Hierarchically Enhanced Impact Resistance of Bioinspired Composites

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An order of magnitude tougher than nacre, conch shells are known for being one of the toughest body armors in nature. However, the complexity of the conch shell architecture creates a barrier to emulating its cross-lamellar structure in synthetic materials. Here, a 3D biomimetic conch shell prototype is presented, which can replicate the crack arresting mechanisms embedded in the natural architecture. Through an integrated approach combining simulation, additive manufacturing, and drop tower testing, the function of hierarchy in conch shell’s multiscale microarchitectures is explicated. The results show that adding the second level of cross-lamellar hierarchy can boost impact performance by 70% and 85% compared to a single-level hierarchy and the stiff constituent, respectively. The overarching mechanism responsible for the impact resistance of conch shell is the generation of pathways for crack deviation, which can be generalized to the design of future protective apparatus such as helmets and body armor.

Damage of materials is difficult to avoid over the course of their operational lifetime. Human safety becomes a concern especially when these materials are used in protective gear. Helmets and armor, for example, aim to provide efficient absorption and dissipation of the impact energy, minimizing damage to the wearer’s body. In the case of helmets, which have received significant attention, any deficiency in quality can cause harm to the skull and brain, and potentially lead to traumatic brain injury, or TBI.[1] It has been recognized that TBI can occur when the brain is injured even without skull fracture. In traditional helmet designs, metals are used which are disadvantageous due to their high inflexibility, weight, and cost of production.[2] The state of the art in helmet design features hard fiberglass outer material and soft inner padding usually made up of polyurethane (PU), offering higher flexibility in comparison to earlier designs based on metallic materials.[2] Despite technology advancement, TBI is still of a concern among military troops, a group of individuals very prone to repetitive head trauma.[3]

Therefore, it remains necessary to develop future superior protective systems through novel, ingenious designs.

Natural protective materials offer unparalleled solutions toward simultaneously lightweight, flexible, hard, and tough armor designs.[4–6] Nature has been iteratively solving an optimization problem through evolution driven by organism survival and functions, though constrained by limited natural building materials.[7,8] What is intriguing about the work of nature is its dual proficiency in achieving high strength and toughness, seemingly circumventing the trade-off faced by conventional engineering materials. Seashells, made up of calcium carbonate and organic biopolymer, simultaneously possess high mechanical strength and toughness. The hard calcium carbonate phase gives the shell stiffness and strength, and the protein layer between these mineral sheets provides compliance and also energy-dissipating mechanisms, making it much harder to fracture. Seashells as a whole are orders of magnitude tougher than their constituents and have therefore earned the reputation for being one of the best natural body armors due to the levels of hierarchy evolved in their multiscale architectures.[9]

In particular, conch shells, which need to withstand predators’ sharp-toothed attacks, have a unique three-tier hierarchical lamellar structure; it is noteworthy that this architecture creates many crack deflection pathways during loading.[9,10] The layered structure of conch shells consists of outer, middle, and inner layers (Figure 1). Each of these layers is composed of first (5 μm thick, many μm wide), second (5–30 μm thick, 5–60 μm wide) and third (60–100 nm thick, 100–380 nm wide) order aragonite lamellae.[9,11] The cross-lamellar structure consists of crisscrossed sheets of calcium carbonate separated by protein layers, with each sheet oriented at right angles to its top and bottom neighbors. The layered makeup of the conch shell ingeniously compartmentalizes crack propagation, leading to high toughness.[12] Cracks forming in the inner layer have a difficult time reaching the middle layer due to their arrest at the rotated interface. Studies have shown that the work of fracture for the conch shell is 1000 times higher than that of its mineral phase,[9] and ten times higher than that reported for nacre.[12] These unparalleled characteristics make conch shells a compelling candidate for biomimicry studies aimed at creating tougher materials.

Biomimicry has become an appealing field of research since the discovery of natural material’s exemplary performance.[11–21] For instance, many research groups have successfully...
mimicked bone and nacre and highlighted their superior performance in comparison to their constituents. However, the complexity of the conch shell architecture creates a barrier for replication via synthetic routes. Previous attempts at mimicking the conch shell laminate architecture did not fully capture the complexity of the hierarchy.[11,22] Meanwhile, there is still a lack of fundamental understanding regarding the role of hierarchy on the overall impact performance. We focus on exploring the unique characteristics associated with the conch shell, through capturing the complex and hierarchical architecture at different length scales for integration into a biomimetic design.

