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A comprehensive review of selected biological armor systems – from structure-function to bio-mimetic techniques

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Abstract

This paper explores several lamellar structures found in nature, which have been shown to possess superior armor systems. In particular, the hard armor systems of nacre and conch shells, and the flexible armor system of fish scales are the focus of this review due to their high relevance to the protective structural engineering discipline. The structure-function relationships that govern the superior mechanical performance of these systems are attributed to their well-organized composite hierarchical structures. The paper also reviews advancements in additive manufacturing techniques for proof-of-concept prototyping, as well as advanced modeling techniques that have been employed to capture the complex geometries of biological structures and the interactions between their constituents. Finite element modeling and 3D printing were found to be the most popular techniques, as they automate the process of modeling and manufacturing complex bio-mimetic composites from a computer-aided design. Finally, attempts to apply bio-mimicry to the structural engineering discipline have been identified, which remains a new and exciting area of research.

Keywords: nacre, conch, fish scale, armor, structure, protective, finite element, 3D printing, additive manufacturing, prototyping.

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1. Introduction

Biological structures have received significant attention from engineering researchers over the past few decades due to their unique structural configurations [1-14]. They offer superior mechanical performance [15-19], lightweight and durability to maximize mobility [20, 21] and survival under harsh environmental conditions. Only recently has the attention of the bio-mimetic discipline been linked to protective structural engineering, a significant area where extreme loadings including blast, impact, earthquake, windborne debris and fire are claiming lives and causing severe damage to infrastructure worldwide [2, 3, 6, 22-35]. Many efforts have been dedicated to the development of novel structures and materials, such as negative Poisson's ratio (NPR) structures to counteract localized blast loads [36-42], innovative polymers for improved energy absorption under impact [43-47], nanoclay additives for enhancing fire resistance [48, 49], lightweight concrete and nanosilica cement paste for improved durability and thermal efficiency [50-52], and so on. However, these structures and materials tend to suffer from performance issues, which include localized buckling of NPR cellular structures under high strain rates, which diminishes their energy absorbing capacity; high combustibility of composites under fire; and reduced strength in lightweight concrete due to the lack of control over its porosity distribution. Learning from the well-organized hierarchical structures found in nature can significantly enhance the performance and resilience of structures to extreme loads, thereby saving lives and reducing damage to infrastructure.

1.1 Modern reviews on biological structures and materials

There is a wealth of information and modern reviews on many biological structures from various perspectives, which can be generally categorized into structural- and materials-based investigations. These focus on: keratinous bio-materials [53]; fibrous, helical, gradient, layered, tubular, cellular, suture and overlapping structures [10]; biopolymer, interfacial, shell and foam materials [54]; structural and functional biological materials [55]; ceramics/ceramic composite, polymer and polymer composite, elastomers, and cellular materials [56]. These types of structures and materials are summarized in Table 1 with examples provided for each type. Other reviewers have focused on specific high-performance biological structures and materials due to the amplification in fracture toughness and energy absorption over their individual constituents, as well as their attractive structural features for mimicry. Examples of these reviews include: nacre, bone and wood [57]; bone, nacre, shrimp dactyl club, teeth and

bamboo [58]; shell, crab exoskeleton, avian feather and beak, and antler and bone [59]; abalone shell, river clam, arthropod exoskeletons, tusks and teeth, toucan and hornbill beaks [60]; spruce wood, bone and glass sponge [61]; and sponge spicules, nacreous shells, conch (Strombus) shells, toucan and hornbill beaks, and crab exoskeleton [62]. It is important to note that although these reviews characterize biological structures into a particular structural group, their unique configurations at different multi-scale hierarchical levels can fall into several categories. In terms of their high relevance to protective structural engineering applications and their well-defined structural features, lamellar structures form the focus of this review. Many of these types of structures, in particular, shell structures such as nacre and conch, have been shown to exhibit excellent damage tolerance due to their well-organized structure at different length scales, regardless of their mainly brittle composition. These impressive features make lamellar structures ideal as lightweight multi-functional armor systems.

Table 1: Recent reviews on biological structures and their characterization into structural and material groups.

Review	Structural/Material Groups	Examples of biological Structures
Wang et al. [53] on keratinous bio-materials	α -keratin	Wool and hair, quills, horns, hooves
	β -keratin	Feathers, beaks, claws
	α - and β -keratin	Reptilian epidermis, hard and soft epidermis of Testudines, pangolin scales
Naleway et al. [10] on different biological structural groups	Fibrous: Structures with numerous aligned fibers	Non-mineralized: Muscle, tendon, silks Mineralized: Chitin fibers in arthropod exoskeletons, collagen fibers in bones
	Helical: Numerous fibers, fibrils at various angles	Crustacean exoskeletons, dactyl club, fish scales
	Gradient	Human teeth, squid beak, fish scales
	Layered	Nacre from abalone shell, fish scales
	Tubular	Horse hooves, ram horns
	Cellular	Trabecular bone, porcupine quills
	Suture	Carapace of turtles, mammalian skulls
	Overlapping	Seahorse tails, shark skin, alligator gar
Meyers et al.	Biopolymer, interfacial, shell	Abalone shell, lobster, deer antler, deep-

[54]	and foam materials	sea sponge
Meyers et al. [55]	Structural and functional biological materials	Abalone shell, toucan beaks, gecko feet, tree frog
Meyers et al. [56]	Ceramics, polymers and cellular materials	Nacreous shells, conch shells, bone, ligaments, toucan beaks and so on

Based on their geometric arrangements, lamellar structures (Figure 1) can be classified into several groups as follows:

- Staggered masonry-like (Figure 1a): Several thin layers of tablets that are stacked into a bricks and mortar-like arrangement, and bonded by a soft organic ductile matrix e.g. the polygonal tablet layers in nacre from abalone shells.
- Cross-lamellar planks (Figure 1b): Several nano-sized wood-like planks stacked together at approximately 45° and bonded by a thin organic matrix e.g. the tough protective middle layer of conch shells.
- Orthogonal plywood-like (Figure 1c): Thin laminates with fibers oriented in perpendicular directions e.g. the interior collagen layers of fish scales.

Figure 1: Schematics of different biological lamellar structures: (a) Staggered polygonal masonry-like (nacre); (b) Cross-lamellar planks (conch); and (c) Orthogonal plywood-like (fish scales).

1.2 Structure of this review paper

This paper provides an overview of selected lamellar structures, namely nacre from mollusk shells, conch shells and fish scales. Their structural features are correlated to their mechanical

function, which can be exploited in the context of protective structural engineering applications. Section 2 discusses the structure-function relationships of these types of biological systems, which are extracted from the mechanical characterization efforts of researchers in the field. Section 3 reviews the different techniques employed to manufacture bio-inspired structures at the macro level and the micro/nano-scales. Section 4 reviews the multi-scale modeling strategies employed to understand the mechanical behavior of novel biological systems. Section 5 reviews the attempts of bio-mimicry for structural applications. Section 6 provides concluding remarks and future recommendations.

2. Structure-function relationships of biological lamellar structures

2.1 Nacre from mollusk shells (*Haliotis Rufescens*)

Mollusks, which appeared millions of years ago and exist in many thousands of species, have been found to exhibit remarkable strength and toughness [63-65]. We focus our attention on bivalves, gastropods, and cephalopods [63] as they exhibit structural characteristics that are most relevant for inspiring the design of protective structural systems. Briefly, bivalves are marine mollusks with a hinged shell that encloses its compressed body e.g. oysters, scallops, mussels and so on. Gastropods include snails and slugs of all kinds and sizes (microscopic to large) e.g. edible sea snails such as abalone seashells (Figure 2a), land snails, and so on, which can live on land or in water. Cephalopods are marine animals that are bilaterally symmetric (or mirrored about the sagittal plane) with a head and a set of arms or tentacles e.g. squid, octopus and so on.

Mollusk shells comprise a two-layer armor system (Figure 2b): a shell consisting of a hard brittle outer calcite layer and a tough nacreous layer at its inner surface [11, 66]. These layers work together to protect the soft body of the mollusk from external loads that may arise, for example, from predator attacks and collisions with rocks transferred by the ocean current. Specifically, the outer layer of the shell is made of large calcite (a calcium carbonate mineral with high hardness, CaCO_3) grains, making it highly strong for preventing the shell from being breached or penetrated. Over many years of evolution, the mollusk has evolved a tough inner nacreous layer to optimize its defense mechanisms, which can dissipate a significant amount of energy in the event that the outer shell is breached i.e. before the energy is imparted to the soft body of the animal.

It is now well-established that many mollusk shells from the bivalve and gastropod species have evolved a protective composite structure at the interior surface of the shell, namely nacre, which is also known as the mother of pearl [63, 67]. The nacreous layer, although relatively similar in structure among bivalves, gastropods, and cephalopods, exhibits varying microstructural arrangements among the different species, which will be explored below.

Figure 2: (a) Red abalone seashell; (b) The protective armor system; (c) The bricks and mortar microstructure; (d) A polygonal layer with cohesive bonds indicated between adjacent tablets; (e) Staggered overlapping multi-layer arrangement [68].

Nacre has attracted much attention over the past ten years because of the toughness and strength improvements over its constituents are profound [56]. However, the mechanisms by which nacre achieves simultaneously high strength and toughness are only partially understood, and these form the key focus of this review due to their relevance to protective structural engineering. Some of these mechanisms have been observed under limited modes of loading over several length scales, e.g. planar tension, compression and shear [64, 69, 70]. We first turn our attention to nacre's hierarchical structure and composition and relate these observations to its toughening mechanisms.

Nacre exhibits a hierarchical structure, which has been observed over several length scales (from macro to nano) [61, 71, 72]. We have seen earlier that the outer shell consists of a two-layer armor system (Figure 2b) comprised of a brittle outer calcite layer and a tough inner nacreous layer at the macro-scale. At the meso-scale, organic bands, which are approximately 8 μm thick, have been observed. These are referred to as growth lines, which separate larger 300 μm thick layers of nacre [56]. Some researchers have reported that these growth lines

indicate pauses in the growth process due to sporadic interruptions in the animal's diet [73] but are also believed improve the fracture toughness of the structure by deflecting cracks [74].

At the micro-scale, we focus our attention on one layer of nacre, which is 300 μm thick as previously mentioned. At the most elementary level, many researchers have correlated nacre's microstructure to a brick wall [75-79]. Generally, nacre's microstructure can be grouped into two arrangements, namely columnar and sheet [63]. Columnar nacre consists of stacks (columns) of tablets, which are staggered from one layer to the next but arranged in an ordered fashion [80, 81]. Hence, like a bricks and mortar structure, an overlap area can be defined between the bricks in such an arrangement. Sheet nacre, on the other hand, consists of tablets arranged randomly between adjacent layers [63, 82]. The platelets (tablets or bricks), which are composed of aragonite (a brittle mineral and a form of calcium carbonate, CaCO_3) are 0.5 μm thick polygons, which are stacked on top of one another to form several layers of nacre's microstructure [83-86]. For example, nacre in a red abalone shell has a columnar type arrangement with a defined overlap length of 1.6 μm between adjacent layers (Figure 2c). Typically, protein inclusions are embedded into the aragonite tablets as a result of the biomineralization process (the process by which the mollusk transforms its organic matter into the mineral matter, aragonite in this case), which basically makes the tablets sensitive to flaws [87, 88]. The aragonite tablets are mineralized by the animal through complex processes [89] and constitute 95% of nacre's volume [90-92].

At the nano-scale, several distinct features have been observed. Using atomic force microscopy, the aragonite tablets were found to be composed of nanograins with a consistent crystallographic texture [82, 93]. Li et al. [94] claimed that the nanograins in the tablets were ductile but this nanostructure appeared to have minimal impact on large-scale material properties of nacre. For instance, the elastic properties of the tablets were found to be similar to single-crystal aragonite, despite the existence of nanograins and inclusions (organic molecules) [95]. All nacles, whether columnar or sheet, comprise of an organic matrix, which is 20-30 nm thick and accounts for 5% of the volume of nacre [90]. This highly ductile matrix acts as glue, which bonds the tablets together. In an attempt to identify the composition of the matrix, the Fourier transform infrared spectroscopy (FTIR) was performed, which is a technique where the absorption or emission spectra of the material in response to infrared

(IR) radiation is analyzed to identify its chemical components [96]. These studies found that the organic matrix is mainly comprised of proteins, chitin (a silk-like protein) and polysaccharides (complex carbohydrate polymers) [97, 98]. The function of the soft organic layer is to maintain the cohesion of the tablets over large deformations, whilst promoting ductility [91, 99, 100].

Recalling that the hierarchical structure of nacre consists of tablets, which are irregularly shaped polygons, several researchers have correlated the tablet shapes to a Voronoi diagram [71, 82, 97]. The surface roughness of the tablets is facilitated by nano-asperities, which were observed using atomic force microscopy (AFM) [101-103]. The height of the nano-asperities varies from 10 to 30 nm while their average spacing is of the order of 100 to 200 nm [95]. The average tablet length is approximately 8 μm and approximately one-third of the area of each tablet overlaps its neighbor between adjacent layers, in the columnar arrangement found in a red abalone shell [69, 70, 104]. The tablet interface is wavy with an average amplitude of 100 nm and a wavelength of 5 μm [92]. Furthermore, reinforcing mineral bridges connecting the tablets between adjacent layers were observed using a transmission electron microscope (TEM) [89, 105, 106]. The bridges appeared roughly circular and measured 46 nm in diameter, with a height of 26 nm (equal to the thickness of the organic matrix). The structural features discussed above are summarized below in Table 2 along with their function. Furthermore, ductile ligaments have been found between the tablets by observing their spacing upon stretching [107] (from 25 to 600 nm in their unstretched and stretched state, respectively). Efforts by researchers to link these key structural features to their mechanical function are explored hereafter.

The structure-function relationships of the key features of nacre have been established through rigorous mechanical testing: tension [63, 92, 99, 107]; compression [64, 73]; bending [63, 91, 99]; shear [73, 92]; and indentation [90, 95]. Tension is believed to be the most common type of loading that nacre's staggered structure is built for. Although there are many efforts in the literature to establish the structure-function relationships of nacre, several examples to extract the important features/mechanisms under various types of loading are explored in adequate detail hereafter.

Tension: Currey [63] was one of the first researchers to perform tension tests on three classes of nacre (bivalves, gastropods, and cephalopods) and found that nacre has a tensile strength in

the range of 35 to 115 MPa. The maximum tensile strain observed was 0.018, which indicates that the plastic deformation was not excessive. In the load-deformation curve, they observed a linear elastic region followed by a region of plastic deformation with a hardening phase. Hence, regardless of the well-organized geometry of the columnar samples, noticeable variations in the tensile strength exist between the bivalve and cephalopod species. The large scatter in tensile strength observed may be attributed to the intragranular fracture in the nacre tablets, which are sensitive to flaws, as opposed to the fracture or delamination that occurs between the grains and in the matrix. Regardless, columnar nacre specimens showed a lower scatter in tensile strength than the sheet nacre samples, as the latter has a random tablet arrangement.

Furthermore, Smith et al. [107] performed a novel study to evaluate the mechanical properties of the nacre matrix on a molecular level. They found adhesive ligaments between the tablets by observing the scanning and transmission electron micrographs of a cleaved red abalone specimen. Upon loading, the space between the tablets increases from 25 nm to approximately 600 nm, which indicates that the ligaments can undergo significant stretching and maintain the integrity of the matrix over large deformations. The force-extension curve was presented for several types of stretched molecules (the lustrin A protein was isolated). The shorter molecules correspond to typical adhesives between two surfaces, which exhibit high strength with little toughness. Once the strong bonds (covalent or ionic) between the two surfaces are broken, the integrity of the adhesive is lost. The longer molecules, on the other hand, can undergo significant stretching but the area under the force-extension curve is still relatively small. This is because their length facilitates stretching over larger distances until the bond between the molecule and the adhering surfaces fails. However, the folded molecules in nacre have several modules (loops), such that intermediate strength sacrificial bonds (stronger than van der Waals but weaker than covalent) exist in the folded domains. Once the molecule is stretched, these bonds take some energy to break them, thereby unfolding the molecule and exposing a hidden length. This process of breakage of intermediate bonds continues, thereby exhibiting a sawtooth pattern in the force-extension curve. Finally, the strong bond between the adhered surfaces breaks when a failure occurs. Thus, there is a remarkable increase in toughness compared to the longer molecule without modules. Given that the nacre matrix is made from layers of proteins and polysaccharides with many molecules present, its characterization is relatively difficult, and it is practical to mimic the aforementioned mechanism through simpler means.

Jackson et al. [99] tested several specimens of dry and wet *Pinctada* nacre in tension to establish the effects of hydration on the mechanical response. A Young's modulus of 70 GPa was obtained for the dry samples and 60 GPa for the wet samples. Tensile strengths of 167 ± 22 MPa and 130 ± 24 MPa were also obtained for dry and wet nacre, respectively. These values are significantly higher than the maximum obtained by Currey [63], which indicates that different species of nacre were used in both experiments. As per the above study by Smith et al. [107], the cyclic fracture of bonds and exposure of hidden lengths can cause this behavior.

Tang et al. [92] investigated the behavior of a red abalone specimen under quasi-static tension and shear to establish the key features that are responsible for nacre's remarkable toughness. Firstly, a dog-bone shaped specimen was tested in tension in its dry and hydrated states, and its stress-strain response was compared to that of bulk aragonite (the main constituent of nacre). Hydrated nacre initially exhibits a linear elastic response followed by a hardening phase until a failure strain of approximately 1% is reached. In its dry state, nacre behaves in a brittle manner, similarly to its bulk constituent, aragonite. The mechanism that was attributed to nacre's superior toughness over aragonite was sliding between the tablets followed by a hardening effect induced by the wavy interface between the adjacent tablet layers, which was reported to impede the sliding mechanism via interlocking. The nano-asperities on the tablet surface were stated to have no contact beyond a sliding distance larger than 10 - 30 nm, which was ten times less than the observed sliding distance (100 - 300 nm). In other words, the nano-asperities cannot sustain contact over large sliding distances. A similar observation was made for the mineral bridges, which are also relatively small in size i.e. they have a thickness of 26 nm, which is of the order of the matrix thickness. Hence, the hardening mechanism was observed to occur at the micro-scale since the tablet interfacial waviness is 100 nm in amplitude and 6 μ m in wavelength. However, a similar number of tablets were seen to have flat tablet interfaces compared to those with a wavy interface. The Young's modulus and strength of hydrated nacre obtained from this test were $E = 70$ GPa and $\sigma = 70$ MPa, respectively, while the failure strain was 0.8%.

