicules. The uniformity in nanomechanical properties is consistent with the uniformity of the optical properties across the diameter and suggests that sponge spicules are not graded index fibers.

Table-I: Mechanical properties of the siliceous materials.

Material	**Nanohardness** H (GPa)	Elastic Modulus[4] E (GPa)	Fracture Strength[5] σ_F (MPa)	Fracture Toughness[6] (MPa-$m^{1/2}$)	Fracture Strain[7] (%)
Optical fiber[1]	7.80±0.80[8]	63.16±3.28[8]	-	-	-
Fused silica	7.50±0.50[8]	70.00±2.00[8]	-	-	-
Silica rod[2]	-	-	200±15[9]	0.78 ± 0.05[10]	1.0±0.1
Spicule[3]	3.22±0.33[8]	38.05±2.90[8]	880±15[9]	2.26-5.60 ±0.10	3.5±0.1

Notes: 1. From Corning Inc.; 2. From General Electric Co.; 3. Rosella; 4. Young's modulus; 5. 3-point bend test; 6. Calculated from Griffith's formula [8]; 7. From 3-point bend test; 8. Nanoindentation; 9. 3-point-bend test; 10. From Sarikaya *et al.* (2001).

Concluding Remarks and Future Prospects:

The structure-property correlations offer possible design guidelines for potential novel, damage tolerant optical fibers via biomimetics. Despite physical layering, the refractive index is constant throughout thickness; therefore, irrespective of optical properties, layering should be an important design feature that significantly increases the mechanical performance of the fiber. For a more robust design of glass fibers for multifunctional engineering applications, further studies are necessary, including micromechanics of layering, nature of the hydrated spicular silica compared to synthetic optical fibers, and formation mechanism of the spicule.

NACRE: MOTHER-OF-PEARL OF MOLLUSK SHELLS

The nacre, mother-of-pearl, is found in the shells of many families of mollusks, e.g., gastropods, cephalopod, and bivalves (Currey, 1987). In red abalone (*Haliotis rufescens*, a gastropod), nacre is composed of 300±100 nms thick, hexagonally-shaped aragonitic (orthorhombic; $CaCO_3$) platelets that are surrounded by a thin film (10±5 nms) organic matrix that are successively stacked to form a layered nanocomposite. The platelets are closed-packed at a given layer, but they are staggered through the thickness forming a brick-mortar structure (Fig. 2(a)). Nacre offers a biomimetic model for design of segmented, layered synthetic materials for practical applications (Sarikaya & Aksay, 1992).

The standard tests performed on nacre included four-point and three-point bend tests, respectively, to obtain fracture toughness ($K_{IC}=10\pm4$ MPa-m$^{1/2}$) and specific strength ($\sigma_F=200\pm40$ MPa/(g-cm^3)). The combination of these mechanical properties are better than those of high technology ceramic materials fabricated by using the standard bulk techniques and are comparable to ceramic-matrix (e.g., ZrO_2-Al_2O_3) and metal-matrix (WC-Co) composites. Toughening effects of the layered structure of nacre is evident from highly tortuous fracture surface with exposed aragonite platelets. However, the extraordinary increase in toughness, in conjunction with increase in strength, cannot be explained with the energy dissipation mechanism associated with creation of new surface due to high tortuosity alone (Katti *et al.*, 2001).