With the advent of multimaterial additive manufacturing, it is now possible to manufacture more complex geometries than ever before.[23–27] Here, we present for the first time a multilayer, biomimetic, 3D conch shell prototype using additive manufacturing, which can replicate the crack-arresting feature at the interface. Additionally, in this study we present a 3D finite element model of the conch shell architecture, building on previous simulation studies that focused primarily on a 2D model.[28,29] This work uses a combination of simulation, additive manufacturing, and drop tower testing to expound the role of multiscale hierarchical architectures in seashells’ enhanced impact resistance. Exploration of these layered structures can guide designs toward future protective systems such as helmets and body armor.

The geometry of the layered composite presented here mimics the *Strombus gigas* conch shell. The top, middle, and
bottom layers of the shell are stacked in a 0°, 90°, and 0° sequence (Figure 1). The synthetic conch shell in this study is built up from a unit cell which is repeated in-plane then stacked into its final laminate design (Figures S1 and S2, Supporting Information). In comparison to the real conch shell architecture (Figure 1), our design is similar and has alternating criss-crossed patterns in each individual layer aligned 45° relative to each other; this will be termed as the Hier-2 design. To investigate the effects of hierarchy on impact performance, we also build a Hier-1 design which only includes the first order hierarchy of the conch shell (Table 1), without the cross-lamellar features seen in the Hier-2 design. Both designs are fabricated using multimaterial 3D-printing, and their impact performance will be compared to each other.

We use drop tower testing to compare the impact performance of the 3D-printed Hier-1 and Hier-2 composite designs (Figure S7, Supporting Information). The difference in the architectures between these two designs is clearly revealed in the impact responses observed at different velocities (Table 1). The Hier-2 design prevents the perforation of the projectile for all three different impact velocities, while the Hier-1 design is only able to halt the projectile impacting at a velocity of 2.3 m s⁻¹. Results of the Bulk stiff material for an impact velocity of 2.3 m s⁻¹ are also presented for comparison showing that even at the lowest testing velocity, bulk stiff is not able to prevent projectile perforation. It should be noted that the higher percentage of soft material in the Hier-2 design is intended to provide more complex crack deflection mechanisms in the microstructure and its effect on stiffness is negligible (Figure S7, Supporting Information). As evident from the results in Table 1, both designs experience almost the same level of maximum load during impact. However, the fate of these structures is distinguished beyond this load. For the Hier-1 design, the force drops to zero almost instantly due to rapid crack propagation and coalescence, leading to low deflection at the end of the test (Table 1). Nevertheless, the Hier-2 design still resists the projectile travel beyond the peak load as it is highly probable that microcracks generated in this structure are arrested and deflected, thereby delaying complete perforation (Figure 2a). Multiple tests at different velocities are conducted to obtain the critical impact energy for Hier-1, Hier-2, and bulk stiff material. The damage patterns on the top and bottom surfaces are also compared for the Hier-1 and Hier-2 composites at a velocity of 3 m s⁻¹ (Figure 2). The Hier-1 design experiences severe damage and catastrophic failure at this velocity, while the cracks visible on the Hier-2 surfaces do not penetrate deep into the material, maintaining the integrity of the composite at the end of the test. These results suggest that the Hier-1 design performs better than bulk, but that the Hier-2 design exceeds both in impact resistance.

We further study the damage mechanisms occurred during the impact experiments to gain a better understanding on why the Hier-2 composite outperformed the bulk and the Hier-1 designs in terms of impact performance. Figure 2 shows the cross-sectional images of the Hier-2 design after an impact testing which results in no perforation (v = 2.3 m s⁻¹). We first follow the propagation path of the crack shown in Figure 2a, where initiation occurs in the hard material at the bottom of the first layer. While passing through a crisscrossed interface, the crack takes a different path and continues its growth toward the interface between layers 1 and 2. Thereafter, it experiences another deflection, tunneling into layer 2. It ultimately stops at the interface between layers 2 and 3 and cannot reach to the top of the sample. Crack propagation does not reach the third layer presumably due to the presence of the complex architecture of the design, as such impact energy is not sufficient to tunnel through the hierarchy. In another example, the crack shown in Figure 2a initiates at the bottom of layer 1 and propagates along the crisscrossed soft material. Once it reaches the interface between layers 1 and 2, it deflects and kinks into the interface before tunneling into the second layer. Thereafter, the crack continues its growth and reaches to another interface, this time between layers 2 and 3. Such interface stops the crack propagation, again protecting layer 3 from fracturing.