Compression: An et al. [64] investigated the microstructure and toughening mechanisms of red abalone nacre under compression in both the parallel and perpendicular directions to the tablet surface. They reported compressive strengths of 420 MPa and 500 MPa for the parallel

loading case (a) and the perpendicular loading case (b), respectively. The load-deflection curve for case (a) showed several cycles of loading and unloading. This may be attributed to buckling of the platelets, which was referred to as platelet crunching, and the collapse of the mineral bridge reinforcements between the tablets. Contrary to this, case (b) shows a linear elastic relationship between the load and deflection followed by brittle failure, where the platelets cannot disengage from each other as with case (a). This shows that the matrix had little contribution in resisting the applied load since there is relatively little plastic deformation. This behavior is different from that of the above studies on the behavior of nacre under bending and tension, where the matrix undergoes significantly large deformations. Hence, nacre appears to be built for flexure and tension under large deformations and compression under localized loading. It can also be deduced that the load carrying capacity of nacre is highly dependent on its orientation. The indication, when compared to the previous studies, is that nacre prefers tensile loading along the grains such that cracks propagate through the highly deformable matrix to activate energy dissipation mechanisms throughout its composite structure.

Menig et al. [73] analyzed the quasi-static and dynamic response of red abalone shells (*Haliotis Rufescens*) under compression. Recall that red abalone nacre has a columnar tablet arrangement. They loaded several specimens parallel and perpendicular to the tablet facets, in a similar manner to that of the above study. Of particular interest is the dynamic compression of red abalone nacre perpendicular to the tablet plane because extreme loads on structures typically occur transversely. Firstly, under quasi-static compression perpendicular to the tablet facets, nacre behaves linear elastically up to a strength between 450 to 700 MPa followed by sudden failure. Contrary to this, when loaded in the direction parallel to the tablet facets, a significant reduction in the peak strength was observed (around 200 MPa). This may be attributed to the micro-buckling phenomena, which shows kinks along the grain boundaries that create an eccentricity between the applied load and the tablet centroids. Hence, the load carrying capacity in nacre under compression is orientation dependent. Under dynamic compression perpendicular to the tablet facets, a significant increase in strength (up to 1000 MPa) was observed. Hence, the response of nacre is highly strain rate-dependent, which makes it ideal for extreme loads. A large variation in the fracture stress was observed, which may be attributed to the statistical orientation of the tablet geometries and the imperfections present in the tablets.

Bending: Currey [63] performed notched three-point bending tests to establish the fracture toughness of small prismatic specimens of *Pinctada margaritifera* (sheet nacre). The work of fracture for *Pinctada margaritifera* across the grain and along the grain was reported as 1650 Jm^{-2} and 150 Jm^{-2} , respectively. By observing the damage in the nacreous specimens, they found that this high variation is attributed to crack propagation through the tablets. Hence, it is important that the crack propagates through the matrix to maintain the integrity of the composite over large deformations. This significant variation also indicates the highly anisotropic nature of nacre's staggered composite structure.

Wang et al. [91] performed three and four-point bending tests on shells from California red abalone (*Haliotis rufescens*), and South Sea pearl oysters (*Pinctada maxima*), which exhibit a columnar and sheet type tablet arrangement, respectively. They found that the random sheet nacre arrangement found in pearl oyster shows a higher strength than the red abalone columnar tablet arrangement. Similar to the aforementioned studies, a region of elastic deformation was observed followed by a plateau region with inelastic strain hardening up to a failure strain of 1%. This is similar to the failure strain of 0.018 reported by Currey [63] for the *Pinctada* sheet nacre species. It was observed that both specimens fail in a brittle manner under compression. Furthermore, large inelastic deformations occurred ahead of the crack tip, thereby blunting it. This shows that nacre has a tremendous ability to arrest crack propagation, which is consistent with the hardening phase observed in the load-deformation curve. The tensile strength and Young's modulus of the red abalone specimens (columnar nacre) were reported as $223 \pm 7 \text{ MPa}$ and $69 \pm 7 \text{ GPa}$, respectively. For the pearl oyster specimen (sheet nacre), the tensile strength and Young's modulus were reported as $227 \pm 13 \text{ MPa}$ and $77 \pm 12 \text{ GPa}$, respectively. Furthermore, tablet junction openings were observed in both red abalone and pearl oyster nacre. The relatively uniform distribution of these openings indicates that crack bridging plays a prominent role in arresting crack propagation in nacre, which may be responsible for the prolonged hardening phase observed in the stress-strain curve.

Jackson et al. [99] performed three-point bending tests on single edge notched *Pinctada* nacre specimens and reported that the variation in the work of fracture across the platelets was in the range of 350 (dry) to 1240 Jm^{-2} (wet). Hence, the toughness of nacre is highly sensitive to the degree of hydration, which can significantly increase the ductility of the matrix by plasticizing it such that debonding occurs near the crack tip. In the dry case, nacre behaves

similarly to its bulk ceramic, namely aragonite. The stress intensity factor was also used as a measure of toughness but became less sensitive in the hydrated samples because significant ductility was present. The crack propagation between the grains was observed to meander, which means that more fracture surfaces will be created such that the energy required to drive a crack increases. Several regions of exposed stretched ligaments were also observed between the tablets, which indicate that there is reinforcement between the tablets that can also contribute to the toughness amplification found in nacre.

Shear: Tang et al. [92] performed shear testing on a red abalone specimen. In this case, dry nacre was seen to behave in a more ductile manner. This was attributed to the activation of more sliding sites at the interface because the interface was directly sheared. Consequently, the tablets were not subjected to large non-uniform tensile stresses, which would then need to be transferred through the interface between them. This reason was identified to be the key contributor as to why the strain at failure was seen to be much larger than that of the tension case (around 15% as opposed to 1%). These two tests consistently showed that the key load transfer mechanism in nacre is via shear at the interface. Furthermore, Tang et al. [92] observed significant expansion across the tablet layers, which suggested that the tablet layers must climb a type of obstacle to initiate the tablet sliding process. From this test, a shear modulus of $G = 14 \text{ GPa}$ and a shear strength $\tau = 20 \text{ MPa}$ were obtained for hydrated nacre, with a failure strain of 15%. From the inverse rule of mixtures (Voigt model), the shear modulus of nacre and the shear modulus of aragonite were used to approximate the shear modulus of the interface as $G_I = 0.8 \text{ MPa}$.

Furthermore, Menig et al. [73] tested six red abalone nacre specimens in shear and obtained an average shear strength of $29 \pm 7.1 \text{ MPa}$. They also found a significant increase in the failure strain (0.4), which shows that nacre prefers to transfer loads via shear through the interface, where the matrix can sustain large deformations. By directly shearing the nacre specimen, the tablets are not subjected to a significantly large tensile load, which thereby increases the ductility of the composite.

Indentation: Wang et al. [90] performed a micro-indentation experiment on a bivalve mollusk (*Cristaria plicata*) to identify the mechanisms responsible for the large sustained deformation and fracture in nacre. The indentations were applied in both directions, namely perpendicular to the tablet surface plane and the cross-sectional surface parallel to the

interface. Three main toughening mechanisms were observed, namely fiber pullout, crack deflection and organic matrix bridging. The crack growth between the nacreous tablets indicates that in the staggered configuration, crack bridging contributes to meandering the crack path, thereby deflecting cracks between the tablet layers. This process forces cracks to develop over a longer path, thereby increasing the damage energy dissipation in nacre. Furthermore, the tablet sliding mechanism that occurs between tablets in adjacent layers indicates that the matrix undergoes significantly large plastic deformations under mechanical loads. Large deformations at the crack tip are well known to effectively blunt cracks. This stepwise pattern in crack propagation is similar to that observed by Wang et al. [91], who performed three and four-point bending tests on several columnar and sheet nacre specimens. It is important to note that although fracture occurred in a small number of tablets, this may be more prominent under extreme loads, where tablet fracture can compromise the integrity of the structure. Thus, ductile tablets may be desirable for this purpose.

Barthelat et al. [95] performed nanoindentation experiments on a red abalone nacre (*Haliotis rufescens*) specimen to establish the mechanical properties of its constituents and link them to its mechanical response. Note that red abalone nacre exhibits a columnar arrangement with a defined overlap length between the tablets. The force-displacement curve showed a region of initially low stiffness followed by a rapid increase in stiffness. This was attributed to the nano-asperities at the interface, which give rise to voids at the interface and flatten out such that the tablet is then engaged in resisting the load. Hence, the asperities tend to soften the composite under localized indentation. The force-displacement curves were processed using an existing technique for determining the hardness and elastic modulus in indentation experiments [108]. It was mentioned previously that the tablets have nano-inclusions due to the biomineralization process (the process where organic matter is formed into minerals). Regardless, the measured properties obtained from Barthelat et al. [95] were found to be similar to bulk aragonite, namely the Young's moduli $E_1 = 144$ GPa, $E_2 = 76$ GPa, and $E_3 = 82$ GPa, the Poisson's ratios $\nu_{12} = 0.44$, $\nu_{13} = -0.06$, and $\nu_{23} = 0.18$, and the Shear moduli $G_{12} = 47.2$ GPa, $G_{13} = 25.6$ GPa, and $G_{23} = 41.3$ GPa. Hence, the properties of the tablets are orthotropic and are not sensitive to nano-inclusions. The stiffness of the confined interface was found to be $E_i = 2.84 \pm 0.27$ GPa. These findings indicate that nacre utilizes its tablets as a structural scaffold and employs its toughening mechanisms at its soft interface to maintain structural integrity.

Table 2: The key structural features of nacre and their functions.

Feature	Geometry	Structural Function
Organic growth bands	8 μm thick	Crack deflection between adjacent nacreous layers.
Nacre's overall thickness	300 μm	Facilitates many staggered layers to form through the thickness, thereby increasing the effectiveness of crack bridging.
Tablets (95 % vol. of nacre)	Polygonal shape 0.5 μm thick 8 μm length Overlap: $\sim 1.6 \mu\text{m}$ (approx. one-third of tablet area)	Polygonal tablet shapes contribute to in-plane crack deflection. Tablet aspect ratio enhances bridging forces. Overlap allows for contact interactions at the interface between adjacent tablets.
Mineral bridges reinforcing the matrix	46 nm diameter 26nm thick	Contribute to the strength of the natural composite by connecting the tablets together with a strong mineral.
Nano-asperities on the tablet surfaces	10 – 30 nm height 100 – 200 nm spacing	Provide sliding frictional resistance between adjacent tablets but not under large deformations. Soften the composite by flattening out under localized indentation.
Tablet interface waviness	100 nm amplitude 5 μm wavelength	Provide interlocking forces under large deformations i.e. strain hardening effects.
Organic matrix (5 % vol. of nacre)	20 – 30 nm thick	Maintain the integrity of the natural composite over large deformations.
Stretched protein ligaments between tablets	25 – 600 nm	Provide sacrificial bonds and exposed hidden lengths for dissipating energy and maintaining the integrity of the bonds between adjacent tablets over large deformations.

2.2 Conch (*Strombus gigas*) shell

Conch (*Strombus gigas*) shell is a large gastropod that is composed of inner, middle and outer crossed lamellar macro-layers (Figure 3) [109]. Each layer shows a hierarchical structure over several different length scales (nano to macro) [110-114] and is composed of a number

of parallel first order lamellae, which are several micrometers wide and 5-60 μm thick [110, 111, 115]. The first order lamellae are sheets that are composed of unidirectional layers of second order lamellae, which alternate in a direction between two orthogonal orientations, typically $\pm 45^\circ$ [110, 111, 115, 116]. The second order lamellae are rectangular beams that are 5–30 μm thick, 5–60 μm wide, and up to several hundred micrometers in length [110, 111]. Each second order lamella is composed of tens of thousands of third order lamellae, which are stacked in parallel [110, 111]. The third order lamella, which is the building block of *Strombus gigas*, is made up of nano-twinned aragonite platelets, and shows a rectangular plank-like structure that is approximately 150 – 200 nm wide by 75 – 100 nm thick and several micrometers in length (100 – 400 nm). These lamellae are surrounded by a thin organic matrix (approximately 0.1% wt.) and tightly interlocked [110-112, 115]. The strategic placement of the organic matrix, which separates the lamellar orders of the stiffer mineral phase, significantly affects the mechanical response of the shell [115]. In other words, the conch shell is made of 99.9% wt. ceramic and is reminiscent of plywood or crossed-ply fiber-reinforced laminated composites, with the macroscopic inner, middle and outer layers playing the roles of the plies [112, 115]. The third order planks (or lamellae) are ductile and assembled from fourth order particles (Figure 3b), which are highly dense nano-scale growth twins with a crystallographic orientation of 30° [110, 111]. These particles are aligned in parallel within a single lamella. Using transmission electron microscopy (TEM), it was confirmed that the twin thickness varied from 2 – 20 nm with a mean value of approximately 8 nm [111], whereby the twin boundaries were coherent and free of defects. The microstructural and crystallographic characterizations revealed nanotwinned aragonite platelets as the basic building blocks of *Strombus gigas* conch shells [111]. Efforts by researchers to link these key structural features to their mechanical functions are explored hereafter.

Figure 3: a) Conch shell with normal ($\hat{n}$) and tangential ($\hat{t}_1, \hat{t}_2$) axes labeled [110]; and b) Schematics of the three-order crossed-lamellar structure and the building block (nano-scale aragonite twins) [111].

The remarkable toughness of conch shells is attributed to several structural features that work to deflect and arrest fracture. Several attempts have been made to establish the structure-function relationships of conch shells through mechanical testing: indentation [110, 117, 118] [111]; compression [15, 116]; and bending [15, 112, 115, 116]. Central to these investigations is the crossed-lamellar structure, which is the most common feature associated with the highest nominal fracture toughness, K_{Ic} i.e. fracture (crack deflection and bridging) is the focus of most of the aforementioned investigations. It is remarkable that the conch shell, which is mainly composed of a brittle mineral (over 99% wt.), exhibits prominent energy-dissipating fracture mechanisms, where the surfaces of an emanating crack are bridged by the microstructural features of the cross-lamellar structure [113, 115].

Although the tensile strength of conch shells is 50% lower than that of nacre from mollusk shells, the conch shell has a work of fracture that is nearly ten times higher [112]. This led to numerous efforts to uncover the mechanisms behind this significant structural advantage. Recall that the direction of the first order lamellae is nearly perpendicular between the adjacent macro-layers of a conch shell, which forces a crack to propagate along the weak

direction. The crack is thereby deflected at the interfaces between the adjacent first order lamellae [110]. In other words, cracks can propagate along two principal directions within a first order lamella, namely along the weak interfaces between the second order lamellae or through the second order lamellae [110]. As such, cracks along the weak direction of the first order lamellae are bridged by the perpendicular second order lamellae in the adjacent first order lamellae [110]. Furthermore, the roughness of the interfaces between the first order lamellae causes interlocking, which increases their adhesion strength and thereby dissipates energy between the neighboring first order lamellae [110, 113, 115]. Although multiple channel cracks along first-order interfaces develop in the inner layer at small loads, they are arrested by the tough middle layer, which mitigates catastrophic failure until much higher loads are encountered. From a fracture mechanics point of view, the mutual shielding produced by the interaction of these closely spaced cracks that propagate along first-order lamellar interfaces results in a higher stress required to achieve catastrophic failure. This thereby results in a higher work of fracture compared to singly cracked specimens [115]. The hierarchical nature of the crossed lamellar structure significantly influences its mechanical properties given that there is an increase in the rate of crack nucleation within the third order lamellae compared to regular (abiotic) aragonite. This is facilitated by the hierarchical internal third order nanostructure [117]. The mechanical investigations that have been conducted by researchers to establish these important mechanisms are explored hereafter.

Indentation: Romana et al. [117] performed nano-indentation tests on a conch shell (*Strombus gigas*) using a Berkovich tip at a strain rate of 0.05/s. They measured the hardness and Young's modulus as a function of the indentation depth in the directions perpendicular and parallel to the growth axis of the shell and found a reasonable level of anisotropy in both directions. For the perpendicular surface, a hardness of 3.9 GPa and a Young's modulus of 84 GPa were obtained at an indentation depth of one micron and for the parallel surface (perpendicular to the outer surface of the shell), they obtained a hardness of 5.6 GPa and Young's modulus of 99 GPa. By measuring the Young's modulus and hardness of geological aragonite, they concluded that the different modulus and hardness values measured on the bio-aragonite samples (conch) are mainly due to the anisotropic properties of the aragonite phase and not to the micro-architecture of the bio-composite. However, as the indentation depth increases, the mechanical parameters were observed to evolve differently. Load plateaus were also observed in the load-displacement curves, referred to as pop-in events in fracture mechanics, in which the indentation depth increases suddenly at a constant load. The

pop in events observed on the load-displacement curves was attributed to the propagation of nano-cracks in the tested materials.

Salinas et al. [110] investigated the influence of different microstructural (lamellar) orientations on the fracture behavior of a conch shell (*Strombus gigas*) using nanoindentation. Crack opening (mode I fracture) was observed during delamination between the third-order lamellae, which resulted in bundles of third-order lamellae being strained until they fractured. Evidence of shearing (mode II fracture) between the third-order lamellae was also observed in the form of buckled third-order planks along the flat parallel indenter face. Additional fractures were observed primarily traveling laterally between rows of third-order lamellae, where they encountered resistance from the interfaces between these lamellae. Arching fractures were also seen to originate from the sides of the indenter, taking a tortuous path by traveling diagonally between rows and columns of third-order lamellae. Hence, the third-order lamellae had the effects of delocalizing fracture by deflecting cracks.