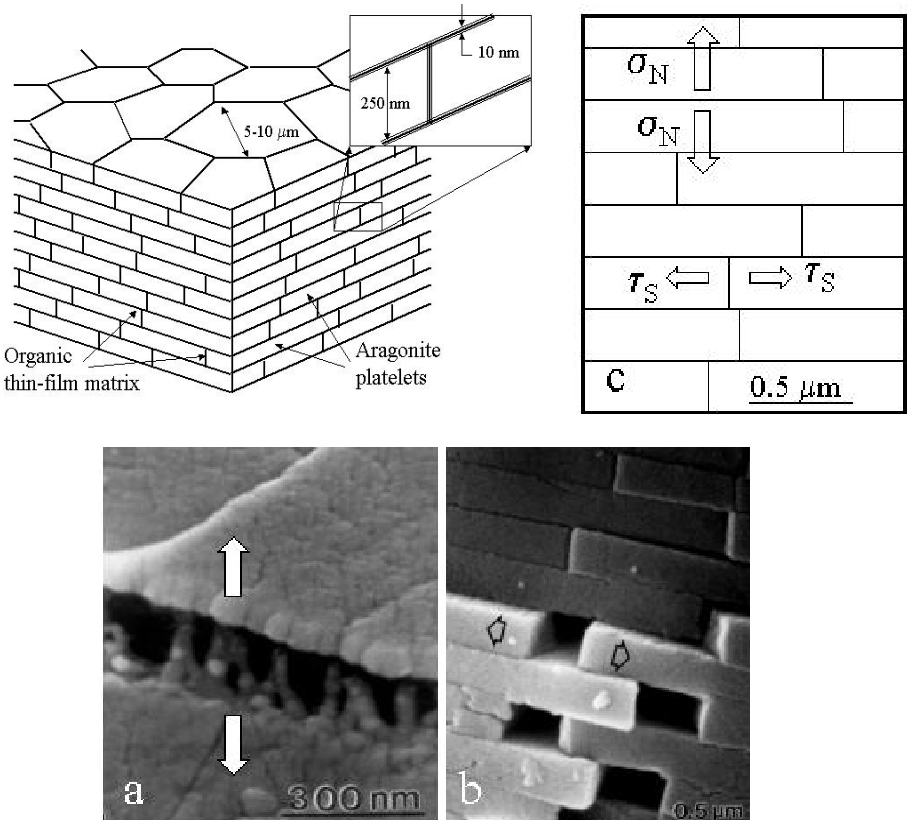

Fig. 2 – Schematic illustration of nacre (inset). (a) and (b) SEM images demonstrating deformation behavior of nacre under static loading, representing normal and shear resolved stresses, respectively (shown in (c)).

The segmented nature of nacre has consequences in its orientational behavior under stress. As illustrated in Fig. 2, when the resolved stresses are normal to the platelet plane, the organic matrix bridges between the platelets, keeping them together and preventing uncontrolled crack growth. On the other hand, if the resolved stresses are shear, then the platelets slide successively over the organic matrix. Conformation of the organic matrix with applied stress may be an important feature of the organic matrix (a strong binder). The bridging behavior implies strong interfaces of the organic matrix and inorganic platelets, and that a component of the protein can form ligaments which itself implies superplastic deformation (Jackson *et al*., 1988).

Concluding Remarks and Prospects:

Foregoing discussions suggest that layered materials could be further toughened and strengthened for use in practical applications by using the segmented design encountered in nacre. The dimensional features, edge size and the thickness of the rigid phase in the form of thin bricks and the thickness and (nano)composite aspects of the soft organic phase, are also critical factors. Furthermore, the soft phase has to be chosen to be multifunctional, which probably derives this property from its nanocomposite nature. Finally, interfaces between the soft and the hard phase are both physically and chemically stable so that they are strong to accommodate large stresses.