As a final example for damage mechanisms in the Hier-2 design, the crack shown in Figure 2c, forms in the bottom layer and propagates along the crisscrossed soft material. Similar to the previous cases, the crack deflects at the interface between layers 1 and 2 before finding its way into the second layer. This time the crack changes direction at the interface between layers

Table 1. Drop tower testing results. Two different designs based on the natural conch shell microstructure are used to study and compare the effects of hierarchy on impact performance. The Hier-1 design represents the first order of hierarchy in the conch shell. The Hier-2 design represents a second order of hierarchy and contains crisscrossed layers within each ply. Both designs, in addition to the bulk (stiff) material, are fabricated using additive manufacturing with the same thickness for all specimens.

<table>
<thead>
<tr>
<th>Composite type</th>
<th>Hier-1</th>
<th>Hier-2</th>
<th>Bulk</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incident velocity [m s⁻¹]</td>
<td>2.3</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Max load [kN]</td>
<td>2.5 ± 0.1</td>
<td>2.7 ± 0.2</td>
<td>3.0 ± 0.2</td>
</tr>
<tr>
<td>Max deflection [mm]</td>
<td>8.0 ± 0.1</td>
<td>7.0 ± 0.7</td>
<td>9.1 ± 1.5</td>
</tr>
<tr>
<td>Residual velocity [m s⁻¹]</td>
<td>0.0</td>
<td>1.5 ± 0.3</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>Perforated?</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Critical impact energy [J]</td>
<td>14.8</td>
<td>25.2</td>
<td>13.5</td>
</tr>
</tbody>
</table>
2 and 3, and then goes into the third layer. Finally, it reaches a slanted interface and finds its way along this soft layer to the top of the sample. These crack paths observed in different locations of the composite cross-section demonstrate that damage is not concentrated in the area beneath the projectile, but rather the entire composite in different sections is working in concert to take the load and toughen the structure. Additionally, the complex nature of its architecture forces the cracks to constantly change direction at the layered interfaces, creating more energy dissipating mechanisms. Consequently, the Hier-2 design can absorb higher impact energy before experiencing complete fracture compared to the bulk material and the Hier-1 composite.

We simulate the impact using finite element method and analyzed the results to further explicate the internal mechanisms occurring during loading in the Hier-2 design. Good agreement between force– and velocity–displacement curves (Figure 3) obtained from experiment and simulation implies that our finite element (FE) model can reveal the dynamics of crack propagation in the composite design. Additionally, numerical simulations also adequately capture the velocity profile observed in experiment, and these results strongly suggest that the hierarchical composite is capable of halting the projectile (down to a velocity of zero) to avoid complete perforation. In the simulation, it is noted that during the impact of the Hier-2 design, initiation of small cracks is clearly evidenced in the soft regions, as shown in Figure 3, which could presumably alleviate the stresses and subsequently dissipate the impact energy. Furthermore, it is clear from the simulation images that these cracks are not localized but distributed over various regions underneath the projectile. However, the complex architecture of the Hier-2 design imposes considerable restrictions on crack propagation and coalescence. This is partly due to the fact that alternating sheets of lamellae are positioned at right angles to each other, thus cracks can only propagate through the material by following a tortuous zig-zag path, which would require greater energy to achieve complete fracture (Figure 3). This phenomenon is in good agreement with the literature findings on conch shell failure and also with our impact experiments. Along with interface failure, cracking of the stiff constituent also occurs in the hierarchical composite design, similar to our experimental observations (Figure 3).

Contribution of each level of hierarchy in the conch shell architecture translates into a higher overall fracture toughness for this natural material. High toughness of the conch shell has been explained based on the crack mitigation mechanisms in its different lamellas.[9,11] In our study, we created prototypes to compare designs with one level (Hier-1) or two levels (Hier-2) of hierarchy. In comparison with the impact deformation and damage of both composite materials (Figure 2), we find that the Hier-2 design exhibits a significantly different mode of failure compared to the Hier-1 design. Whereas initiation of distributed cracks is only seen in the Hier-2 design, complete penetration and a perforated hole arise in the Hier-1 composite.
Correspondingly, the hierarchically superior Hier-2 design exhibits an 85% improvement with respect to the threshold impact energy in comparison with the bulk stiff material, while the threshold impact energy of the Hier-1 design is only 10% higher (Table 1). This finding clearly demonstrates that increasing the level of hierarchy from Hier-1 to Hier-2 significantly improves the impact properties for the samples tested. The soft bulk material is not compared here because its extent of deformation under impact is too high, which is not practical for use in most helmets applications, where a high threshold velocity along with a low back-face deflection are required. In fact, these requirements can be achieved through the hierarchical design of the conch shell. These results show promise that this conch shell’s architecture offers smart solutions for new armor and helmet designs.