Li et al. [118] investigated another species of conch (*Busycon carica*) using micro- and nano-indentation. A Vickers indenter was employed to simulate attacks by a predator with sharp teeth, which a conch shell may experience over its lifetime. The top, middle and bottom macro layers showed similar damage patterns i.e. stress concentrations were observed around the corners of the indenter tip. Contrary to polycrystalline metals and ceramics, the conch shell had short major cracks that were scattered along the indenter margins. In conch shells, the short major cracks formed primarily at the first-order lamellar interfaces and were deflected into these interfaces. The cracks were then further branched along the second- and third-order boundaries. The elongated crack paths due to crack deflection in the lamellae of a conch shell showed evidence for its enhanced toughness. Nanoindentation tests were further performed on individual third-order lamellae to determine that the aragonite lamellae were ductile, which contradicts the previously-assumed brittle characteristic for the aragonite phase of the conch shell. The brittle aragonite lamellae behaved in a ductile manner because the viscoelastic-plastic biopolymer between the nanoparticles acts as rubber-bands, which thereby contributes to the deformability of the individual third-order lamellae.

Shin et al. [111] conducted in-situ transmission electron microscopy (TEM) nanoindentation experiments on nanotwinned aragonite (extracted from the conch shell) and its single-crystalline (twin-free) counterpart, to quantitatively determine the fracture toughness by

measuring the crack tip opening displacement (CTOD). From the sequence of TEM images of crack propagation in the nanotwinned and single-crystalline aragonites, respectively, it was observed that the main crack propagates rapidly along a cleavage plane and a few deformation twins form near the crack tip or some other sites with a stress concentration. Contrary to this, for the nanotwinned aragonite, the main crack propagates nearly perpendicular to the twin boundaries and is then highly deflected by these boundaries. Again, crack deflection was observed to be a key contributor to the enhanced fracture toughness of the conch shell, this time at the twin boundaries of the aragonite lamellae.

Compression: Menig et al. [116] performed compressive testing on a conch shell (*Strombus gigas*) in the directions parallel and perpendicular to the outer surface under quasi-static and dynamic (loading rates between 10,000 GPa/s and 25,000 GPa/s) conditions. By compressing the specimen in different directions, they found that the orientation of the lamellae greatly affected its strength. Uncertainties were identified (e.g. variable layer thickness, flaws, existing cracks) that warranted a Weibull statistical analysis to quantify the quasi-static and dynamic properties of the shell. Note that this technique is normally employed to obtain flexural strengths. Compressive strengths between 180-210 MPa along with failure strains between 0.7-0.8 % were obtained for the case of quasi-static loading perpendicular to the outer surface of the shell. It was observed that the material exhibits damage-induced softening after the peak of the stress-strain curve was reached. A softening slope of about 8 GPa was obtained, which is approximately one-quarter of the elastic stiffness (30 GPa). This behavior was contrasted to monolithic ceramics, which are known to fracture catastrophically. For the case of quasi-static loading parallel to the outer surface, compressive strengths between 210 and 310 MPa, and failure strains between 0.9 and 1.3% were obtained. Furthermore, the dynamic response of the conch samples compressed perpendicular to the outer surface of the shell showed failure strains between 0.005 and 0.012, and a maximum stress between 230 and 300 MPa. The dynamic stress-strain response of the conch shell was also obtained for loading parallel to the outer surface. The maximum stress was found to be between 320 MPa and 410 MPa, and failure strains between 0.008 and 0.011. Hence, there is high variability in the mechanical properties between the specimens due to the uncertainties stated above.

Lin et al. [15] also investigated the behavior of conch shells (*Strombus gigas*) in both the parallel and perpendicular directions to the outer surface under quasi-static and dynamic

(between 200/s and 500/s) strain rates. The test samples were cut into rectangular prisms in different orientations with respect to the shell layers. Again, a Weibull statistical analysis was used to obtain a quasi-static compressive strength between 166 MPa and 218 MPa (failure probability of 50%) in the perpendicular and parallel directions of loading, respectively. The 50% failure probabilities of the conch shell were reported at 249 MPa and 361 MPa under dynamic loading perpendicular and parallel to the layered structure, respectively. The conch shell was seen to fail similarly to most brittle materials under compressive loading via an axial splitting mechanism, in which fracture occurs parallel to the loading direction. Crack propagation was observed to be blunted along the organic-inorganic interface in the middle macro layer before traveling through the second-order lamellae. Furthermore, a zigzag pattern was observed during failure whereby the cracks are bifurcated and delocalized, which increases the toughness of the material.

Bending: Kuhn-Spearing et al. [112] investigated the performance of conch shells (*Strombus gigas*) using displacement controlled four-point bending experiments under quasi-static loading (0.1 mm/min), under both dry and wet conditions. Channel cracking was observed at the interface of the outer and middle macro layers at an average stress of 35 MPa for the dry samples, and at much lower stresses for the wet samples, indicating that the strength of the organic component is significantly affected in the hydrated state. In the parallel orientation, channel cracks initiated between the first-order layers and propagated rapidly to the interface of the macroscopic layer. These cracks were arrested and deflected along the interface, which is parallel to the neutral axis of the beam. Due to the variability of the shell (e.g. layer thickness, multiple cracks and so on), there is considerable uncertainty associated with calculating the stress in this middle layer, which warranted the use of beam bending equations to calculate the flexural strength. The average flexural strengths for the dry and wet crossed-lamellar samples in the parallel orientation were found to be 56 MPa and 84 MPa, respectively. In the transverse direction, the average flexural strength of the wet and dry samples was 107 MPa. Considering the large extent of delocalized cracking observed, a high fracture toughness was obtained: 4 kJm⁻² for the dry shell specimens and 13 kJm⁻² for the wet shell specimens tested in the parallel orientation. Several mechanisms were found to contribute to the high work of fracture of the shell, namely a higher channel crack density, additional delamination at the inner/middle interface and multiple cracks in the middle layer penetrating partially through its thickness. Again, the jagged crack path through the cross-lamellar structure, combined with frictional dissipation between the fractured lamellae was

reported to be responsible for the superior toughness of the shell. From this study, a bio-inspired design including layering schemes at three to four length scales was recommended.

Kamat et al. [115] also performed bending tests on conch shells (*Strombus gigas*). As per the above investigation, they observed multiple channel cracks along the first-order interfaces, which initiated in the inner layer at low loads but were arrested by the tough middle layer such that catastrophic failure was mitigated. The mutual shielding produced by the interaction of these closely spaced cracks was reported to contribute to a higher stress for catastrophic failure, which consequently increases the work of fracture significantly as opposed to singly cracked specimens. From observations of the cracked specimen, the crack front cleaved the interfaces between second-order lamellae and every other first-order lamella remained intact, which reduced the crack opening displacement (COD). The stiffness of the first-order lamellae influenced the net bridging tractions on the strength-defining crack. In summary, the high fracture toughness was attributed to the onset of channel cracking, interlayer delamination and crack tortuosity. Using notched fracture-mechanics bending specimens, several samples were cut from the inner layer and the middle layer. An important observation in the middle layer was that the cracks propagated directly along the second order interfaces, namely at 45° to the applied stress.

Menig et al. [116] harvested specimens from conch (*Strombus gigas*) and investigated their behavior under bending. They tested four configurations, where the samples were cut such that the lamellar orientations were: parallel to the outer surface with the outer surface perpendicular (C) and parallel (E) to the loading direction; and perpendicular to the outer surface, with the outer surface perpendicular (D) and parallel (F) to the loading direction. The results of the bending tests evidenced the high anisotropy of the shell. From the four orientations tested, C and E showed the highest strength. Orientations D and F had a strength of approximately half that of orientations C and E. The tensile strength was observed to vary from 24 to 74 MPa (average of 46.5 MPa) as measured from the bending tests, depending on orientation. The ratio between the compressive and tensile strengths was reported as 4.1, which is a significantly low ratio compared to that of monolithic ceramics, which is typically in the range of 8-12. This difference is attributed to the toughening mechanisms of the conch shell. Based on these observations, they concluded that the hierarchical structure of the conch shell enhances its toughness significantly by providing several damage mitigation

mechanisms, namely viscoplastic deformation and crack deflection within the organic layer, and delocalization of damage due to the cross-lamellar structure.

Lin et al. [15] performed a similar investigation for assessing the performance of conch (*Strombus gigas*) under quasi-static three-point bending. They reported average flexural strengths of 74 MPa for the configuration where the layered structure was parallel and the outer surface was perpendicular to the loading direction and 29 MPa where the layered structure was perpendicular to the loading direction. The fracture surface of a sample under tension induced by bending along the growth axis of the shell showed separation along this axis, which thereby exposed all three orders of lamellae. Similar to the above investigations, it was concluded that the hierarchical lamellar microstructure of the conch shell is responsible for its toughness, whereby the crack tips are delocalized by a large number of smaller cracks over a broader region, which alternate directions at each lamellar level or order.

Table 3: The key structural features of conch shells and their functions.

Feature	Geometry	Structural Function
Inner middle and outer layers	See the dimensions for each of the first- to third-order lamellae below	<p>Surface roughness increases their adhesion strength and dissipates forces between neighboring first-order lamellae.</p> <p>Has a weak direction, which when loaded in tension, results in delamination between the first-order lamellae.</p> <p>Multiple channel cracks emanate from the outer layer, which activates several damages dissipating mechanisms via cracks deflection at the middle layer.</p> <p>Macrocracks passing through the outer macro layer are deflected by the middle macro layer with a deflection angle that is comparable to the orientation of the cross-lamellar structure.</p>
First-order lamellae (sheets)	Several microns wide 5 – 60 μm thick	<p>Allow cracks to propagate along the weak principal direction.</p> <p>The micro-buckling/kinking phenomenon has</p>

		been observed at this lamellar order, which has also been observed in nacre under compression.
Second-order lamellae (beams)	5 – 30 μm thick 5 – 60 μm wide Several microns in length $\pm 45^\circ$ orientation	Bridges cracks that propagate through the weak direction of adjacent first order lamellae.
Third-order lamellae (rectangular planks)	150 – 200 nm wide 75 – 100 nm thick 100 – 400 nm long	Provide the building blocks for the crossed-lamellar conch structure. Surrounded by organic material for improving adhesion.
Fourth-order particles (nano-twinned aragonite platelets)	2 – 20 nm thick	Crack deflection and enhancing fracture toughness.
Organic matrix	0.1% wt.	Large viscoplastic deformation and crack deflection occur within the matrix. Facilitates large viscoelastic deformation of the third-order lamellae, thereby enhancing ductility.

2.3 Fish scales

Fish scales are often well recognized as plywood-like, cross-laminated structures. They are a key component of the *Arapaima gigas*, which is one of the largest freshwater fish in the world that can grow to a length of about 2–2.5 m and a mass over 150 kg [20]. This fish inhabits the Amazon River Basin in South America, which is home to the piranha. For this reason, it has been proposed that the scales provide protection against the sharp piranha teeth. Furthermore, the function of scales as armor has been demonstrated for *Polypterus senegalus*, a species also referred to as dragon fish [20]. These types of armor systems have gained interest because they possess light weight and high flexibility, as they must not affect the mobility of the fish. To this end, numerous studies on fish scales have been conducted to understand their structural arrangement, which includes the formation of collagen and its orientation [18, 20]. The scales have dimensions of 5–7 cm in length (up to 10 cm in large fish) and

approximately 4 cm in width. The scales overlap with an areal fraction of approximately 0.6 to form armor-like protection [20, 119, 120].

Most scales are mainly composed of type I collagen fibers and hydroxyapatite, which are the material components found in bone and also teeth [13, 20]. Similar to cortical bone, the collagen fibers are usually densely packed lamellae with different orientations from layer to layer, thereby forming a plywood structure [20, 121, 122]. Among the different species, the dimensions of the laminates vary with the thickness of the scale. For instance, in *P. reticulata* (guppy), the lamellae are approximately 1 μm thick whereas in *C. auratus* (goldfish), they have a thickness of around 5 μm [13, 20]. The angles between the layers also vary for different species, from 36° for teleosts to 90° for *Poecilia reticulata* and *Pagrus major*. This type of plywood structure has been proposed to form the well-known Bouligand arrangement, which consists of the superposition of different layers with the fibers forming a helical pattern. Bones also have this type of structure, except that the fibers are twisted/wrapped around a cylinder between the laminates around the central axis [13, 20].

There are two main distinguishable sections in the *Arapaima* scale, namely an embedded part with a thickness of approximately 1 mm and an exposed section, which has a thickness of 2 mm. The *Arapaima* scale is thicker than most other fish scales, which can be as low as 1 – 2 μm in the case of *Pagrus major* [13, 20, 119]. The scale has a laminated structure, which is composed of an external highly mineralized bony layer with ridges and internal fibrous layers [20, 123]. The collagen fibrils have a diameter of approximately 100 nm and are bundled together to form collagen fibers with a diameter of 1 μm [20], which are in turn assembled into lamellae with a thickness of approximately 50 μm [20]. The collagen fibrils in the central lamella are oriented in one direction. A network of cracks in the layers has been observed to propagate between the fibers, which are induced by shrinkage stresses from the drying process. When the fibers are oriented parallel to the surface, no cracks have been observed [20]. These cracks have been used to estimate the fiber angles in the different layers, which suggested that the angle between layers is approximately 75° .

The structure of the scales has also been observed after deproteinization i.e. with the collagen phase removed to determine the morphology of the platelets, which are the characteristic elements of the entire deproteinized scale structure with a random orientation. The platelets

have a thickness of 50 nm and a diameter of 500 nm and are assembled to form three semicircles along a common axis. The significance of this arrangement is that it does not disrupt the parallel alignment of the collagen fibrils. As such, it is suited for the mineral to form a semi-continuous or even continuous network in the aligned collagen fiber network. The density of the platelets has been estimated to be less than 0.1 by assuming they are contiguous spheres [20]. The mechanical investigations conducted by researchers to establish these important structural features and link them to their function are explored hereafter.

Figure 4: Schematic of the fish scale: a) The lamellar structure of the internal and external layers; b) The orthogonal plywood-like lamellar structure with the building block (nano-scale collagen fibril) [20].

Several mechanical tests have been performed to establish the structure-function relationships of fish scales: tension [13, 20, 123, 124]; perforation/puncture [123]. Tension is the most common due to the fibrous plywood-like nature of the scale.

Tension: Ikoma et al. [13] performed tensile tests on *Pagrus major* fish scales and obtained an average strength of 93 MPa. The tensile curve showed an initially linear elastic region with a Young's modulus of 2.2 GPa. They attributed the low modulus to the low mineral content (46%) of the scale. Following the elastic zone, there was considerable plastic yielding before fracture at a strain of 5%. They attributed the yielding zone to the sliding and pullout of the collagen fibers (2 to 3 microns thick) within the lamellar structure. They also found that demineralized scales have a tensile strength of 36 MPa and a Young's modulus of 0.53

GPa. This indicates that the interaction between the apatite crystals and collagen fibers are paramount to the mechanical performance of the scale, despite that the fracture behavior was similar to that of the mineralized tissue.

Zhu et al. [123] performed quasi-static tensile testing on individual fish scales from striped bass (*Morone saxatilis*) under hydrated conditions. They harvested samples with a gage length of 4 mm, gage width of 1.5 mm and an average thickness of 0.2 mm, which were cut at 0°, 45° and 90° from the longitudinal axis of the fish. The stress-strain curve displayed an initially quasi-linear region with an initial tensile modulus of 600 – 850 MPa followed by slight softening until a tensile stress of 30 – 50 MPa was reached. They attributed this behavior to sudden cracking of the bony layer from optical observations. Following this behavior, the collagen layer detaches progressively from the stiff bony layer by tearing the collagen plies (one after the other), which was responsible for the stair-like patterns on the stress-strain curve up to a failure strain of 40%. Additional tests were conducted on the collagen layer alone (with the bony layer removed). The stress-strain response consisted of a linear elastic regime with a modulus of 450 MPa, followed by progressive failure up to a peak stress of 65 MPa. The ultimate failure strain was the same as that without the bony layer.

Lin et al. [20] performed quasi-static (0.0001/s) and quasi-dynamic (0.01/s) tensile testing on *Arapaima gigas* fish scales under both dry and hydrated conditions. They obtained an elastic modulus of 1.2 GPa and 0.1 GPa, and a tensile strength of 47 MPa and 25 MPa under dry and hydrated conditions, respectively. The hydrated scales showed much higher deformation prior to failure, whereby the failure strain was less than 10% under dry and 30 – 40% under hydrated conditions. This indicates that the scales required high flexibility to flex with the body of the fish during swimming. They inferred that the high difference in the mechanical properties of *Arapaima gigas* compared to the *Pragus major* scales investigated by Ikoma et al. [13] was attributed due to the low ductility observed under dry testing conditions. They also found that the elastic modulus was highly rate-dependent i.e. 118 MPa (quasi-static) to 404 MPa (quasi-dynamic). They also observed different collagen fiber orientations in different lamellae on the fracture surface, whereby the angle between the fibers in adjacent lamellae is 90°. In addition to fracture of the collagen, tearing was also observed, which split the fibers away from each other. This indicates that the fracture mechanism appears to be a combination of fracture and pull out of the collagen fibers in a single layer.

Torres et al. [124] also performed tensile tests on fish scales (*Arapaima gigas*) under dry and hydrated conditions and obtained a tensile strength of 54 MPa and 22 MPa, and a Young's modulus of 1.38 GPa and 0.84 GPa under dry and hydrated conditions, respectively. However, the peak failure strain was lower in the hydrated state (2%) than that of the dry state (3%). This contradicts the results obtained by Lin et al. [20] who found that the failure strain was less than 10% for dry and 30-40% for hydrated conditions. The fact that the soaked samples have a water content of around 30% of their dry weight reduces the volume fraction of hydroxyapatite crystals, thereby reducing the mechanical properties of the scale.

Puncture: Zhu et al. [123] performed a perforation/puncture test to simulate the impact of a sharp tooth on a fish scale (striped bass). They used a sharp steel needle with a radius of 25 microns, which is at a similar size to a predator's tooth, and drove it into the scale at a speed of 0.005 mm/s. Remarkably, the fish scale provided significantly higher resistance to puncture compared to high performance engineering polymers such as polystyrene and polycarbonate. The isolated collagen layer was easily penetrated, providing only half of the puncture resistance in terms of force. Therefore, the bony layer is an important component of the system, which operates with the collagen layer to increase the performance of individual scales.

Table 4: The key structural features of fish scales and their functions.

Feature	Geometry	Structural Function
Fish Scale	Thickness: 1 mm (embedded section) Thickness: 2 mm (exposed section) 5 – 10 cm in length 4cm in width Overlap: On average 3 layers (areal fraction of 0.6)	Overlap one another to form a characteristic armor-like protection. Bony layer resists localized perforation while the collagen fibers bridge cracks.
Lamellae	50 microns thick Cross-ply plywood like	Consist of different fiber orientations to resist damage in different directions.

	structure with a 90° orientation Twisted plywood is also possible, varying at 36° between layers	Reminiscent of a cross-plywood like structure, which is effective at bridging cracks.
Collagen fibers	1 micron diameter Bundles	Bundles of fibrils aligned consistently to provide a flexible armor system.
Collagen fibrils	100 nm diameter	Contributes to the tensile strength of the scale. Fiber bridging in the presence of cracks, thereby increasing toughness.
Mineral phase (platelets)	50 nm thickness and 500 nm diameter	Provides the compressive strength of the scale. High resistance to perforation, particularly at the bony layer.

3. Multi-scale manufacturing of bio-mimetic structures

3.1 3D printing (macro- to micro-scale)

3D printing is a process that creates three-dimensional objects by joining or solidifying materials with the help of a computer [125]. A review on different methods of 3D printing and the materials employed, as well as the applications and challenges arising from this method was conducted by Ngo et al. [126]. Among numerous methods that could be categorized as 3D printing, filament extrusion-based and powder-based are two common methods that have been employed for manufacturing bio-mimetic prototypes. In filament extrusion-based printing, a continuous thermoplastic filament is extruded to print objects layer-by-layer through the print head's nozzle. This process basically involves a filament being drawn through an extruder, which is then heated using a nozzle (hot end). The heated filament is then deposited onto a hot surface to build the model layer by layer. No further treatments are required for the filament-based 3D printing method. This technique is attractive for developing bio-mimetic samples due to the ease of manufacturing and readily available 3D printer technologies. It is worth noting that nowadays, dual extrusion printers are available for printing two materials simultaneously to develop composite specimens. On the other hand, in powder-based printing, a thin layer of powder is spread onto a surface and

connected by binders. Only powder in the designed area is connected by binders to form the designed geometry. The binders can be liquids [127] or laser beams [128, 129] while the powders are normally metal alloys. The unbound powder will be removed after the object is printed. This method provides higher manufacturing accuracy compared to the filament extrusion-based method. Similar to the powder-based method, there is another method that uses an ultraviolet (UV) beam to cure photopolymers. This method uses photo-sensitive polymeric materials as a replacement for powders. The 3D printing samples are manufactured by pointing the beam to the designed areas to cure the materials. In all the aforementioned methods, the objects are created layer by layer.

3D printing is quite popular due to its ease of manufacturing and is mainly used to mimic biological structures at the macro- to micro-scale. The key advantage is that it can fabricate multi-material composite structures at high precision, which are easily adapted from computer-aided design (CAD) geometry with a high degree of complexity. The rapid development of 3D printing technology nowadays has enabled the capability to easily and quickly manufacture complex bio-inspired structures directly from a Standard Triangle Language (STL) file, which is converted from a standard CAD model. Although the cost of 3D printed products can be relatively high, manufacturing prototypes for fundamental research is feasible since the cost is driven down by the small scale of the samples.

The 3D printing technique has been used to mimic different bio-inspired structures such as nacre-inspired [130], conch [110, 131], fish scale amour structures [14] and so on [127-129, 132-134]. In filament based, materials for 3D printing were acrylonitrile butadiene styrene (ABS) [130, 135], poly lactic acid (PLA) [130, 136], thermoplastic polyurethane (TPU) [130], polyethylene [110], VeroWhite (VW) and TangoPlus (TP) [14]. Powders in powder based 3D printing were the mixture of Sr-HT powder, aluminum oxide powder and zirconia balls [134], calcium polyphosphate [127], Ti6Al4V [128], titanium – titanium boride whisker [132]. Examples are provided hereafter.

Tran et al. [130] employed the fused filament fabrication 3D printing technique to manufacture a bi-material nacre-inspired structure. Two separate CAD models for the soft and strong phases were prepared before carrying out the printing process, which was controlled by a G-code file (3D printing hardware instructions). Acrylonitrile butadiene styrene (ABS) was used as the strong/stiff material to mimic the nacre-like tablets, and poly

lactic acid (PLA) or thermoplastic polyurethane (TPU) was used to mimic the ductile matrix. The authors successfully mimicked the complex nacre-inspired structure, which consisted of several ABS polygonal tablets connected by cohesive/adhesive bonds made from TPU and PLA. They were also able to print a curved composite structure by mapping the flat multi-layered structure to a generalized arbitrary surface using non-uniform rational basis splines (NURBS), which are well-known in the field of computational geometry, and also implemented in commercial computer-aided design (CAD) software packages.

Figure 5: 3D printed nacre-like panels: a) Flat and b) curved composites composed of hard tablets (ABS) bonded by a soft material (PLA); and c) ABS tablets bonded by flexible polyurethane.

Tiwarly et al. [136] explored 3D printing techniques to manufacture seashells of various shapes and tested them under compression. Poly-lactide (PLA) was used to manufacture the seashell prototypes. To achieve this, the dimensions of the general shape of the shell were obtained using a digital caliper while scanning electron microscopy (SEM) was used to obtain the measurements for the surface patterns. To generate an approximate CAD model of the shell, a cone was generated and a helix of varying radii was constructed on the surface of the cone. The CAD model was exported into a 3D printing format and printed using layer-by-layer deposition. This process basically involves a filament being drawn through an extruder, which is then heated using a nozzle (hot end). The heated filament is then deposited onto a hot surface to build the model layer by layer. This technique is attractive for developing bio-mimetic samples due to the ease of manufacturing and readily available 3D printer technologies. It is worth noting that nowadays, dual extrusion printers are available for printing two materials simultaneously to develop composite specimens.

Salinas et al. [110] developed third-order lamellar conch-like samples by 3D printing with polyethylene. They investigated the influence of different layer orientations on the mechanical properties of the conch-shell lamellar structure under indentation. The fracture patterns in the biomimetic samples were observed experimentally and used to validate the developed finite-element model. The sample dimensions were 50 x 50 x 60 mm. Each sample consisted of numerous 1 x 0.5 mm planks, for which the alignment angles were 0° , 45° or -45° . These planks were covered by a thin layer of resin (0.1 mm). The results showed that the abrasion resistance of the samples under indentation was significantly correlated with the orientation of the planks. From the experimental observations and finite element model predictions, the alignment angles of $\pm 45^\circ$ were reported to provide the highest resistance to penetration.

Based on the same principle of the powder-based 3D printing method, liquid materials (photopolymers) are deposited and cured by a UV beam to create the samples. By employing this method, Rudykh et al. [14] mimicked the structure of a fish scale using multi-material 3D printing to investigate the mechanisms responsible for its high resistance to perforation. The fish scale biomimetic composite samples were printed from a hard and a soft material. The hard material was VeroWhite (VW) while TangoPlus (TP) was used as the soft material. The Young's modulus of VeroWhite and TangoPlus are 1.2 GPa and 0.78 MPa, respectively. Both of these materials are photo-sensitive polymeric materials. The biomimetic samples were fabricated with a size of 150 x 10 x 20 mm. Several configurations with different inclination angles, and various material volume ratios between the stiff and soft phase were created. By performing indentation tests and three-point bending tests, the authors successfully provided the best configuration in terms of the optimal inclination angles and material volume ratios to significantly achieve both penetration resistance and flexibility simultaneously.

The same method was used by Gu et al. [131] to mimic the second-order lamellar structure of a conch shell. VeroMagenta and TangoBlackPlus were employed as stiff and soft materials to manufacture two small panels. They did not specify the size of the panel, but it was built from three layers of rotated lamellae (45° on the top and bottom layers, and horizontal in middle). The authors investigated the performance of this structure under low velocity impact (2.3 to 3 ms^{-1}) using a drop tower. Two designs were studied, namely the first order hierarchy (in-plane) and the cross-lamellar design (out of plane). The conch-like design showed no

perforation compared to an equivalent bulk sample made from the same stiff material. Cracks propagated along the soft interface through the weak adhesive zones. The cracks were forced to propagate along a zigzag path similar to that observed through experimental investigations.

Table 5: Properties of 3D printing techniques for manufacturing proof-of-concept bio-mimetic structures.

Material	Method	Resolution/ accuracy	Printer	Mimicked Structure	Reference
ABS (strong) and TPU (soft)	Filament extrusion based	Layer thickness 0.1 mm	Makerbot dual extrusion 3D printer	Nacre	Tran et al. [130]
PLA	Filament extrusion based	Nozzle size 0.3 mm	In-house assembled extrusion-based 3D printer	Seashells	Tiwary et al. [136]
Polyethylene and Resin	Filament extrusion based	Not specified	3D printing	Conch shell	Salinas et al. [110]
Verowhite (strong) and TangoPlus (soft)	Liquid deposited and cured by UV	Printer resolution $16\ \mu\text{m}$	Connex3 Objet500	Fish scale	Rudykh et al. [14]
VeroMagenta (strong) and TangoBlackPlus (soft)	Liquid deposited and cured by UV	Printer resolution $16\ \mu\text{m}$	Connex3 Objet260	Conch shell	Gu et al. [131]

3.2 Laser cutting/engraving and CNC machining (macro)

Mirkhalaf et al. [137] took inspiration from nacre's crack meandering mechanisms, which are facilitated by its microarchitecture, to toughen glass. They employed a laser engraving technique to machine flaws in a glass specimen. Basically, the technique involves reflecting a laser beam off a set of glass mirrors and employing a lens to focus the heat at a particular

point in the glass specimen. This, in effect, generates hoop stresses that open up cracks in the specimen. Jigsaw-like interfaces were machined ahead of the crack tip of the glass sample to facilitate crack meandering mechanisms to arrest crack propagation. Two types of specimens were developed, one engraved with plain jigsaw-type flaws and the other with jigsaw-type flaws infiltrated with polyurethane. Engraved glass infiltrated with polyurethane exhibits higher toughness compared to plain engraved glass. Furthermore, the engraved glass was found to be 200 times tougher than ordinary glass, which has no microstructure. Hence, this bio-inspired technique can be employed to toughen ceramics quite effectively. Generally, the idea that can be taken from this experiment is to develop several distributed cracks in the material and guide those cracks along jagged paths to dissipate energy while delaying their propagation.

Narducci et al. [12] mimicked the tablet architecture of nacre by using a laser cutter to engrave dovetail patterns into carbon-fiber/epoxy composite laminates prior to layup and curing. They were able to achieve a tablet size of 600 μm to a high degree of accuracy and repeatability. By conducting three-point bending tests on the engraved samples and using scanning electron microscopy (SEM) to observe the damage distribution in the nacre-like composite, they concluded that the micro-structure of nacre functions to deflect cracks via interlocking, thereby preventing sudden and localized failure. Hence, the interface between the nacre-like tablets can be optimized to improve the damage distribution throughout the composite structure. Furthermore, it was recommended that a more ductile matrix and a lateral compressive force can also enhance the interlocking mechanism, which would also help to further increase the diffusion of damage and thereby improve the toughness of the structure. It is worth noting that other bio-mimetic principles have been employed to improve the performance of laminated composites [138-142]. For example, Apichattrabrut et al. [143] mimicked the twisted plywood like structure found in different biological animals such as fish scales to enhance the performance of a laminated composite structure. To this effect, they manufactured composites with 40 layers, where the individual laminates were stacked with fiber orientations of 10° relative to each other i.e. [180/170/160/.../0]. It was observed that the bio-mimetic fiber orientations improved the energy absorption of the composite by limiting the development of transverse cracks due to fiber bridging.

Barthelat et al. [144, 145] developed a nacre-mimetic prototype, which mimics the dovetail geometry of the tablets and tablet sliding under tension using computer numerical control

(CNC) machining. Basically, the CNC machining technique guides a tool head (such as a drill bit, saw and so on) through a material according to the geometry provided in a computer-aided design (CAD) file. The technique can machine 2D and 3D geometries, and is thereby capable of mimicking the 3D waviness observed on the nacre-like tablet surfaces. The nacre-like prototype was made from dovetail shaped poly methyl methacrylate (PMMA) tablets, which is also known as acrylic glass. The tablets were chosen for ease of machining and their brittleness, with the objective of making a ductile material out of brittle tablets. Bolts were inserted through the thickness of the tablets to introduce interlocking forces that arise when the tablets slide on one another as the composite is loaded in tension. It was observed that the snug tight configuration produces the lowest strength and toughness as opposed to the higher tightening configurations. In particular, a linear elastic region was observed on the stress-strain curve followed by a hardening phase up to failure strains of about 10%. This is a significant improvement over PMMA, which has a failure strain of about 1 to 2%. Although this composite is limited by its low strength for engineering applications, the remarkable improvement in the ductility of a brittle prototype inspires further study into the mimicry of nacreous composites that can achieve high strength and toughness simultaneously.

3.3 Other manufacturing techniques

Other novel manufacturing techniques have been employed to fabricate bio-mimetic structures at the micro- to nano- scales, which are more scarce than the aforementioned techniques in the literature, perhaps due to their complexity: Hot press assisted slip casting (HASC) (micro) [67], ice templating with polymer infiltration (micro) [146]; magnetic freeze casting (micro) [147]; trench etching of the silicon layers and filling of the trenches with photoresist [148]; lost mold fabrication (micro) [149]; colloidal assembly (nano) [150]; nano-particle reinforced composites by nano-grafting (nano) [151]; electrospinning (nano) [152]; pH driven self-assembly (nano) [153]; facile hydrothermal process coating [120]; and thermal processing [13].

Ekiz et al. [67] fabricated nacre-mimetic bulk nano-laminar composites using Hot-press Assisted Slip Casting (HASC). The technique, which combines hot pressing and slip casting to improve the alignment and volume fractions in a reinforced matrix, was employed to manufacture alumina (Al_2O_3) flake-reinforced epoxy matrix nano-laminar composites. The alumina flakes were approximately 10 μm in diameter and 0.35 μm thick, which yielded an

aspect ratio that was similar to that of the aragonite tablets found in nacre. Basically, alumina flakes were manually mixed in epoxy, which was added with the suitable amount of hardener suggested by the manufacturer. This resulted in an inorganic phase volume fraction of 20%, which was deemed to be the highest practical flake content to retain a usable mixture viscosity. A disposable porous plaster mold was prepared and placed at the bottom of a stainless-steel die. The mixture containing alumina flake and epoxy was then poured into the steel die and the die assembly was placed in a custom-made laboratory type hot-press. Excess resin was first forced through the porous mold by applying an initial pressure. Once the desired pressure level was obtained, the temperature was increased to 150°C in 30 min and this pressure was maintained to cure the epoxy matrix, which was then cooled in air at the end of the cycle. The fracture surface, which was obtained from a three-point bending experiment, does not show similar behavior to nacre, which exhibits a uniform tablet sliding mechanism and crack bridging. The stress-strain curves indicate that the specimen fabricated using the HASC technique yielded higher strength than the simply mixed specimen, with exponential failure beyond the linear elastic zone. The plain epoxy resin showed linearly elastic behavior with higher toughness than the HASC and simply mixed specimens but abrupt failure thereafter. Hence, this technique may not be desirable for fabricating composites to resist extreme loads.

Naglieri et al. [146] employed a two-phase process to manufacture hybrid nacre-mimetic composites. The freeze casting method, also known as ice templating, was first employed to manufacture a silicon carbide (SiC) scaffold structure. Mineral bridges can be observed in the scaffold structure, in which the porosity was controlled to be unidirectional. The lamella thickness (δ) and wavelength (λ) are of the order of 6 μm and 25 μm . These parameters are heavily influenced by the freezing front velocity. The freeze casting method basically templates a porous ceramic by exploiting the highly anisotropic solidification behavior of a solvent in a well-dispersed slurry. The slurry may be formed by mixing a ceramic powder (such as SiC) with sintering aids such as water and a binder. The reader may refer to [154] for a detailed explanation of the process employed to manufacture the SiC scaffold structure. The SiC scaffolds were then infiltrated with poly methyl methacrylate (PMMA) to form a nacre-like composite, which mimicked the staggered architecture and many features of the inorganic phase (tablets) e.g. ceramic bridges and so on. The fracture morphology for a SiC/PMMA composite specimen under three-point bending showed fractures in the SiC ceramic nacre-like tablets with significant plastic deformation observed in the PMMA matrix.

Several samples with different volume fractions of SiC and PMMA were tested and the average flexural strength obtained was 130 MPa, which depends on the morphology of the ceramic SiC scaffolds. The fracture resistance was up to 0.85 kJ/m² at crack extensions of roughly 300 μ m. Thus, the freeze casting and polymer infiltration processes can be combined to produce composites that mimic nacre's high strength and toughness quite well. Other researchers have used the freeze-casting method to fabricate a helix-reinforced zirconium dioxide (ZrO₂) epoxy composite, which showed enhanced torsional properties due to the helicoidal orientations of the reinforcements [147].

Chen et al. [148] developed a conch-like crossed-lamellar micro-composite using silicon to represent the brittle/strong aragonite phase, and photoresist to mimic the tough and relatively weak organic matrix. This is a proof of concept study that is limited to these two materials to ascertain whether some of the energy dissipation mechanisms observed in conch shell structures can be achieved. The fabrication process consisted of two steps, namely trench etching of the silicon layers and filling of the trenches with the photoresist polymer. The photoresist is a ductile polymer that is typically used to form a patterned coating on a surface due to its sensitivity to light. Under three-point bending, although the bio-mimetic crossed-lamellar microstructure did not produce as many tunnel cracks that have been observed in conch shells, cracking patterns induced by delamination, as well as bridged cracks were seen to develop. As a result, a significant strength and work of fracture were achieved.