DENTIN-ENAMEL JUNCTION: MECHANICAL COUPLING DENTAL TISSUES

Mammalian tooth is an intricately structured and functionally gradient composite material containing both enamel (on the outside) and dentin (on the inside) that are coupled through an interface region called dentin-enamel junction. Tooth is an engineering tool performing daily functions of mastication. Because of the various sets of stresses involved in the process of chewing, tooth, necessarily, is a complex material both structurally and mechanically. Enamel is the most mineralized biological tissue in the human body, which at the nanometer scale, is composed of long, hydroxyapatite (HAP) crystallites (~50 nm in diameter) packed as bundles in enamel rods (Moss-Salentijin & Hendricks-Klyvert, 1990). The enamel rods (5 µm diameter) are organized unidirectionally normal to the surface of the tooth (µm hierarchy). This results in a hard, wear resistant tissue that is highly packed with HAP crystals (98% by vol.). Dentin is primarily composed of mineralized collagen fibrils (nm hierarchy) that form a randomly intertwined, continuous network (µm hierarchy) making it a soft but highly fracture resistant tissue. Combining enamel and dentin, a functionally gradient composite material emerges as a cutting and grinding tool that is both hard and tough. A study of structure and detailed mechanical properties is necessary for establishing the structure-function relation of the dentin-enamel junction (DEJ) in mammalian teeth as it plays a critical role in transferring stress from hard enamel to soft dentin efficiently in order to preserve the longevity of tooth. An understanding of this relation would also provide a basis for enamel regeneration, designing new crowns for enamel or dentin, and would furnish biomimetic lessons for coupling hard and soft materials for a wide variety of engineering applications.

The teeth used in this study were adult human incisors, cut approximately through the center along the axial direction exposing the axial planes of enamel, dentin, and pulp (Fig. 2 inset). The nanoindentation system described above allowed precise positioning of indentation locations as well as imaging the areas of interest before and after indentation. The values of hardness (H) and elastic modulus (E) were determined following the procedures of Oliver and Pharr (1992).

A detailed analysis of the interface region between dentin and enamel was carried out using both SEM and AFM imaging (Fong *et al*., 2000). The enamel rods and dentin tubules in the XZ plane and their cross sections in the XY plane are simultaneously shown in Fig. 3(a), where the ripple-like morphology at the DEJ with an average period of ~30 μm is revealed. This image clearly shows that the DEJ in human tooth is not a planar joint of dentin and enamel but has two distinct interpenetrating regions at this junction. Furthermore, a higher resolution AFM imaged DEJ shown in Fig. 3 reveals an even smaller scale corrugation, on the order of a few micrometers. Therefore, it appears that the interfacial region may be fractal in nature suggesting that interpenetration between enamel and dentin takes place at many dimensional scales.

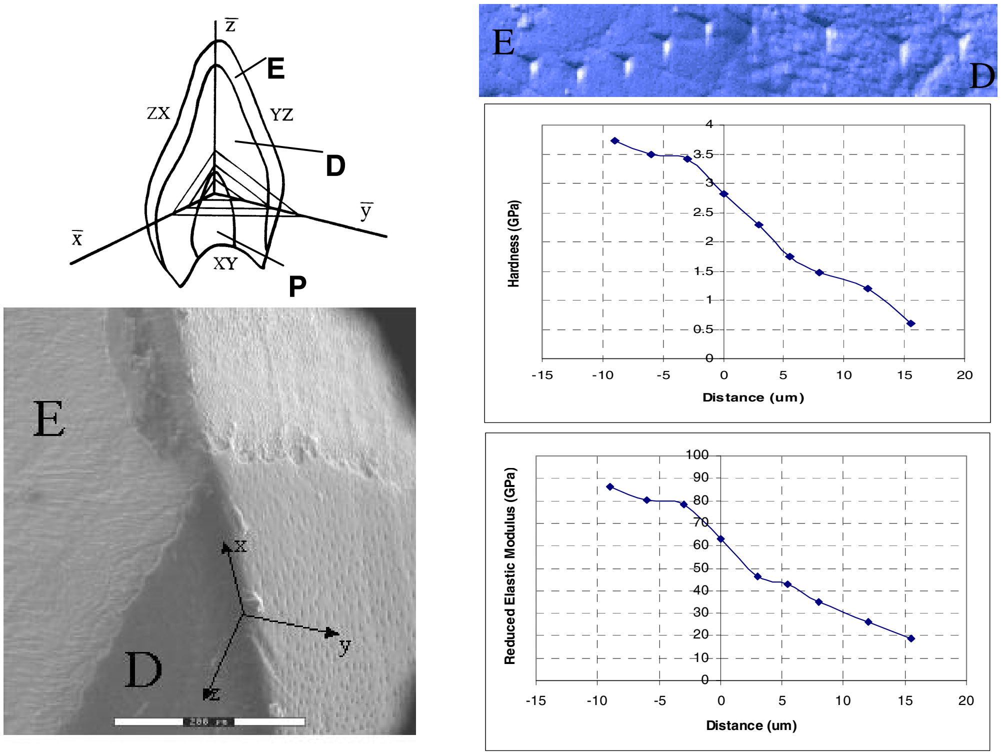

Figure 3 (a) Schematic cross section of human incisor tooth. (b) SEM image reveals two perpendicular surfaces of the sample at the DEJ region (bar: 200 μm). (c) and (d) Nanomechanical profiles across DEJ of a human incisor tooth: Nanohardness (GPa) and elastic modulus, (GPa), respectively. The inset (above) is an AFM image of the indents across the DEJ.

Nanoindentation measurements were made initially within enamel and dentin away from the interface. Indentation (contact depth) was kept to ~100 nm by adjusting the load. At this depth, the side of the triangular footprint was ~ 1 μm. From the measurements, the average hardness (H) and elastic modulus (E) of enamel were 4.46±0.26 GPa and 94.4±4.6 GPa, respectively. There was no trend established in the profiles from the surface of the tooth to ~20 μm from the DEJ. For dentin, the average values of H and E were 0.76±0.04 GPa and 23.6±1.2 GPa, respectively. In dentin, all indentations were made in the intertubular region (by avoiding the peritubular areas) and no significant change from these values was observed from 20 μm away from the DEJ to 50 μm away from the pulp. Nanoindentation profiles across the DEJ were taken within a 50 μm-width on either side of the DEJ zone as significant differences were only observed within this strip of interface region. As shown in Fig. 3, the determined H and E profiles reveal a gradual decrease in these properties from the enamel to dentin regions.

The corrugated structural characteristics of the interface along with the gradual change in mechanical properties are of significant consequence on the durability of the tooth in order to sustain minor damage in the enamel through microcrack formation and propagation. Throughout the lifetime of a tooth, creation of microcracks in the enamel as a result of everyday mastication is highly probable. For human incisors, since enamel rods are oriented normal both to the tooth surface and the DEJ, cracks (most likely generated between rods) would generally be directed toward the DEJ. At this point, it can deflect along the interface, terminate at the interface, or penetrate into the dentin and terminate immediately. Deflecting cracks along the interface can be detrimental as it can cause delamination of enamel from the underlying dentin, thereby mechanically decoupling the two regions. Both microindentation as well as nanoindentation results indicate that crack generation in the enamel tend to terminate near the DEJ. Mechanistically, cracks most likely penetrate into the dentin tissue and terminate immediately due to blunting of the crack by local plastic deformation at the crack tip, or internal pores present in the dentin. There are two features that favor a crack to propagate into dentin. These may be explained by considering the effect of orientation of the interface with respect to that of the crack. A crack is more likely to penetrate if the interface is normal to the crack. As the angle between the crack and the interface plane decreases, the probability of the crack deflection increases. By having a rippled, or saw-tooth shaped geometry along the interface (Fig. 2), a crack penetration is favored at the DEJ. This is because, regardless of the angle between the approaching crack and the interface, the crack will eventually find a normal orientation to the interface, upon which, penetration will be favored. In addition, crack penetration is also favored if the reduced elastic moduli between the two materials of concern are closely matched. In the case of the DEJ zone, this condition is satisfied by the presence of the gradual change of reduced elastic modulus over a width of 15 to 25 μm.

CONCLUDING REMARKS

Potentially useful structure-function relationships were discussed for biomimetic design of materials. These relationships may be applicable for materials at the size scale investigated and, for larger materials used for more practical engineering applications, the size effect may have to be taken into account. New design criteria, including the size effects, may be achieved either by physically constructing structures and experimentally testing them or by using advanced theoretical modeling, such as finite element analysis.

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