To further provide insight for future applications of this design, we take an analytical approach to crack propagation in its intricate architecture. Cross-section images of the Hier-2 design after impact testing (Figure 2) reveal various interactions between cracks propagating toward the soft interfaces. In general, a crack reaching an interface can take one of the three paths: first, the crack can arrest at the interface; second, the crack can deflect into the interface; and finally, the crack can traverse the interface penetrating into the matrix (Figure 4a).

The following analysis will assume homogenous, elastic, isotropic materials for the composite constituents. The competition between deflection and penetration at the interface is readily understood by linear elastic fracture mechanics which sets the conditions for fracture initiation; no fracture occurs so long as the crack intensity factor or energy release rate is less than the fracture toughness of a given material. In the case of interfaces, crack deflection would mean the interfacial fracture. On the other hand, the crack goes through the interface, penetrating into the matrix. The condition for crack deflection into the interface can then be formulated as

$$\frac{G(\beta, v_2)}{G_i(v_1)} \geq \frac{\Gamma_{ln}(v_2)}{\Gamma_{Ma}(v_1)}$$

where $G(\beta, v_2)$ and $G_i(v_1)$ are the energy release rates for the deflected and penetrated cracks, respectively, and $\Gamma_{ln}(v_2)$ and $\Gamma_{Ma}(v_1)$ are the fracture toughness of the interface layer and matrix, respectively.

The left-hand side of Equation (1) can be formulated as

$$\alpha_{d}k_i^2(v_2) \left( \frac{3 \cos \beta}{2} + \cos \frac{3 \beta}{2} \right)^2 + \alpha_{d}k_i^2(v_2) \left( \frac{\sin \beta}{2} + \sin \frac{3 \beta}{2} \right)^2$$

where

$$\alpha_{d} = \frac{\alpha_{d,l}}{\alpha_{d,i}} \frac{D_i}{D_l}$$

$\alpha_{d,l}$ and $\alpha_{d,i}$ are the crack propagation coefficients for the localized and interfacial fracture, respectively. $D_i$ and $D_l$ are the thickness of the interface layer and matrix, respectively.
Figure 4. Crack deflection or penetration. a) Schematic showing crack traveling toward the interface (left) and could either deflect into the interface or penetrate through the interface. \( v_1 \) and \( v_2 \) are the incident and deflected crack speeds, respectively. \( \beta \) is the interfacial angle starting from the horizontal axis and ending at the interface. b) For our 3D-printed system, crack deflection into the interface will occur when \( \beta < 50° \), while the crack will traverse the interface for \( 50° < \beta < 90° \).

\[
D = 4\alpha_a\alpha_d - (1 + \alpha_d^2)^2
\]

and \( \alpha_s \) and \( \alpha_d \) are the shear and dilatational wave speeds of the matrix material. The universal functions of the crack tip speed, \( k_1 \) and \( k_{11} \), are defined as follows

\[
k_1(v) = \frac{1 - \frac{v}{c_s}}{1 - \frac{v}{c_d}}, \quad k_{11}(v) = \frac{1 - \frac{v}{c_d}}{1 - \frac{v}{c_s}}
\]

where \( c_R \) is the Rayleigh wave speed of the material.