Sabree et al. [149] employed a manufacturing method named modified "lost-mold" to create ceramic scaffolds for tissue engineering applications. In this method, a polymer mold was created by stereolithography in which a mixture of liquid polymer and resin were solidified layer by layer with the help of a laser beam. After the CaO-SiO₂ powder was mixed with a gel casting suspension and filled in the mold, the final slurry of the powder and the suspension liquid was treated to form the designed shape. Finally, removal of the polymer mold was carried out via heat treatment. They successfully developed scaffolds with three different pore sizes of 300 μ m, 400 μ m and 600 μ m.

Martikainen et al. [150] employed a technique that mimics the sacrificial bonds observed in the ligaments connecting the tablets of nacre by functionalizing polymer-coated colloidal nanoplatelets with guanosine groups. The basic idea was to introduce weak bonds between the platelets to promote slippage and sacrificial bonds between the platelets, as opposed to

covalent or ionic bonds, which are found in stiff adhesives. Firstly, the colloidal nacre-mimicking nanoclay platelets were prepared by coating Anionic montmorillonite (MTM) with cationic poly (diallyldimethylammonium chloride) (PDADMAC). The remaining chloride counterions were then allowed exchange to functional anionic 2'-deoxyguanosine 5'-monophosphate (dGMP) counterions, containing hydrogen bonding donors and acceptors. Hence, the counterions promoted hydrogen bonding interactions between the platelets. Several tension tests were then performed on the samples with and without dGMP at 50% humidity. It was found that the addition of dGMP increased the lamellar spacing between the clays from 1.85 to 2.14 nm. This also increased the elastic modulus, tensile strength, and strain by 33%, 41% and 6%, respectively. Specifically, the elastic modulus was increased to 13.5 GPa whilst the tensile strength increased to 67 MPa, leading to improved toughness. However, the failure strain remained at 1% in both cases. Another study was conducted on the samples with and without dGMP at various humidity. By vacuum drying the samples, the samples with dGMP exhibited a linear-elastic response with little plastic deformation, whilst the samples without dGMP exhibited lower strength and higher toughness. Hence, the samples with dGMP mimicked nacre's behavior under dry and hydrated conditions, since nacre is well-known to exhibit a brittle response under dry conditions. By increasing the humidity to 75%, the failure strain of the samples with dGMP increased significantly (up to 2%). Hence, it appears that mimicking the sacrificial bonds of nacre are of high interest to extreme loading applications, which require significant amounts of toughness amplification.

Sun et al. [120] mimicked the stacked structure of fish-scales to manufacture nanostructured coatings by employing a facile hydrothermal process. This process consists of continuous and repeated steps such as reactions between different chemicals, heating, stirring and spinning. The fish-scale inspired nanostructured coatings were made from clean glass, which consists of varied densities of ZnO seeds at the nano-scale. The authors stated that the mimicked structure had remarkable characteristics such as tunable optical properties and a self-cleaning surface. In terms of mechanical properties, the behavior of this bio-inspired structure was adjustable based on the scale-stacking mode and nanostructured coatings.

Funk et al. [119] manufactured a man-made fish scale structure by sewing a cellulose acetate butyrate scale to a polypropylene mesh. The bio-inspired scales were made from cellulose acetate butyrate in rectangular sheets of 9.5 x 12.7 mm. These scales were attached to the polypropylene mesh by a cotton thread such that half of each scale was below the mesh while

the rest stood on top of the mesh. The man-made fish scale structure successfully represented a low-modulus elastic mesh and relatively rigid scales that partially overlap adjacent scales. According to this study, the polypropylene was believed to provide in-plane strength and offer a platform for the interaction between scales when they rotated. This phenomenon was similar to the structure of the natural teleost fish skin. The mechanical behavior of the bio-inspired structure in terms of bending, in-plane deformations and indentation showed good agreement with natural teleost fish skin.

4. Multi-scale modeling of bio-composites

4.1 Macro-scale

Nacre: Ghazlan et al. [68, 155] performed numerical simulations to investigate the mechanisms responsible for nacre's superior toughness amplifications over its brittle constituents under transverse impulsive loading. Voronoi diagrams were employed to mimic the polygonal tablet structure observed in an individual layer of nacre. They employed a computer algorithm to automatically insert the cohesive bonds between the tablets and thereby generate a masonry-like structure that is reminiscent of nacre's tablet architecture. The nacre-like structure (Figure 6) showed significantly higher energy dissipation compared to an equivalent bulk panel. The governing energy dissipation mechanisms were observed to be crack bridging, which was facilitated by the number of staggered layers through the thickness of the bio-mimetic panel, and also in-plane crack deflection through the cohesive bonds between the oblique tablet boundaries in each layer.

Figure 6: a) 3D view of a five-layer nacre-like composite model; b) The Voronoi polygons are bonded by zero-thickness cohesive elements and the composite laminates are bonded by adhesive layers; c) The FE mesh of the adhesive layer; and d) A close-up view of the FE mesh for the adhesion layer.

Flores-Johnson et al. [156] mimicked part of nacre's microstructure to develop an armor grade aluminum panel and simulate it under close-range blast loading. The blast pressures were applied to the front surface of the plate with a peak pressure p_0 in the range of 125 to 1250 MPa. The features they chose to mimic were the multilayer architecture, adhesive bonds between the aluminum layers and sinusoidal waviness at the interface between the layers. The nacre features were mimicked at the macroscopic level with plate dimensions of 200 x 200 x 5.4 mm. The Johnson-Cook plasticity and damage models were employed to simulate the rate-dependent constitutive behavior of the armor graded aluminum alloy AA7075-T651. A cohesive zone model was employed to simulate fracture in the epoxy resin interfaces between the aluminum layers. The crack propagation was compared between a monolithic aluminum panel of equal mass and the nacre-like panel. It is clear that the nacre-like panel did not experience any cracking at the back face but rather, at the interface closest to the blast face upon rebound. Furthermore, the back face velocity of the nacre-like panel was lower than that of the monolithic panel (200 m/s as opposed to 250 m/s). They attributed these improvements to the hierarchical structure of nacre, which facilitates globalized energy absorption by inter-layer interlocking, delamination and friction. Even though several simple features of nacre's microstructure have been mimicked in this case, it exhibits significant potential when applied to critical structural components under extreme events such as blast loading. A step further may be taken in terms of mimicking the tablet geometries and cohesive bonding between adjacent tablets in the same layer, which may distribute fracture more uniformly throughout the composite. This may enhance the energy dissipated in the panel through additional uniformly distributed fracture sites.

Flores-Johnson et al. [157] also investigated the behavior of a nacre-mimetic panel under impact loading. A similar panel to that described in the aforementioned study was used but cohesive bonds between adjacent square tablets in the same layer were mimicked in this study. Although the projectile penetrated both the nacre-like and monolithic plates in all cases, the nacre-like plate showed a notable reduction in the residual velocity of the

projectile. However, this comparison was highly sensitive to the thickness of the plate and impact velocity, where the thickest nacre-like plate (9.6 mm) showed a higher residual velocity than the monolithic plate at impact velocities lower than 700 m/s. Hence, in the case of impact loading, a stiff brittle plate may be required to transfer the load from the projectile since the cohesive bonds between the adjacent nacre tablets in the same layer fracture catastrophically near the projectile impact location. Recall that the mollusk shell comprised a two layers armor system with a stiff brittle outer calcite layer for transferring impact loads from predator bites to the inner nacreous layer. This is imperative under impact loading, which is highly localized.

The performance of a nacre-mimetic panel under impact loading from a fragment simulating projectile (FSP) was investigated by Grujicic et al. [158]. The authors developed a finite element model to capture the ballistic impact behavior and penetration resistance of the nacre-like panel, which is composed of seven layers of strong boron carbide (B_4C) ceramic tablets bonded by a ductile elastomer (polyurea). The FSP was modeled as a solid right circular cylindrical fragment-simulating projectile made from a tungsten heavy-alloy with a diameter and height of 10 mm. The projectile impacted the target at 90° and 75° to the surface with an incident velocity of 600 m/s. Interlocking between layers was simulated by adjusting the surface profile to create dovetail geometries at the tablet interfaces. The roughness of the surface between layers was also considered in this study. The performance of the nacre-like composite panel was compared to a monolithic B_4C plate with an identical areal density. The residual velocity of projectile after penetrating the nacre-mimetic panel was found to be 10 times lower than that of the monolithic panel. The nacre-mimetic panel also significantly reduced the mass and velocity of fragments. The research also studied the effects of tablet-surface profiling, roughness and mineral bridges, and provided an optimized configuration for the nacre-like armour.

Gu et al. [131] studied the impact behavior of a bio-inspired composite panel that was based on the hierarchical structure of conch shells. A 3D finite element (FE) model was developed to capture the velocity profile, crack propagation and crack distribution. The authors also performed drop tower tests to validate the FE model. The simulation results strongly agreed with the experiment in terms of predicting the dynamic crack propagation in the hierarchical composite structure. In addition, the FE model successfully captured the velocity profile obtained from the experiment. These results demonstrated the strong capability of the cross-

lamellar structure in preventing perforation. The simulation also showed that cracks were distributed area throughout the composite structure rather than being localized. Crack propagation occurred through tortuous rather than straight paths.

Funk et al. [119] developed a finite element model to capture the in-plane and flexural deformation of a man-made fish scale structure. This structure, which consists of a flexible polypropylene mesh and comparatively rigid plastic scales, represents the structure of the natural teleost fish skin. The modeled mesh was composed of many beams that represented fibers while each scale was replaced by a spring. Because the ratio between the length and the depth of the fibrous beam was too small, the authors neglected shear effects in the fiber model. The spring stiffness was dependent on the type of simulation to account for compression, tension, bending, and in-plane or out-of-plane rotation of the scale. Similarly, the interactions between adjacent scales in bending were simulated by springs. The finite element model was able to capture the deformation mechanisms of the bio-mimetic fish scale structure, which were observed experimentally.

4.2 Meso-scale

Vernerey et al. [18] presented a two-dimensional model to investigate the relationship between the fish scale structure and its bending behavior. In this idealized model, straight scales were attached to a straight support with a rigidity that was larger than that of each individual scale. The displacement of a scale was restrained by a support and an additional rotational spring. The support was modeled as a homogeneous material and assumed to experience the same curvature under bending. The deformation of the support caused the deformation and rotation of the scales, as well as contact forces between adjacent scales. Hence, the bending stiffness of the fish scale structure was attributed to the elastic energy of the scales and support deformation. The model was built on two hypotheses, namely that the arrangement of the fish scales is periodic and the bending deformation for all scales is identical. With these hypotheses, the fish scale structure was represented by only one scale. The interaction between adjacent scales was simulated as concentrated forces on contact points while the support was replaced by a force and a moment. The simplified model of the scale successfully captured the effects of scale density, attachment stiffness and bending stiffness on strain stiffening, average bending stiffness, mass density and resistance to fracture. Specifically, an increase in scale density resulted in an increase in the average bending stiffness and mass density, and a decrease in the strain stiffening effect. On the other

hand, strain-stiffening decreased with an increase in the ratio between the attachment stiffness and bending stiffness of the scale. The simulation also had some limitations such as neglecting the underlying skin elasticity, ignoring the three-dimensional structure of the fish scale and the impact of other organs such as the skeleton, tendons and muscle.

4.3 Micro-mechanical

Nacre: Several attempts were made to link the mechanical properties of nacre to the mechanisms by which it achieves superior toughness through simplified modeling approaches. To this effect, Wei et al. [70] employed a shear lag modeling approach to investigate the quasi-static behavior of nacre at a unit cell level. This modeling approach is typical for lap joint connections, for which the tensile load is assumed to be transferred between two plates via shear at the interface [159]. From the aforementioned experimental investigations, a strong indication is given that nacre is built for tensile loading parallel to the plane of its tablets. The shear lag model also assumes that the tablets in the same layer are not bonded by the matrix, and that failure occurs via plastic deformation in the matrix while the tablets remain linear elastic. This is a reasonable assumption since relatively few tablets fracture under tensile loading. Wei et al. [70] obtained a closed form solution for the normal (σ) and shear stress (τ) stresses by employing a continuum approach. From these expressions, they were able to obtain a strain energy density function to predict the energy absorbed in the composite unit cell. By maximizing the strain energy density, they obtained an optimal overlap length of $1.6 \mu\text{m}$ between the tablets in the adjacent layers, which was close to that found in nacre.

Similarly, Wei et al. [70] investigated the behavior of a representative unit cell of nacre under tension where the matrix was assumed to exhibit elasto-plastic behavior. Again, it was assumed that the tensile stress was transferred between the stiff tablets via shear in the softer matrix. The shear stress transferred through the matrix has three zones of interest, namely an elastic zone, plastic zone and failure zone. Again, failure was predicted to occur at the edges of the matrix, where the shear stress is at a maximum. By using the shear lag modeling approach, they obtained an optimal overlap length of $1.7 \mu\text{m}$ in this case. The criterion employed in this case was that failure occurs in the tablets and matrix simultaneously i.e. the stress/strain limits of the tablets and matrix were reached. Hence, it was concluded that nacre chooses its overlap length between adjacent tablets to maximize the shear transfer efficiency through the matrix. However, this simplified modeling approach does not consider the wavy

geometry observed on the surface of nacreous tablets, nor the polygonal geometry of the tablets.

Askarinejad et al. [160] investigated the influence of several microstructural features of nacre under bending using finite element analysis. The model is composed of beam elements (aragonite platelets), which were connected by link elements (mineral bridges, organic matrix and nano-asperities). Each platelet had an estimated length and thickness of 4 μm and 0.52 μm , respectively. The gap between two adjacent platelets and layers are approximately 20 nm and 24 nm, respectively. The contribution of each component to the overall stiffness of the sample was investigated by comparing the numerical model with an existing four-point bending test. The ultimate strength of the nacre-like structure is highly dependent on the area fraction of the asperities and bridges rather than the stiffness of the organic matrix. However, the stiffness of the organic layer strongly affects the stiffness of the multilayered material. The overall tensile toughness and strength have a strong correlation with the aspect ratio of the platelets while the area fraction of the bridges is proportional to the highest tensile toughness. Remarkably, the study pointed out the significant effects of the mineral bridges on the mechanical properties of abalone nacre. The existence of mineral bridges enhanced the tensile toughness and strength of nacre. Moreover, by improving the stiffness of the organic matrix, they indirectly stiffen the structure of nacre.

Kotha et al. [69] investigated the quasi-static behavior of *Pinctada* nacre under tension using a modified two-dimensional shear lag model. The matrix interface was also assumed flat in this study. In this case, the model was used to predict Young's modulus of nacre. To this effect, a closed form solution was obtained to relate the elastic modulus of the composite to its material properties, which were obtained from the literature. Note that this model is only applicable to high volume fractions of platelet reinforcements (>90 %), as they did not account for the normal stress transferred in the overlap region of the unit cell. This is reasonable given that nacre consists of 95% vol. aragonite. The model predicted Young's modulus of 64 GPa for hydrated nacre, which is in close agreement with experimental observations (around 70 GPa). Furthermore, the same trend of load transfer in the matrix was observed, namely that the shear stress is at a maximum at the edges of the unit cell and gradually falls to a minimum in the middle of the cell. However, the stress-strain curve showed a linear increase beyond yielding in the matrix up to failure, which is similar to the behavior of bulk aragonite. In contrast, the stress-strain curve of nacre shows a linear-elastic

region followed by a hardening phase. Hence, the simplified assumption that there are no organic matrix bonds between adjacent tablets in the same layer may be attributed to this discrepancy.

Dutta et al. [161] also investigated the mechanical behavior of nacre at the unit cell level via a shear lag modeling approach under tension but applied dynamic loading pulses (triangular and sinusoidal) to the unit cell that are reminiscent with that of a Split Hopkinson Pressure Bar (SHPB). They also used the properties of spider silk and collagen fibrils in tendon/bone from the literature, which also exhibit a staggered microstructure, to investigate the efficacy of the modeling approach in predicting an optimal overlap length. To obtain the critical overlap length, Dutta et al. [161] minimized the peak shear stress in the interface. This gave optimal overlap lengths of 2.5 μm for nacre, 5 nm for spider silk and 36 nm for collagen fibrils in tendon/bone, which are close to the average overlap lengths obtained from microscopy observations. Hence, two contradictory criteria were chosen to obtain the critical overlap lengths, which happened to be close to the average tablet overlap length found in nacre. This raises the question of whether nacre elects to minimize the shear stress transferred in the matrix, which reduces the energy absorbed by the unit cell, or maximize the strain energy density of the overall unit cell, which does the opposite. Ultimately, finite element techniques need to be employed to investigate the effects of the geometry of the tablets and the organic matrix bonds between adjacent tablets on the damage distribution in the composite. This will provide further insights into the influence of the tablet overlap length on the damage mitigating mechanisms found in nacre.

Dutta et al. [162] investigated the influence of the overlap length in nacre in minimizing the crack driving force at the interface. This is another independent criterion used to determine the influence of the overlap length on delamination at the interface. Again, the shear lag modeling approach was used to quantify this behavior based on a unit cell model of the staggered tablet arrangement at the intrinsic region ahead of the crack tip. In their schematic of a cracked nacre sample, they identified the intrinsic and extrinsic toughening regions as crack initiation and crack growth regions, respectively. The unit cell model analyses the crack initiation zone and the toughening mechanisms associated with it. Note that the model assumes that a crack propagates through the thickness of nacre, thereby ignoring damage to the cohesive bonds between the tablets in the same layer as with the aforementioned unit cell models. They observed that the crack driving force is highly influenced by the overlap length

between the tablets in adjacent layers, such that it approaches a minimum at an overlap length of approximately $1.6\ \mu\text{m}$, which is the tablet overlap length observed in nacre. Note that this simplified model assumed that the tablet and matrix exhibit linear elastic behavior with no bending or rotation about the y-axis. Given that the model also assumes that the integrity of the in-plane cohesive bonds between the tablets is maintained, further investigation is required to verify the influence of the tablet overlap length using numerical methods that account for the polygonal tablet geometries.

Barthelat et al. [163] identified several mechanisms that may be responsible for nacre's remarkable toughness, namely intrinsic toughness in the absence of other toughening mechanisms, crack bridging and the contribution of the wake of the crack process zone. They employed the J-integral approach, which is a common approach used in fracture mechanics to estimate the fracture energy of red abalone nacre in the presence of plastic deformation, to predict the toughness due to crack bridging ($0.012\ \text{kJ/m}^2$) and the fracture toughness contribution due to the wake ($0.75\ \text{kJ/m}^2$). By comparing these results with those observed in a three-point bending experiment, where the fracture toughness is of the order $0.5 - 1.5\ \text{kJ/m}^2$, they found that crack bridging does not contribute much to nacre's superior toughness. The trend observed shows that the fracture toughness of nacre keeps increasing as the crack propagates. This was attributed to the generation of new inelastic regions, which generally require more input energy to drive an advancing crack. The dissipative mechanisms in the biopolymer interface were identified to be responsible for this superior toughening mechanism, along with progressive sliding and locking due to the dovetail shape of the tablets. Hence, the toughening mechanisms of nacre are not well understood, and comprehensive numerical modelling is required to alleviate the simplifications associated with the J-integral approach. This study indicates that the influence of the cohesive bonds on nacre's fracture toughness may be particularly important because they facilitate the opening of cracks between adjacent tablets in the same layer, thereby giving rise to a potentially large number of crack initiation sites, which can maximize the energy dissipation mechanisms across the entire composite. However, the influence of the cohesive bonds between the nacre tablets continues to be ignored in this and the aforementioned analyses.

Shao et al. [164] employed a discontinuous crack bridging model to investigate the origin of the fracture toughness of nacre. This model simplifies the tablets that are contributing to closing the crack as a series of concentrated forces. The crack bridging forces were

determined based on a previous study by Tang et al. [92], who modeled the constitutive behavior of the nacre matrix using a trapezoidal cohesive law. Recalling the aforementioned shear lag modeling approaches, the tensile force in the tablets is transferred via shear at the interface. Thus, the crack bridging forces were determined from the tablet sliding displacement and the shear stress across the tablet interface. They observed that an increase in the thickness of the tablets results in lower toughness, which suggests that the contribution of crack bridging to nacre's toughness is highly dependent on the characteristic size of the tablets. However, one must account for the high tensile stress transferred through the tablets, which may cause them to fracture before the cohesive force in the matrix is activated. Specifically, higher fracture toughness was achieved by tablets with a thickness of less than 1 μm but not thinner than tens of nanometers because this would cause the tablets to break under tension. Although Shao et al. [164] found that crack bridging was a significant toughening mechanism, the aforementioned study by Barthelat et al. [163] found that it was quite small compared to the extrinsic toughness that was compared to a three point bending experiment of a nacre specimen. Hence, the origin of the superior toughness of nacre remains inconclusive.

Tang et al. [92] obtained the contours of nacre's tablet geometry through optical imaging of a red abalone specimen. They constructed a finite element model of a representative volume element (RVE) of nacre by inserting cohesive elements between the tablet boundaries, which were identified as junctions. The tablet interfaces were also modified between adjacent layers to approximately follow a sinusoidal wave, with the exact data obtained from laser profilometry. The cohesive behavior was modelled by a trapezoidal cohesive law using several observations from a tension experiment on a nacre specimen, namely that tablet sliding began at a displacement of 0.9 nm, followed by a plateau region that ended at the maximum opening between adjacent tablets (250 nm) and finally a linear decrease in strength up to an opening displacement of 600 nm, which is the length of the longest ligament connecting two tablets. This cohesive law assumes that the hardening effect in nacre is attributed to the waviness and not the constitutive behavior of the matrix i.e. the matrix only contributes to large plastic deformation such that it maintains cohesion between the tablets over large sliding distances. A cohesive strength of 25 MPa was obtained from the shear experiment. It was observed from the stress-strain curve that the model with a flat tablet interface failed prematurely at a much lower strain than that of the model with the wavy

interface. This was attributed to the interlocking between the tablets when they slid on one another, thereby inducing a strain hardening effect.

Tran et al. [165] developed a nacre-mimetic composite panel and assessed its performance when subjected to underwater blast loading using a fluid-structure interaction approach, with a coupled acoustic-solid technique to describe the physical interaction between water and the nacre-like composite panels. The panel consisted of several layers of e-glass fiber/epoxy composite laminae (0.6 mm thick), which were bonded together by 0.1 mm thick layers of vinylester. Each layer consisted of dovetail shaped tablets and was modelled using continuum shell elements, and cohesive zone elements were used to bond the adjacent layers. Rate-dependence was incorporated in the bi-linear traction-separation law to simulate the constitutive behavior of the cohesive bonds. The performance of the nacre-like panel was compared to a monolithic panel of equal mass. The nacre-like panel was found to alleviate stress concentrations and showed more a uniform damage distribution across the entire composite than the monolithic panel. The dovetail shaped geometry reduced delamination between the interlayer adhesive bonds, which was attributed to interlocking between the adjacent tablets. Hence, nacre-mimetic composites show promising behavior under extreme loading in terms of superior energy dissipation compared to their monolithic counterparts. Recall that the dovetail geometries observed in the aforementioned experimental studies were highlighted as an important feature of nacre, which was highly responsible for its superior toughness.

Kamat et al. [113] introduced a calibrated model based on experimental results to simulate two unique energy dissipation mechanisms of the conch shell, namely multiple cracking and crack bridging. Multiple cracking in the weak layer of the conch shell was simulated by a plane strain model. The model consisted of a tough and weak layer. Both layers had the same thickness, Young's modulus, and Poisson's ratio but a different fracture toughness. The shell structure was modeled as an elastic homogeneous and isotropic material with an assumption that tunnel cracks (cracks that propagate through the thickness along the weak layers between first-order lamellae) appeared equally on the edge of the specimen. On the other hand, crack bridging was also modeled by introducing non-linear springs across the crack surfaces. These springs followed a cohesive law and were removed if the crack opening reached a predefined value. A crack bridging finite element model was developed to predict the energy dissipation.

This calibrated model predicted a fracture toughness that closely matched that obtained from a four-point bending experiment on a conch specimen.

4.4 Nano-scale

Nacre: On the notion that the mineral platelets must be able to carry large tensile stresses without fracture, such that shear stresses can be transferred efficiently through the protein/mineral interface, Gao et al. [87] investigated the nano-scale fracture mechanics of the tablets using Griffith's fracture criterion for brittle materials. This load transfer mechanism has been the center of much research on nacre's mechanical behavior under tension. Recall that the mineral tablets are sensitive to inclusions during the biomineralization process, where protein inclusions become embedded in the tablets. Hence, the inclusions were modeled as crack-like flaws because the soft protein inclusions within a hard mineral crystal are mechanically equivalent to embedded microcracks due to their low modulus [87]. By employing Griffith's fracture criterion, a critical length scale ($h^* \approx 30$ nm) was found where the nacre tablets would be insensitive to flaws such that the fracture strength is not sensitive to the structural size of the tablets, whereby the tablet material cannot fail due to high stress concentrations at the crack tip. This is similar to the early findings by Griffith, who found that the theoretical strength of glass is not reached at failure due to the presence of flaws, as opposed to individual glass fibers embedded in a matrix, where the length of the fibers is much less than the critical flaw size for fractures to occur. Given that the nacre tablets are thicker than the critical flaw size predicted by the aforementioned model ($h \approx 500$ nm), they are sensitive to flaws, and fractures have been observed in some of the tablets under tension in the aforementioned experimental studies.

Katti et al. [166] postulated that the interlocks between the tablets are responsible for nacre's superior toughness over its main brittle constituent. They developed a finite element (FE) model based on images obtained from a scanning electron micrograph of the fracture surface of the tablets. The FE model incorporates interlocks between the adjacent tablets. The interpenetrating tablets generate corresponding lateral forces that impede tablets sliding, with the organic matrix thickness still intact at 20 nm. The stress-strain curve shows the typical behavior observed in nacre, a linear-elastic region followed by a hardening phase. It was observed that the FE model undergoes several phases, with the interlocks failing near the loading face first (A), followed by failure at the interlocks opposite to the loading face (B), the interlocks on the sides subsequently fail (C) and finally all of the interlocks fail (D). The

FE model is not able to capture neither the strength of nacre under tension (70 MPa) nor the failure strain (1%) observed experimentally. This suggests that there may be another hardening mechanism present, namely the waviness at the tablet interface observed in the aforementioned study by Tang et al. [92], or that the interlocks cause premature failure due to stress concentrations at the jagged edges, whereas nacre tends to build smoother surfaces at the interface between adjacent tablets.

5. Discussion on bio-mimetic features for civil/structural applications

Limited studies have also been conducted to investigate the performance of bio-mimetic composites in the context of structural applications. Chen et al. [167] mimicked the sacrificial bond and hidden length feature of nacreous ligaments to develop a model of an optimized bio-inspired base isolation system. They found that the proposed system showed significant advantages compared to traditional passive isolators (e.g. the lead rubber bearing system), particularly under near-fault earthquake excitations. By mimicking the same feature, Kwon et al. [168] investigated the performance of a bio-inspired damper for mitigating wind excitations on buildings. They subjected a single degree of freedom (SDOF) model to a range of resonant frequencies reminiscent of vortex shedding and found that the peak displacement was reduced by 43% compared to a conventional tuned mass damper. Constantz et al. [169] took inspiration from the mineral crystals found in bone to develop bio-inspired concrete by using precursors of amorphous calcium carbonate to form rapid-setting high strength cement. This can result in the mass production of calcium carbonate-based cement using waste materials in the future, which can address global sustainability issues.

Ghazlan et al. [68] mimicked the polygonal bricks and mortar structure of nacre to investigate the performance of a bio-inspired composite panel under blast loading. They observed that the nacre-like panel dissipated a significant amount of energy compared to a monolithic panel of equal mass, which was attributed to crack deflection and bridging facilitated by the mortar-like bonds. Similarly, Flores-Johnson et al. [157] mimicked the staggered structure of nacre to simulate the behavior of a bio-inspired composite panel under impact loading, which showed a notable reduction in the residual velocity of the impacting projectile compared to an equivalent monolithic panel. Tran et al. [165] also developed a nacre-inspired composite panel by mimicking the interfacial waviness between adjacent bricks in nacre. They observed well-distributed damage at the interface of the composite under underwater blast loading,

which resulted in prominent energy dissipation. Ghazlan et al. [170] developed an analytical model to capture the influence of nacre's interfacial geometry on its energy absorption capacity. They employed a typical lap joint modeling approach used in structural engineering, which assumes that tension through the brick-like tablets is transferred via shear through the interface. The results indicated that the waviness of the nacreous tablets amplifies the energy absorbed by the composite whilst improving the distribution of shear forces along the interface. Ghazlan et al. [171] also investigated the performance of a nacre-like composite panel under quasi-static loading, which they validated with experimental data. They found that the oblique orientations of the tablet bonds deflect cracks. Furthermore, by investigating different constitutive laws to model the behavior of the inter-tablet and inter-layer bonds, they found that the cohesive law governs the hardening behavior at the interface. This finding contradicts prior results, which indicate that the interfacial waviness was a prominent toughening mechanism.

Other studies on biomimetics in the context of structural applications include bio-inspired magnetorheological dampers for vibration mitigation under earthquake loading [172], staggered nacre-like composite beams [173, 174], meso-scale investigations on durable and sustainable cement paste inspired by nature [175], bio-inspired ceramic jackets for enhancing the performance of concrete under projectile impacts [176], and design of T-joints in composite bio-inspired hierarchical structure [177].

6. Conclusions

A comprehensive review was conducted on selected lamellar structures found in nature to extract the structure-function relationships that govern their performance in the context of protective structures. The latest manufacturing techniques were also explored to assess the advantages and drawbacks of modern methods that have been employed to fabricate proof-of-concept bio-mimetic composites. Additive manufacturing techniques such as 3D printing and laser cutting were to be the most popular because they can fabricate complex bio-mimetic prototypes at the micro- to macro-scale most efficiently, by automatically converting computer-aided designs into a physical model. Modeling approaches that have been employed at different length scales to predict the performance of biological structures have also been explored. Finite element modeling was found to be dominant because it can capture the complex geometries and constitutive behavior of intricate biological structures at different

length scales with the highest computational efficiency. A common trend observed between nacre, conch and fish scales was that crack deflection and bridging through different lamellae were the governing toughening mechanisms. The arrangement of each individual lamella is quite important. As such, natural structures can simultaneously achieve high stiffness and toughness by deflecting cracks, and high strength in different directions, due to the orientations of the individual lamellae. Several attempts to mimic biological structures from a modeling and manufacturing perspective have also been explored, which are quite new to the structural engineering discipline. It is important to progress this exciting area of research to a level of producing the protective structures of the future through advanced modeling and manufacturing technologies.

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8. References

1. Wang, Z., Z. Li, W. Zhou, and D. Hui, *On the influence of structural defects for honeycomb structure*. Composites Part B: Engineering, 2018. **142**: p. 183-192.
2. Wu, Y., Q. Liu, J. Fu, Q. Li, and D. Hui, *Dynamic crash responses of bio-inspired aluminum honeycomb sandwich structures with CFRP panels*. Composites Part B: Engineering, 2017. **121**: p. 122-133.
3. Liu, Q., J. Ma, Z. He, Z. Hu, and D. Hui, *Energy absorption of bio-inspired multi-cell CFRP and aluminum square tubes*. Composites Part B: Engineering, 2017. **121**: p. 134-144.
4. Hu, Z., K. Thiyagarajan, A. Bhusal, T. Letcher, Q.H. Fan, Q. Liu, and D. Salem, *Design of ultra-lightweight and high-strength cellular structural composites inspired by biomimetics*. Composites Part B: Engineering, 2017. **121**: p. 108-121.
5. Tan, C. and H.M. Akil, *Impact response of fiber metal laminate sandwich composite structure with polypropylene honeycomb core*. Composites Part B: Engineering, 2012. **43**(3): p. 1433-1438.
6. Khatam, H. and M.-J. Pindera, *Microstructural scale effects in the nonlinear elastic response of bio-inspired wavy multilayers undergoing finite deformation*. Composites Part B: Engineering, 2012. **43**(3): p. 869-884.

7. Chen, P.-Y., J. McKittrick, and M.A. Meyers, *Biological materials: Functional adaptations and bioinspired designs*. Progress in Materials Science, 2012. **57**(8): p. 1492-1704.
8. An, B. and H.D. Wagner, *Protection mechanisms of the carapace of a box turtle*. Journal of the mechanical behavior of biomedical materials, 2017. **71**: p. 54-67.
9. Seki, Y., M.S. Schneider, and M.A. Meyers, *Structure and mechanical behavior of a toucan beak*. Acta Materialia, 2005. **53**: p. 5281-5296.
10. Naleway, S.E., M.M. Porter, J. McKittrick, and M.A. Meyers, *Structural Design Elements in Biological Materials: Application to Bioinspiration*. Adv. Mater., 2015. **27**: p. 5455-5476.
11. Currey, J.D. and J.D. Taylor, *The mechanical behaviour of some molluscan hard tissues*. Journal of Zoology, 1974. **173**: p. 395-406.
12. Narducci, F. and S.T. Pinho, *Exploiting nacre-inspired crack deflection mechanisms in CFRP via micro-structural design*. Composites Science and Technology, 2017. **153**: p. 178-189.
13. Ikoma, T., H. Kobayashi, J. Tanaka, D. Walsh, and S. mann, *Microstructure, mechanical, and biomimetic properties of fish scales from Pagrus major*. Journal of Structural Biology, 2003. **142**: p. 327-333.
14. Rudykh, S., C. Ortiz, and M.C. Boyce, *Flexibility and protection by design: imbricated hybrid microstructures of bio-inspired armor*. Soft Matter, 2015. **11**: p. 2547-2554.
15. Lin, A.Y.M., M.A. Meyers, and K.S. Vecchio, *Mechanical properties and structure of Strombus gigas, Tridacna gigas, and Haliotis rufescens sea shells: A comparative study*. Materials Science and Engineering C, 2006. **26**: p. 1380-1389.
16. Rho, J.Y., L. Kuhn-Spearing, and P. Zioupos, *Mechanical properties and the hierarchical structure of bone*. Medical Engineering and Physics, 1998. **20**: p. 92-102.
17. Chen, P.Y., A.Y. Lin, J. McKittrick, and M.A. Meyers, *Structure and mechanical properties of crab exoskeletons*. Acta Biomater, 2008. **4**(3): p. 587-96.
18. Vernerey, F.J. and F. Barthelat, *On the mechanics of fishscale structures*. International Journal of Solids and Structures, 2010. **47**: p. 2268-2275.

19. Jongpaibojkosit, N. and P. Jearanaisilawong, *Mechanical properties and numerical simulation of Sulcata tortoise carapace*. Journal of the mechanical behavior of biomedical materials, 2017. **72**: p. 261-267.
20. Lin, Y.S., C.T. Wei, E.A. Olevsky, and M.A. Meyers, *Mechanical properties and the laminate structure of Arapaima gigas scales*. Journal of the Mechanical Behavior of Biomedical Materials, 2011. **4**: p. 1145-1156.
21. Sullivan, T.N., B. Wang, H.D. Espinosa, and M.A. Meyers, *Extreme lightweight structures: avian feathers and bones*. Materials Today, 2017.
22. Department, U.S., *National consortium for the study of terrorism and responses to terrorism: Annex of statistical information*. 2013, University of Maryland: Maryland, US. p. 1-11.
23. Librescu, L., S.-Y. Oh, and J. Hohe, *Linear and non-linear dynamic response of sandwich panels to blast loading*. Composites Part B: Engineering, 2004. **35**(6-8): p. 673-683.
24. Anderson, T.A., *An investigation of SDOF models for large mass impact on sandwich composites*. Composites Part B: Engineering, 2005. **36**(2): p. 135-142.
25. Gómez-del Río, T., R. Zaera, E. Barbero, and C. Navarro, *Damage in CFRPs due to low velocity impact at low temperature*. Composites Part B: Engineering, 2005. **36**(1): p. 41-50.
26. Sutherland, L. and C.G. Soares, *Impact behaviour of typical marine composite laminates*. Composites Part B: Engineering, 2005. **37**(2-3): p. 89-100.
27. Bahei-El-Din, Y.A. and G.J. Dvorak, *Enhancement of blast resistance of sandwich plates*. Composites part B: engineering, 2008. **39**(1): p. 120-127.
28. Batra, R. and N. Hassan, *Blast resistance of unidirectional fiber reinforced composites*. Composites Part B: Engineering, 2008. **39**(3): p. 513-536.
29. Taha, M.M.R., A.B. Colak-Altunc, and M. Al-Haik, *A multi-objective optimization approach for design of blast-resistant composite laminates using carbon nanotubes*. Composites Part B: Engineering, 2009. **40**(6): p. 522-529.
30. Jackson, M. and A. Shukla, *Performance of sandwich composites subjected to sequential impact and air blast loading*. Composites Part B: Engineering, 2011. **42**(2): p. 155-166.

31. Porras, A. and A. Maranon, *Development and characterization of a laminate composite material from polylactic acid (PLA) and woven bamboo fabric*. Composites Part B: Engineering, 2012. **43**(7): p. 2782-2788.
32. Boumbimba, R.M., C. Froustey, P. Viot, and P. Gerard, *Low velocity impact response and damage of laminate composite glass fibre/epoxy based tri-block copolymer*. Composites Part B: Engineering, 2015. **76**: p. 332-342.
33. Petrucci, R., C. Santulli, D. Puglia, E. Nisini, F. Sarasini, J. Tirillò, L. Torre, G. Minak, and J. Kenny, *Impact and post-impact damage characterisation of hybrid composite laminates based on basalt fibres in combination with flax, hemp and glass fibres manufactured by vacuum infusion*. Composites Part B: Engineering, 2015. **69**: p. 507-515.
34. Wang, Y., X. Chen, R. Young, I. Kinloch, and G. Wells, *A numerical study of ply orientation on ballistic impact resistance of multi-ply fabric panels*. Composites Part B: Engineering, 2015. **68**: p. 259-265.
35. Caminero, M., J. Chacón, I. García-Moreno, and G. Rodríguez, *Impact damage resistance of 3D printed continuous fibre reinforced thermoplastic composites using fused deposition modelling*. Composites Part B: Engineering, 2018. **148**: p. 93-103.
36. Imbalzano, G., S. Linforth, T.D. Ngo, P.V.S. Lee, and P. Tran, *Blast resistance of auxetic and honeycomb sandwich panels: Comparisons and parametric designs*. Composite Structures, 2018. **183**: p. 242-261.
37. Imbalzano, G., T. Ngo, and P. Tran, *A numerical study of auxetic composite panels under blast loadings*. Composite Structures, 2015. **135**: p. 339-352.
38. Imbalzano, G., P. Tran, T. Ngo, and P.V. Lee, *Three-dimensional modelling of auxetic sandwich panels for localised impact resistance*. Journal of Sandwich Structures and Materials, 2015: p. 1-26.
39. Hou, X., H. Hu, and V. Silberschmidt, *Numerical analysis of composite structure with in-plane isotropic negative Poisson's ratio: Effects of materials properties and geometry features of inclusions*. Composites Part B: Engineering, 2014. **58**: p. 152-159.
40. Kaminakis, N.T. and G.E. Stavroulakis, *Topology optimization for compliant mechanisms, using evolutionary-hybrid algorithms and application to the design of auxetic materials*. Composites Part B: Engineering, 2012. **43**(6): p. 2655-2668.
41. Poźniak, A.A., K.W. Wojciechowski, J.N. Grima, and L. Mizzi, *Planar auxeticity from elliptic inclusions*. Composites Part B: Engineering, 2016. **94**: p. 379-388.

42. Qi, C., A. Remennikov, L.-Z. Pei, S. Yang, Z.-H. Yu, and T.D. Ngo, *Impact and close-in blast response of auxetic honeycomb-cored sandwich panels: Experimental tests and numerical simulations*. Composite structures, 2017. **180**: p. 161-178.
43. Mohotti, D., M. Ali, T. Ngo, J. Lu, and P. Mendis, *Strain rate dependent constitutive model for predicting the material behaviour of polyurea under high strain rate tensile loading*. International Journal of Materials and Design, 2014. **53**: p. 830-837.
44. Mohotti, D., M. Ali, T. Ngo, J. Lu, P. Mendis, and D. Ruan, *Out-of-plane impact resistance of aluminium plates subjected to low velocity impacts*. Materials and Design, 2013. **50**: p. 413-426.
45. Scarponi, C., F. Sarasini, J. Tirillò, L. Lampani, T. Valente, and P. Gaudenzi, *Low-velocity impact behaviour of hemp fibre reinforced bio-based epoxy laminates*. Composites Part B: Engineering, 2016. **91**: p. 162-168.
46. Yu, B., C. Geng, M. Zhou, H. Bai, Q. Fu, and B. He, *Impact toughness of polypropylene/glass fiber composites: interplay between intrinsic toughening and extrinsic toughening*. Composites Part B: Engineering, 2016. **92**: p. 413-419.
47. Alcock, B., N. Cabrera, N.-M. Barkoula, Z. Wang, and T. Peijs, *The effect of temperature and strain rate on the impact performance of recyclable all-polypropylene composites*. Composites Part B: Engineering, 2008. **39**(3): p. 537-547.
48. Nguyen, K.T.Q., T. Ngo, P. Mendis, and D. Heath, *Performance of high-strength concrete walls exposed to fire*. Advances in Structural Engineering, 2017.
49. Nguyen, Q.T., T. Ngo, P.A. Tran, P. Mendis, and D. Battacharyya, *Influences of clay and manufacturing on fire resistance of organoclay/thermoset nanocomposites*. Composites Part A: Applied Science and Manufacturing, 2015. **74**: p. 26-37.
50. Hajimohammadi, A., T. Ngo, P. Mendis, T. Nguyen, A. Kashani, and J.S.J. van Deventer, *Pore characteristics in one-part mix geopolymers foamed by H₂O₂: The impact of mix design*. Materials and Design, 2017. **130**: p. 381-391.
51. Rupasinghe, M., P. Mendis, T. Ngo, T.N. Nguyen, and M. Sofi, *Compressive strength prediction of nano-silica incorporated cement systems based on a multiscale approach*. Materials and Design, 2017. **115**: p. 379-392.

52. Rupasinghe, M., R. San Nicolas, P. Mendis, M. Sofi, and T. Ngo, *Investigation of strength and hydration characteristics in nano-silica incorporated cement paste*. Cement and Concrete Composites, 2017. **80**: p. 17-30.
53. Wang, B., J. McKittrick, and M.A. Meyers, *Keratin: Structure, mechanical properties, occurrence in biological organisms, and efforts at bioinspiration*. Progress in Materials Science, 2016. **76**: p. 229-318.
54. Meyers, M.A., J. McKittrick, and P.Y. Chen, *Structural Biological Materials: Critical Mechanics-Materials Connections*. Science, 2013. **339**(773-779).
55. Meyers, M.A., P.Y. Chen, M.I. Lopez, Y. Seki, and A.Y.M. Lin, *Biological materials: A materials science approach*. Journal of the Mechanical Behavior of Biomedical Materials, 2011. **4**: p. 626-657.
56. Meyers, M.A., P.Y. Chen, A.Y.M. Lin, and Y. Seki, *Biological materials: Structure and mechanical properties*. Progress in Materials Science, 2008. **53**: p. 1-206.
57. Barthelat, F., Z. Yin, and M.J. Buehler, *Structure and mechanics of interfaces in biological materials*. Nature Reviews, 2016: p. 1-16.
58. Wegst, U.G.K., H. Bai, E. Saiz, A.P. Tomsia, and R.O. Ritchie, *Bioinspired structural materials*. Nature Materials, 2014. **14**: p. 23-36.
59. Chen, P.Y., A.Y.M. Lin, A.G. Stokes, Y. Seki, S.G. Bodde, J. McKittrick, and M.A. Meyers, *Structural biological materials: Overview of Current research*. JOM, 2008. **60**(23): p. 23-32.
60. Chen, P.Y., A.Y.M. Lin, Y.S. Lin, Y. Seki, A.G. Stokes, J. Peyras, E.A. Olevsky, M.A. Meyers, and J. McKittrick, *Structure and mechanical properties of selected biological materials*. Journal of the Mechanical Behavior of Biomedical Materials, 2008. **1**: p. 208-226.
61. Fratzl, P. and R. Weinkamer, *Nature's hierarchical materials*. Progress in Materials Science, 2007. **52**: p. 1263-1334.
62. Meyers, M.A., A.Y.M. Lin, Y. Seki, P.Y. Chen, B.K. Kad, and S. Bodde, *Structural Biological Composites: An Overview*. JOM, 2006. **58**(7): p. 35-41.
63. Currey, J.D., *Mechanical properties of mother of pearl in tension*. Proceedings of the Royal Society of London Series B-Biological Sciences, 1977. **196**(1125): p. 443-463.
64. An, Y., Z. Liu, G. Wang, and W. Wu, *Microstructure and toughening mechanism of compressive fractured nacre*. Advanced Materials Research, 2011. **228-229**: p. 727-731.

65. Barthelat, F., *Designing nacre-like materials for simultaneous stiffness, strength and toughness: Optimum materials, composition, microstructure and size*. Journal of the Mechanics and Physics of Solids, 2014. **73**: p. 22-37.
66. Ortiz, C. and M.C. Boyce, *Bioinspired structural materials*. Materials Science, 2008. **319**(5866): p. 1053-1054.
67. Ekiz, O.O., A.F. Dericioglu, and H. Kakisawa, *An efficient hybrid conventional method to fabricate nacre-like bulk nano-laminar composites*. Materials Science and Engineering C, 2009. **29**: p. 2050-2054.
68. Ghazlan, A., T. Ngo, and P. Tran, *Three-dimensional voronoi model of a nacre-mimetic composite structure under impulsive loading*. Composite Structures, 2016. **153**: p. 278-296.
69. Kotha, S.P., Y. Li, and N. Guzelsu, *Micromechanical model of nacre tested in tension*. Journal of Materials Science, 2001. **36**(8): p. 2001-2007.
70. Wei, X., M. Naraghi, and H.D. Espinosa, *Optimal length scales emerging from shear load transfer in natural materials: Application to carbon-based nanocomposite design*. ACSNANO, 2012. **6**(3).
71. Sun, J. and B. Bhushan, *Hierarchical structure and mechanical properties of nacre: a review*. Royal Society of Chemistry, 2012. **2**: p. 7617-7632.
72. Wei, X., T. Filletier, and H.D. Espinosa, *Statistical shear lag model - Unravelling the size effect in hierarchical composites*. Acta Biomaterialia, 2015. **18**: p. 206-212.
73. Menig, R., M.H. Meyers, M.A. Meyers, and K.S. Vecchio, *Quasi-static and dynamic mechanical response of haliotis rufescens (abalone) shells*. Acta Materialia, 2000. **48**(9): p. 2383-2398.
74. Lin, A. and M. Meyers, *Growth and structure in abalone shell*. Materials Science and Engineering A, 2005. **390**: p. 27-41.
75. William Pro, J., R.K. Lim, L.R. Petzold, and M. Utz, *GPU-based simulations of fracture in idealized brick and mortar composites*. Journal of the Mechanics and Physics of Solids, 2015. **80**: p. 68-85.
76. Wilbrink, D.V., M. Utz, R.O. Ritchie, and M.R. Begley, *Scaling of strength and ductility in bioinspired brick and mortar composites*. Applied Physics Letters, 2010. **97**: p. 1-3.
77. Begley, M., N.R. Philips, B.G. Compton, D.V. Wilbrink, R.O. Ritchie, and M. Utz, *Micromechanical models to guide the development of synthetic 'brick and mortar' composites*. Journal of the Mechanics and Physics of Solids, 2012. **60**: p. 1545-1560.

78. Sarikaya, M., *An introduction to biomimetics: A structural viewpoint*. Microscopy Research and Technique, 1994. **27**: p. 360-375.
79. Katti, K.S., B. Mohanty, and D.R. Katti, *Nanomechanical properties of nacre*. Journal of Materials Research, 2006. **21**(5): p. 1237-1242.
80. Feng, Q.L., F.Z. Cui, G. Pu, R.Z. Wang, and H.D. Li, *Crystal orientation, toughening mechanisms and a mimic of nacre*. Materials Science and Engineering C, 2000. **11**: p. 19-25.
81. Song, F. and Y.L. Bai, *Effects of nanostructures on the fracture strength of the interfaces in nacre*. Journal of Materials Research, 2003. **18**(8): p. 1741-1744.
82. Rousseau, M., E. Lopez, P. Stempfle, M. Brendle, L. Franke, A. Guette, R. Naslain, and X. Bourrat, *Multiscale structure of sheet nacre*. Biomaterials, 2005. **26**: p. 6254-6262.
83. Rabiei, R., S. Bekah, and F. Barthelat, *Failure mode transition in nacre and bone-like materials*. Acta Biomaterialia, 2010. **6**(10): p. 4081-4089.
84. Okumura, K., *Fracture strength of biomimetic composites: Scaling views on nacre*. Journal of Physics: Condensed Matter, 2005. **17**: p. 2879-2884.
85. Bertoldi, K., D. Bigoni, and W.J. Drugan, *Nacre: An orthotropic and bimodular elastic material*. Composites Science and Technology, 2008. **68**: p. 1363-1375.
86. Allison, P.G., R.D. Moser, J.P. Schirer, R.L. Martens, J.B. Jordon, and M.Q. Chandler, *In-situ nanomechanical studies of deformation and damage mechanisms in nanocomposites monitored using scanning electron microscopy*. Material Letters, 2014. **131**: p. 313-316.
87. Gao, H., B. Ji, I.L. Jager, E. Arzt, and P. Fratzl, *Materials become insensitive to flaws at nanoscale: Lessons from nature*. Proceedings of the National Academy of Sciences of the United States of America 2003. **100**(10): p. 5597-5600.
88. Blank, S., M. Arnoldi, S. Kohoshnavaz, L. Treccani, M. Kuntz, K. Mann, G. Grathwohl, and M. Fritz, *The nacre protein perlucin nucleates growth of calcium carbonate crystals*. Journal of Microscopy, 2003. **212**(3): p. 280-291.
89. Schaffer, T.E., C. Ionescu-Zanetti, R. Proksch, M. Fritz, D.A. Walters, N. Almquist, C.M. Zaremba, A.M. Belcher, B.L. Smith, G.D. Stucky, D.E. Morse, and P.K. Hansma, *Does abalone nacre form by heteroepitaxial nucleation or by growth through mineral bridges?* Chemistry of Materials, 1997. **9**: p. 1731-1740.

90. Wang, R.Z., H.B. Wen, F.Z. Cui, H.B. Zhang, and H.D. Li, *Observations of damage morphologies in nacre during deformation and fracture*. Journal of Materials Science, 1995. **30**: p. 2299-2304.
91. Wang, R.Z., Z. Suo, A.G. Evans, N. Yao, and I.A. Aksay, *Deformation mechanisms in nacre*. Journal of Materials Research, 2001. **16**(9): p. 2485-2493.
92. Tang, H., F. Barthelat, and H.D. Espinosa, *An elasto-viscoplastic interface model for investigating the constitutive behavior of nacre*. Journal of the Mechanics and Physics of Solids, 2007. **55**: p. 1410-1438.
93. Li, X., W. Chang, Y.J. Chao, R. Wang, and M. Chang, *Nanoscale structural and mechanical characterization of a natural nanocomposite material: The shell of red abalone*. Nano Letters, 2004. **4**(4): p. 613-617.
94. Li, X., Z. Xu, and R. Wang, *In situ observation of nanograin rotation and deformation in nacre*. Nano Letters, 2006. **6**(10): p. 2301-2304.
95. Barthelat, F., C.-M. Li, C. Comi, and H.D. Espinosa, *Mechanical properties of nacre constituents and their impact on mechanical performance*. Journal of Materials Research, 2006. **21**(8): p. 1977-1986.
96. Narasimhulu, K.V. and J.L. Rao, *EPR and IR spectral studies of the sea water mussel Mytilus conradinus shells*. Spectrochimica Acta Part A, 2000. **56**: p. 1345-1353.
97. Espinosa, H.D., J.E. Rim, F. Barthelat, and M. Buehler, *Merger of structure and material in nacre and bone – Perspectives on de novo biomimetic materials*. Progress in Materials Science, 2009. **54**: p. 1059-1100.
98. Song, F., A.K. Soh, and Y.L. Bai, *Structural and mechanical properties of the organic matrix layers of nacre*. Biomaterials, 2003. **24**: p. 3623-3631.
99. Jackson, A.P., J.F.V. Vincent, and R.M. Turner, *The Mechanical Design of Nacre*. Proceedings of the Royal Society of London Series B-Biological Sciences, 1988. **234**(1277): p. 415-440.
100. Meyers, M.A., C.T. Lim, A. Li, B.R. Hairul Nizam, E.P.S. Tan, Y. Seki, and J. McKittrick, *The role of the intertile layer in abalone nacre*. Materials Science and Engineering C, 2009. **29**: p. 2398-2410.
101. Katti, D.R., S.M. Pradhan, and K.S. Katti, *Modeling the organic-inorganic interfacial nanoasperities in a model bio-nanocomposite, nacre*. Reviews on Advanced Materials Science, 2004.

102. Evans, A.G., Z. Suo, R.Z. Wang, I.A. Aksay, M.Y. He, and J.W. Hutchinson, *Model for the robust mechanical behavior of nacre*. Journal of Materials Research, 2001. **16**(9): p. 2475-2484.
103. Katti, K.S. and D.R. Katti, *Why is nacre so tough and strong?* Materials Science and Engineering C, 2006. **26**: p. 1317-1324.
104. Espinosa, H.D., A.L. Juster, F.J. Latourte, O.Y. Loh, D. Gregoire, and P.D. Zavattieri, *Tablet-level origin of toughening in abalone shells and translation to synthetic composite materials*. Nature communications, 2011. **2**.
105. Lopez, M.I., P.E. Meza Martinez, and M.A. Meyers, *Organic interlamellar layers, mesolayers and mineral nanobridges: Contribution to strength in abalone (Haliotis Rufescence) nacre*. Acta Biomaterialia, 2014. **10**: p. 2056-2064.
106. Song, F., X.H. Zhang, and Y.L. Bai, *Microstructure and characteristics in the organic matrix layers of nacre*. Journal of Materials Research, 2002. **17**(7): p. 1567-1570.
107. Smith, B.L., T.E. Schaffer, M. Viani, J.B. Thompson, N.A. Frederick, J. Kindt, A. Belcher, G.D. Stucky, D.E. Morse, and P.K. Hansma, *Molecular mechanistic origin of the toughness of natural adhesives, fibres and composites*. Nature, 1999. **399**(6738): p. 761-763.
108. Oliver, W.C. and G.M. Phar, *An improved technique for determining hardness and elastic-modulus using load and displacement sensing indentation experiments*. Journal of Materials Research, 1992. **7**(6): p. 1564-1583.
109. Karambelas, G., S. Santhanam, and Z.N. Wing, *Strombus gigas inspired biomimetic ceramic composites via SHELL—Sequential Hierarchical Engineered Layer Lamination*. Ceramics International, 2013. **39**: p. 1315-1325.
110. Salinas, C.L., E.E. de Obaldia, C. Jeong, J. Hernandez, P. Zavattieri, and D. Kisailus, *Enhanced toughening of the crossed lamellar structure revealed by nanoindentation*. Journal of the Mechanical Behavior of Biomedical Materials, 2017. **76**: p. 58-68.
111. Shin, Y.A., S. Yin, X. Li, S. Lee, S. Moon, J. Jeong, M. Kwon, S.J. Yoo, Y.M. Kim, T. Zhang, H. Gao, and S.O. Oh, *Nanotwin-governed toughening mechanism in hierarchically structured biological materials*. Nature Communications, 2016: p. 1-10.
112. Kuhn-Spearing, L.T., H. Kessler, E. Chateau, R. Ballarini, and A.H. Heuer, *Fracture mechanisms of the Strombus gigas conch shell: implications for the*

- design of brittle laminates*. Journal of Materials Science, 1996. **31**: p. 6583-6594.
113. Kamat, S., H. Kessler, R. Ballarini, M. Nassirou, and A.H. Heuer, *Fracture mechanisms of the Strombus gigas conch shell: II-micromechanics analyses of multiple cracking and large-scale crack bridging*. Acta Materialia, 2004. **52**: p. 2395-2406.
 114. Zhang, Z., Y.W. Zhang, and H. Gao, *On optimal hierarchy of load-bearing biological materials*. Proceedings of the Royal Society B, 2011. **278**: p. 519-525.
 115. Kamat, S., X. Su, R. Ballarini, and A.H. Heuer, *Structural basis for the fracture toughness of the shell of the conch Strombus gigas*. Nature, 2000. **405**: p. 1036-1040.
 116. Menig, R., M.H. Meyers, M.A. Meyers, and K.S. vECChio, *Quasi-static and dynamic mechanical response of Strombus gigas (conch) shells*. Materials Science and Engineering A, 2001. **297**: p. 203-211.
 117. Romana, L., P. Thomas, P. Bilas, J.L. Mansot, M. Merrifiels, Y. Bercion, and D. Aldana Aranda, *Use of nanoindentation technique for a better understanding of the fracture toughness of Strombus gigas conch shell*. Materials Characterization, 2013. **76**: p. 55-68.
 118. Li, H., Z.H. Xu, and X. Li, *Multiscale hierarchical assembly strategy and mechanical prowess in conch shells (Busycon carica)*. Journal of Structural Biology, 2013. **184**: p. 409-416.
 119. Funk, N., M. Vera, L.J. Szewciw, F. Barthelat, M.P. Stoykovich, and F.J. Vernerey, *Bioinspired Fabrication and Characterization of a Synthetic Fish Skin for the Protection of Soft Materials*. ACS Applied Materials and Interfaces, 2015. **7**: p. 5972-5983.
 120. Sun, Z., T. Liao, W. Li, Y. Dou, K. Liu, L. Jiang, S. Kim, J.H. Kim, and S.X. Dou, *Fish-scale bio-inspired multifunctional ZnO nanostructures*. NPG Asia Materials, 2015. **7**: p. 1-9.
 121. Bigi, A., M. Burghammer, R. Falconi, M.H.J. Koch, S. Panzavolta, and C. Riek, *Twisted Plywood Pattern of Collagen Fibrils in Teleost Scales: An X-ray Diffraction Investigation*. Journal of Structural Biology, 2001. **136**: p. 137-143.
 122. Zylberberg, L., J. Bonaventure, L. Cohen-solal, D.J. Hartmann, and J. Bereiter-Hahn, *Organization and characterization of fibrillar collagens in fish scales in situ and in vitro*. Journal of Cell Science, 1992. **103**: p. 273-285.

123. Zhu, D., C.F. Ortega, R. Motamedi, L. Szewciw, F. Vernerey, and F. Barthelat, *Structure and Mechanical Performance of a "Modern" Fish Scale*. *Advanced Engineering Materials*, 2012. **14**(4): p. 185-194.
124. Torres, F.G., O.P. Troncoso, J. Nakamatsu, C.J. Grande, and C.M. Gomez, *Characterization of the nanocomposite laminate structure occurring in fish scales from Arapaima Gigas*. *Materials Science and Engineering C*, 2008. **28**: p. 1276-1283.
125. Excell, J. and S. Nathan, *The rise of additive manufacturing*. *The engineer*, 2010. **24**.
126. Ngo, T.D., A. Kashani, G. Imbalzano, K.T. Nguyen, and D. Hui, *Additive manufacturing (3D printing): A review of materials, methods, applications and challenges*. *Composites Part B: Engineering*, 2018.
127. Vlasea, M., R. Pilliar, and E. Toyserkani, *Control of structural and mechanical properties in bioceramic bone substitutes via additive manufacturing layer stacking orientation*. *Additive Manufacturing*, 2015. **6**: p. 30-38.
128. Weibmann, V., R. Bader, H. Hansmann, and N. Laufer, *Influence of the structural orientation on the mechanical properties of selective laser melted Ti6Al4V open-porous scaffolds*. *Materials and Design*, 2016. **95**: p. 188-197.
129. Sing, S.L., J. An, W.Y. Yeong, and F.E. Wiria, *Laser and Electron-Beam Powder-Bed Additive Manufacturing of Metallic Implants: A Review on Processes, Materials and Designs*. *Journal of Orthopaedic Research*, 2015: p. 369-385.
130. Tran, P., T.D. Ngo, A. Ghazlan, and D. Hui, *Bimaterial 3D printing and numerical analysis of bio-inspired composite structures under in-plane and transverse loadings*. *Composites Part B*, 2017. **108**: p. 210-223.
131. Gu, G.X., M. Takaffoli, and M.J. Buehler, *Hierarchically Enhanced Impact Resistance of Bioinspired Composites*. *Advanced Materials*, 2017. **29**(28).
132. Sheydaei, E. and E. Toyserkani, *A new approach for fabrication of titanium-titanium boride periodic composite via additive manufacturing and pressure-less sintering*. *Composites Part B: Engineering*, 2018. **138**: p. 140-148.
133. Hu, Y., W. Cong, X. Wang, Y. Li, F. Ning, and H. Wang, *Laser deposition-additive manufacturing of TiB-Ti composites with novel three-dimensional quasi-continuous network microstructure: Effects on strengthening and toughening*. *Composites Part B: Engineering*, 2018. **133**: p. 91-100.

134. Roohani-Esfahani, S., P. Newman, and H. Zreiqat, *Design and Fabrication of 3D printed Scaffolds with a Mechanical Strength Comparable to Cortical Bone to Repair Large Bone Defects*. Scientific Reports, 2016. **6**: p. 1-8.
135. Zou, R., Y. Xia, S. Liu, P. Hu, W. Hou, Q. Hu, and C. Shan, *Isotropic and anisotropic elasticity and yielding of 3D printed material*. Composites Part B: Engineering, 2016. **99**: p. 506-513.
136. Tiwary, C.S., S. Kishore, S. Sarkar, D.R. Mahapatra, P.M. Ajayan, and K. Chattopadhyay, *Morphogenesis and mechanostabilization of complex natural and 3D printed shapes*. Advanced Science, 2015. **1**: p. 1-9.
137. Mirkhalaf, M., A.K. Dastjerdi, and F. Barthelat, *Overcoming the brittleness of glass through bio-inspiration and micro-architecture*. Nature Communications, 2014: p. 1-9.
138. Hosome, T., S. Zaike, and T. Matsumoto, *Bending Characteristics of Helicoidal Laminated CFRP*. Procedia Engineering, 2017. **171**: p. 1325-1331.
139. Shang, J.S., N.H.H. Ngern, and V.B.C. Tan, *Crustacean-inspired helicoidal laminates*. Composites Science and Technology, 2016. **128**: p. 222-232.
140. Ginzburg, D., F. Pinto, O. Iervolino, and M. Meo, *Damage tolerance of bio-inspired helicoidal composites under low velocity impact*. Composite Structures, 2017. **161**: p. 187-203.
141. Grunenfelder, L.K., N. Suksangpanya, C. Salinas, G. Milliron, N. Yaraghi, S. Herrera, K. Evans-Lutterodt, S.R. Nutt, P. Zavattieri, and D. Kisailus, *Bio-inspired impact-resistant composites*. Acta Biomater, 2014. **10**(9): p. 3997-4008.
142. Ribbans, B., Y. Li, and T. Tan, *A bioinspired study on the interlaminar shear resistance of helicoidal fiber structures*. Journal of the Mechanical Behavior of Biomedical Materials, 2016. **56**: p. 57-67.
143. Apichattrabrut, T. and K. Ravi-Chandar, *Helicoidal Composites*. Mechanics of Advanced Materials and Structures, 2006. **13**(1): p. 61-76.
144. Barthelat, F., *Nacre from mollusk shells: a model for high-performance structural materials*. Bioinspiration and Biomimetics, 2010. **5**.
145. Barthelat, F. and D. Zhu, *A novel biomimetic material duplicating the structure and mechanics of natural nacre*. Journal of Materials Research, 2011: p. 1-13.

146. Naglieri, V., B. Gludovatz, A.P. Tomsia, and R.O. Ritchie, *Developing strength and toughness in bio-inspired silicon carbide hybrid materials containing a compliant phase*. Acta Materialia, 2015. **98**: p. 141-151.
147. Porter, M.M., L. Meraz, A. Calderon, H. Choi, A. Chouhan, L. Wang, M.A. Meyers, and J. McKittrick, *Torsional properties of helix-reinforced composites fabricated by magnetic freeze casting*. Composite Structures, 2015. **119**: p. 174-184.
148. Chen, L. and R. Ballarini, *Bioinspired micro-composite structure*. J. Mater. Res., 2006. **22**(1): p. 124-131.
149. Sabree, I., J.E. Gough, and B. Derby, *Mechanical properties of porous ceramic scaffolds: Influence of internal dimensions*. Ceramics International, 2015. **41**: p. 8425-8432.
150. Martikainen, L., A. Walther, J. Seitsonen, L. Berglund, and O. Ikkala, *Deoxyguanosine phosphate mediated sacrificial bonds promote synergistic mechanical properties in nacre-mimetic nanocomposites*. Biomacromolecules, 2013. **14**: p. 2531-2535.
151. Rogel, M.R., H. Qiu, and G.A. Ameer, *The role of nanocomposites in bone regeneration*. Journal of Materials Chemistry, 2008. **18**: p. 4233-4241.
152. Liu, Y., D. Luo, and T. Wang, *Hierarchical Structures of Bone and Bioinspired Bone Tissue Engineering*. Small, 2016. **12**(34): p. 4611-4632.
153. Minardi, S., B. Corradetti, F. Traballi, M. Sandri, J. Van Eps, F.J. Cabrera, B.K. Weiner, A. Tampieri, and E. Tasciotti, *Evaluation of the osteoinductive potential of a bio-inspired scaffold mimicking the osteogenic niche for bone augmentation*. Biomaterials, 2015. **62**: p. 128-137.
154. Naglieri, V., H.A. Bale, B. Gludovatz, A.P. Tomsia, and R.O. Ritchie, *On the development of ice-templated silicon carbide scaffolds for nature-inspired structural materials*. Acta Materialia, 2013. **61**: p. 6948-6957.
155. Ghazlan, A., T. Ngo, N. Lam, and P. Tran, *A numerical investigation of the performance of a nacre-like composite under blast loading*. Applied Mechanics and Materials, 2016. **846**: p. 464-469.
156. Flores-Johnson, E.A., L. Shen, I. Guiamatsia, and G.D. Nguyen, *A numerical study of bioinspired nacre-like composite plates under blast loading*. Composite Structures, 2015. **126**: p. 329-336.
157. Flores-Johnson, E.A., L. Shen, I. Guiamatsia, and G.D. Nguyen, *Numerical investigation of the impact behaviour of bioinspired nacre-like aluminium composite plates*. Composites Science and Technology, 2014. **96**: p. 13-22.

158. Grujicic, M., J. Snipes, and S. Ramaswami, *Ballistic Impact Behavior of Nacre-Like Laminated Composites Consisting of B 4 C Tablets and Polyurea Matrix*. Journal of Materials Engineering Performance, 2016. **25**(3): p. 977-994.
159. Soboyejo, W., *Further Topics in Composites*, in *Mechanical Properties of Engineering Materials*, M.D. AG, Editor. 2003. p. 304.
160. Askarinejad, S. and N. Rahbar, *Toughening mechanisms in bioinspired multilayered materials*. Journal of The Royal Society Interface, 2015. **12**(102): p. 20140855.
161. Dutta, A., A. Tekalur, and M. Miklavcic, *Optimal overlap length in staggered architecture composites under dynamic loading conditions*. Journal of the Mechanics and Physics of Solids, 2013. **61**.
162. Dutta, A. and S.A. Tekalur, *Crack tortuosity in the nacreous layer - Topological dependence and biomimetic design guideline*. Internal Journal of Solids and Structures, 2014. **51**: p. 325-335.
163. Barthelat, F. and H.D. Espinosa, *An experimental investigation of deformation and fracture of nacre - mother of pearl*. Experimental Mechanics 2007. **47**: p. 311-324.
164. Shao, Y., H.P. Zhao, X.Q. Feng, and H. Gao, *Discontinuous crack bridging model for fracture toughness analysis of nacre*. Journal of the Mechanics and Physics of Solids, 2012. **60**: p. 1400-1419.
165. Tran, P. and T. Ngo, *Bio-inspired composite structures subjected to underwater impulsive loading*. Computational Materials Science, 2014.
166. Katti, K.S., D.R. Katti, S.M. Pradhan, and A. Bhosle, *Platelet interlocks are the key to toughness and strength in nacre*. Journal of Materials Research, 2005. **20**(5): p. 1097-1100.
167. Chen, X., H.T. Yang, J. Shan, P.K. Hansma, and W. Shi, *Bio-inspired passive optimized base-isolation system for seismic mitigation of building structures*. Journal of Engineering Mechanics, 2015. **142**(1): p. 04015061.
168. Kwon, I.Y., H.T. Yang, P.K. Hansma, and C.J. Randall, *Bioinspired Tuned Mass Damper for Mitigation of Wind-Induced Building Excitation*. Journal of Structural Engineering, 2017. **143**(10): p. 04017142.
169. Constantz, B.R., M.A. Bewernitz, C.L. Camire, S.H. Kang, J. Schneider, and R.R. Wade, *Bioinspired concrete*, in *Biotechnologies and Biomimetics for Civil Engineering*, L.J. Pacheco Torgal F., Diamanti M., Yu CP., Lee H., Editor. 2015, Springer, Cham.

170. Ghazlan, A., T.D. Ngo, and P. Tran, *Influence of interfacial geometry on the energy absorption capacity and load sharing mechanisms of nacreous composite shells*. Composite Structures, 2015. **132**(0): p. 299-309.
171. Ghazlan, A., T. Ngo, and P. Tran, *Influence of geometric and material parameters on the behavior of nacreous composites under quasi-static loading*. Composite Structures, 2017.
172. Kim, Y., C. Kim, and R. Langari, *Novel bio-inspired smart control for hazard mitigation of civil structures*. Smart Materials Structures
2010. **19**(11): p. 115009.
173. Pacheco-Torgal, F. and J. Labrincha, *Biotechnologies and bioinspired materials for the construction industry: an overview*. International Journal of Sustainable Engineering, 2014. **7**(3): p. 235-244.
174. Soltan, D., R. Ranade, and V. Li, *A Bio-inspired Cementitious Composite for High Energy Absorption in Infrastructural Applications*. Blucher Material Science Proceedings, 2014. **1**(1): p. 1-4.
175. Palkovic, S.D., D.B. Brommer, K. Kupwade-Patil, A. Masic, M.J. Buehler, and O. Büyüköztürk, *Roadmap across the mesoscale for durable and sustainable cement paste-A bioinspired approach*. Construction Building Materials, 2016. **115**: p. 13-31.
176. Sun, Y., Z. Yu, Z. Wang, and X. Liu, *Novel protective covering to enhance concrete resistance against projectile impact*. Construction and Building Materials, 2015. **96**: p. 484-490.
177. Burns, L., A. Mouritz, D. Pook, and S. Feih, *Bio-inspired hierarchical design of composite T-joints with improved structural properties*. Composites Part B: Engineering, 2015. **69**: p. 222-231.