We apply these equations to the 3D-printing materials system, with the stiff material as the matrix and the soft material as the interface (Figure 4). Details of the matrix and interfacial properties can be found in the Supporting Information. To determine whether an incident crack will zip across the interface, the normalized energy release rate, the left-hand side of Equation (1), is plotted as a function of crack incident angle, \( \beta \). For the stiff/soft combination, crack deflection into the interface will occur when \( \beta < 50° \), while the crack will traverse the interface for \( 50° < \beta < 90° \). The value of the threshold incident angle is obtained from the intersection of the horizontal line that corresponds to the ratio of the dynamic fracture toughness of the interface to the matrix material (Equation (1)). This analysis is instrumental to understand the effects of incident angle on crack propagation and deflection. It can be shown that the soft interface dictates the system response, as the weaker the interfacial strength, the larger the range of angle where deflection occurs. However, as the interface material gets weaker, the system may lose stiffness and cause early delamination, so striking a balance between the two materials is important. What is also interesting to note is that from this analytical study, the critical angle appears to be \( 50° \), which makes the natural conch shell angle (\( 45° \)) and the angle adopted in our biomimetic design (\( 45° \)) in a range that deflection is more probable during impact. This analysis suggests that when designing a cross-lamellar composite, using an angle around \( 50° \) will tend to prevent perforation and allow for crack deflection.

We also calculate the ratio of the fracture toughness of the interface to the matrix material (right hand side of Equation (1)) for the natural conch shell system to make a comparison with the current system. From literature, this ratio is estimated to be 0.6\(^{[33,34]} \) (approximated using aragonite as the bulk material (10 J m\(^{-2} \)) and nacre’s interfacial properties (5.5 J m\(^{-2} \)) since they are both made up of similar materials that exist in nature) and for our biomimetic design, it is 1.5 (from the Supporting Information). These ratios are thus in the same order of magnitude and according to Figure 4b, both result in crack deflection. In general, based on this study’s findings, the proposed microstructural design can be applied to brittle materials to gain toughness enhancement. This, however, requires a good bonding between the inner soft material and the brittle matrix which is the case for ultraviolet cured 3D-printed materials used in this work. In addition, the fracture toughness of the interface relative to the bulk material should promote crack deflection (Equation (1)). In such a scenario, the overall fracture toughness of the brittle material can be enhanced with the introduction of soft fillers in a designed architecture. For instance, if our analytical approach is applied to a Si\(_3\)N\(_4\)/BN combination, materials previously used to make nacre-like composites\(^{[33,34]} \), we obtain a value of 1.1 on the right hand side of Equation (1) (details outlined in the Supporting Information), which is on the same order of magnitude as our 3D-printed system. This shows that even though the analysis was based on additive manufactured materials, it can be applied to other material systems as well. Future work could involve using multimaterial additive manufacturing of a ceramic and polymer system.

In this paper, we elucidated a novel approach detailing the progress in creating a biomimetic conch shell prototype, using additive manufacturing. The prototypes are able to achieve on-demand impact enhancements by recreating the complex cross-coupled lamellar architecture seen in natural conch shells. We incorporate two levels of hierarchy into our biomimetic design and show that adding the second level of hierarchy can greatly
Enhance impact performance by 70% compared to the design with only the first level of hierarchy and 85% compared to the bulk stiff material. Moreover, a detailed FE analysis for the impact of conch shell-inspired designs is presented to reveal the crack arresting mechanisms evidenced at the layered interfaces. These results and analyses demonstrate proof of concept that conch shell's architecture offers unmatched solutions for the design of protective wear, such as armor and helmets. Although this study examined the role of hierarchy in impact resistance of conch shells specifically, the methodology presented in our study can be tailored and adapted to gain understanding and insight on impact resistant characteristics of other biological materials. Integrating additive manufacturing into computational modeling can open a wide new avenue of unprecedented applications not possible before.

**Experimental Section**

Experimental Section details can be found in the Supporting Information.

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

The authors acknowledge funding from the National Defense Science and Engineering Graduate (NDSEG), fellowship Nos. ONR-N00014161233 and ONR-DURIP N000141410767. M. Takaffoli appreciates support from the Natural Sciences and Engineering Research Council of Canada (NSERC) fellowship. The authors thank Talal Al-Mulla, Dr. Chun-Teh Chen, from the Natural Sciences and Engineering Research Council of Canada and ONR-DURIP N000141410767. M. Takaffoli appreciates support from the Natural Sciences and Engineering Research Council of Canada (NSERC) fellowship. The authors thank Talal Al-Mulla, Dr. Chun-Teh Chen, Dr. Alex J. Hsieh, Steve Palkovic, Dr. Chian Fong Yen, and Xiaowei Zhang for insightful discussions. Additionally, the authors thank Hyunwoo Yuk and Masoumeh Takaffoli for their invaluable help with pictures.

**Keywords**

3D-printing, biological materials, conch shell, drop tower testing, finite element modeling

Received: January 4, 2017
Revised: February 7, 2017
Published online: