Printing nature: Unraveling the role of nacre’s mineral bridges

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ABSTRACT

Creating materials with strength and toughness has been a long-sought goal. Conventional engineering materials often face a trade-off between strength and toughness, prompting researchers seeking to overcome these limitations to explore more sophisticated materials, such as composites. This paradigm shift in material design is spurred by nature, which exhibits a plethora of heterogeneous materials that offer outstanding material properties, and many natural materials are widely regarded as examples of high-performing hybrid materials. A classic example is nacre, also known as mother-of-pearl, which boasts a combination of high stiffness, strength, and fracture toughness. Various microstructural features contribute to the toughness of nacre, including mineral bridges (MBs), nano-asperities, and waviness of the constituent platelets. Recent research in biomimicry suggests that MBs contribute to the high strength and toughness observed in nacre and nacre-inspired materials. However, previous work in this area did not allow for complete control over the length scale of the bridges and had limitations on the volume fraction of mineral content. In this work, we present a systematic investigation elucidating the effects of structural parameters, such as volume fraction of mineral phase and density of MBs, on the mechanical response of nacre-inspired additive manufactured composites. Our results demonstrate that it is possible to tune the composite properties by tuning sizes and content of structural features (e.g. MBs and mineral content) in a heterogeneous material. Looking forward, this systematic approach enables materials-by-design of complex architectures to tackle demanding engineering challenges in the future.

1. Introduction

The quest for stronger and tougher materials has been an important topic of research for many decades. As most engineering materials sacrifice strength for toughness, and vice versa, researchers strive to overcome these limitations by exploring hybrid materials (Gu et al., 2016a; Kickelbick, 2007; Pedro and Sanchez, 2006; Ritchie, 2011). Heterogeneity embedded in natural materials engenders astounding material properties that have gained them the prestigious title of high-performing structural materials (Tat et al., 2007). Over the course of evolution, these materials make efficient and highly adapted uses of their available resources (Meyers et al., 2013; Wegst et al., 2015a). In fact, many biological systems do not face the tradeoffs in material properties often seen in synthetic engineering materials (Espinosa et al., 2009). Examples of such exemplary natural materials include bone, nacre, wood, and teeth (Wegst and Ashby, 2004; Wegst et al., 2015a). Virtually all of these materials are composites, made up of soft and hard components organized into a multiscale hierarchical structure. Many biological materials show a staggered arrangement (e.g., bone and nacre), which has shown to be optimal for achieving stiffness, strength and toughness (Guo and Gao, 2006).

Nacre, mother-of-pearl, can be found in the inner layer of mollusk shells and has a complex hierarchical architecture that is mostly made up of crystalline aragonite (CaCO\textsubscript{3}) platelets (95 wt%) and a biopolymer (5 wt%), organized in a brick-and-mortar structure. Nacre’s microarchitecture offers an interesting design that allows for the simultaneous presence of stiffness, strength, and fracture toughness, traits usually mutually exclusive in conventional engineering materials (Espinosa et al., 2011; Espinosa et al., 2009; Jackson et al., 1988; Wegst et al., 2015b). Until recently, aragonite mineral platelets were thought to be brittle crystals. However, from recent studies it is evident that these platelets, composed of millions of nanograins with the same orientation and glued together by a biopolymer (Barthelat et al., 2006; Li et al., 2006), show an anisotropic elastic-plastic behavior at the nanoscale (Kearney et al., 2006). Despite a composition, that is predominantly of stiff aragonite, nacre is 20–30 times tougher than aragonite alone (Sarikaya and Aksay, 1995). This enhancement in toughness highlights the role of architecture versus material
composition in dictating a material’s mechanical behavior (Wegst and Ashby, 2004). Besides the architecture, the weak interface between the mineral and the biopolymer and its sophisticated design, also plays a critical role in the overall mechanical performance, promoting ductility, energy dissipation, and self-healing (Barthelat et al., 2016; Khayer Dastjerdi et al., 2013).

When stressed to a point of fracturing, nacre’s hierarchical architecture results in the occurrence of several energy dissipation mechanisms (crack blunting and branching, nucleation of microcracks and microvoids, platelet pullout) operating at multiple length scales during the fracture process (Kakisawa and Sumitomo, 2011). This not only increases the overall fracture toughness but also adds robustness against failure to the structure, as multiple toughening mechanisms can be activated during loading. Various structural features contribute to the toughness of natural nacre, including mineral interconnectivity, bridges, nano-asperities, and waviness of the platelets, among others (Barthelat and Espinosa, 2007; Barthelat et al., 2006; Espinosa et al., 2009; Lopez et al., 2014; Wang and Gupta, 2011). It has been discovered that the thin biopolymer layer is porous and contains holes of diameter 50 nm. These holes enable the creation of mineral bridges (MBs) between the mineral layers (Meyers et al., 2008). These bridges, observed and measured by transmission electron microscopy and scanning electron microscopy (Fan and Yilong, 2001; Song et al., 2003; Song et al., 2002), make the structure a “brick-bridge-mortar” structure rather than a brick-and-mortar one and provide a full continuity of aragonite crystals across the inter-lamellar layers (Cecha et al., 2011).

In earlier literature, most studies on nacre-like composites have focused on mimicking the biological material’s brick-and-mortar microstructure of mineral platelets embedded in a polymer matrix. Thoroughly studied methods to fabricate materials like nacre (and other biological) materials include ice templation, freeze casting, layer-by-layer deposition, hot-pressing, thin film deposition, coextrusion, and self-assembly (Dimas et al., 2013; Grossman et al., 2016; Gu et al., 2016b; Gu et al., 2016c; Launey et al., 2010; Libonati et al., 2016; Munch et al., 2008; Naglieri et al., 2015; Niebel et al., 2016; Sun and Blushan, 2012; Wilkerson et al., 2016). Each method has produced composites whose capabilities well exceed those of their constituents. Recent biomimicry research suggests that mineral nano-interconnectivity contributes to the high strength and toughness seen in these bio-inspired materials. For instance, composites that have interconnected ceramic bonds between platelets, aimed at mimicking the naturally-observed MBs, are significantly stiffer and stronger than composites lacking these connections (Le Ferrand et al., 2015; Munch et al., 2008; Naglieri et al., 2015). Such composites are produced by freeze casting or magnetically assisted slip casting (MASC) of nacre-like ceramic scaffolds, subsequently followed by infiltration with a polymer matrix. It has been shown in freeze cast SiC systems that increasing the number of MBs enhances the flexural strength of the composite (Naglieri et al., 2015). Although claiming the positive effects of mineral bridging and volume fraction on the mechanical performance, previous experimental studies did not have a thorough control over the length scale of the bridges and had limitations on the volume fraction of mineral content. A theoretical approach has been used, instead, to probe the size effect of nanoscale MBs in nacre, through which the interface achieves an optimal strength (Shao et al., 2014).

In this work, we present a systematic investigation of the effects of structural parameters, such as volume fraction of mineral phase and length scale of MBs, on the mechanical response of nacre-inspired additive manufactured composites. With the advent of additive manufacturing, it is possible to quickly design and manufacture an enormous number of diverse and complex geometries, allowing for a methodical study of different designs. In this study, 3D-printing allowed us to exercise complete control over the nacre-like substructure design, systematically changing the volume fraction of the mineral phase and the density of MBs. The present work experimentally and numerically studies the effects of these structural features on toughness and strength in nacre-inspired polymer composites. The results demonstrate the dependence of mechanical properties on the volume content of the brick “mineral” phase and the amount of MBs present.

2. Materials and methods

2.1. Structural designs

Our designs are nacre-inspired composites with a brick-and-mortar-like pattern. In each case, two vastly different constituent materials are simultaneously 3D-printed, one that is stiff and another that is much softer, aiming at emulating the stiff mineral and the soft polymer matrix, respectively. Five different stiff volume fraction contents are studied – 50%, 60%, 70%, 80%, and 90%. The nomenclature for graphs will be 50%, 60%, 70%, 80%, and 90% for the respective volume fractions. The designs and dimensions are shown in Fig. 1(a). The aspect ratio changes with volume fraction but the number of unit cells repeating remains constant. The number of MBs is also varied – 6, 9, 12, 15, and 18 bridges. The nomenclature for the number of bridges (mb) will be listed after the volume fraction amount. For instance, for 70% volume fraction and 6 bridges, it will be 70%-6mb. The bridge thickness is the same...
throughout, but the number of bridges is varied across the platelet length. We include the true volume fraction of the materials with the additional bridges in Supporting Information Table S1, to allow a more accurate comparison among various topologies. An example of a case with and without bridges for 70% design is shown in Fig. 1(b), where pink indicates the stiff material and black indicates soft material. Although the size difference (about 3 orders of magnitude) between the natural nacre and our 3D-printed designs, the latter have been precisely scaled. Table 1 shows a comparison between the parameters of a nacre-like design 90%-12mb (i.e. the design with the volume fraction more similar to real nacre) and those of natural nacre. It can be shown that all parameters are of the same magnitude as natural nacre and that motivates this study to vary and tune these parameters to see the effects on mechanical properties such as strength and toughness. Finally, to compare the number of MBs between the different systems, we define a parameter called shear length, SL, which is the distance between MBs. The structures are designed to be similar on the basis of SL due to the limitations in resolution of the 3D printer; we cannot do the comparison using the same number of bridges as natural nacre. The results would have been using very tiny SL or increasing the sample size that results in high material consumption.

The relevant geometries are generated using AutoCAD 2016 (Autodesk, Inc.). 3D models are created by extruding the 2D design and rendering them into Stereolithography (.stl) files. To prepare the models for fracture testing, an edge crack is incorporated into the design. The crack spans 20% of the specimen's width and is perpendicular to the intended direction of loading for testing. The included crack tip is at a 60° angled point. Each geometry is designed to be 76.2 × 76.2 × 3 mm, plus additional length to allow for gripping during testing (Fig. 2).

Table 1

<table>
<thead>
<tr>
<th></th>
<th>Natural Nacre</th>
<th>Synthetic Nacre</th>
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<tr>
<td>Platelet aspect ratio: ( \frac{pl}{pt} )</td>
<td>16</td>
<td>15</td>
</tr>
<tr>
<td>Mineral bridge a.r.: ( \frac{d}{h} )</td>
<td>1.8</td>
<td>1.9</td>
</tr>
<tr>
<td>Num. of MBs (per platelet)</td>
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<td>12</td>
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<tr>
<td>( \frac{mt}{pl} )</td>
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<td>SL/pl</td>
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An Objet500 Connex3 3D-printer, manufactured by Stratasys, is used to manufacture the various samples. The printer's capability to simultaneously print multiple, distinct, materials with a near-perfect interface makes it ideal for this type of composite testing. Two of Stratasys’ commercial plastics, VeroMagenta (RGD851) and TangoBlackPlus (FLX980), are used for the composite material creation. VeroMagenta makes up the stiff component, representing nacre's calcium carbonate platelets, and TangoBlackPlus is a soft component in place of nacre's soft biopolymer interface, with a stiffness three orders
of magnitude less than that of VeroMagenta (Libonati et al., 2016). Table S2 in Supporting information lists values for material properties.

The two base materials printed are acrylic-based photopolymers. Using Stratasys’ Polyjet technology, the materials are printed simultaneously by two printing heads as liquids, and cured in situ by ultraviolet light. The instant curing creates an interface between the two materials that is stronger than the weaker material, in this case the TangoBlackPlus. This ensures that failure does not occur prematurely at the interface between the materials. After 3D-printing, water jet technology is used to remove the gel-like support material from the samples. To prepare printed specimens for testing, aluminum tabs are glued to the specimens’ gripping ends with a strong epoxy, to avoid stress concentration at the grips and allow for a correct load application. Additionally, the printed notch is sharpened with a razor blade to ensure that crack propagation starts from the tip.

2.3. Mechanical testing

We perform tensile tests on single edge-notched samples using an Instron 5582 universal testing machine with a 100kN load cell in place. The specimens are secured using mechanical vise action grips made of steel. An extension rate of 2 mm/min is employed in the displacement-controlled tests. With tests lasting 2–3 min and a data acquisition frequency of 10 Hz, this displacement condition allows for ample data while keeping the tests timely. The test proceeds until the crack propagates entirely through the material and the load dropped. We could not design this procedure to precisely emulate ASTM standards, which have not yet been established for these composites, but rather used conditions deemed appropriate for this type of plastic composite. We follow the same testing protocol for all the composite samples and the homogeneous materials (VeroMagenta and TangoBlackPlus), allowing for a comprehensive comparison of the results.

2.4. Digital Image Correlation (DIC)

The 3D-printed samples are sprayed on one side in a speckled pattern with black and white paint for digital image correlation (DIC) before testing. DIC is performed using the VIC-2D software created by Correlated Solutions and details are shown in reference (Solutions, 2009). The main parts of the process include a user interface that allows different frames of the deformation at different times to be observed and a camera pointed at the specimen while it is being tested. Tape is placed on the aluminum tabs before spraying to prevent paint from getting on the tabs, which might cause slipping during mechanical testing. The post-processing DIC software measures displacements between the black and white sprayed dots while the sample undergoes deformation, permitting visualization of the strain field for the samples.

2.5. Simulation set-up

A simple finite element (FE) simulation is used to obtain the strain fields from displacements for the nacre-like geometries and allows a direct comparison with the experimental DIC strain maps. The FE method that is used in this study follows closely to reference (Gu et al., 2016a) and will be briefly described here. The geometries possess an edge crack extending 20% of the sample width, and are tested under tensile loading (mode I failure), similar to the experimental set-up. We build a 2D model, with 4-node quadrilateral elements. For the material properties, we adopt a linear elastic model, assuming that the dominating mechanisms occur in the linear elastic regime, as shown by
experimental evidence (Dimas et al., 2013; Libonati et al., 2016). A uniform mesh size consisting of 25,600 elements is used for the problem to compare between geometries and a sufficiently low stiffness ratio is used (0.1) between soft and stiff elements to prevent elastic stress mismatch. Displacement boundary conditions are applied in the loading direction.

3. Results

Tensile tests are performed on all the composite topologies and the base materials. The results are summarized in Figs. 4–5, and Supporting material Fig. S1. The results are very reproducible in terms of stress-strain response and failure modes. For the sake of brevity, we report only one representative curve and failure mode for each sample series. Analyzing the two extremes, the 100% material (i.e. homogeneous stiff material) fails catastrophically, with a very low failure strain and...
relatively high failure stress. The homogeneous soft material, on the other hand, fails with high failure strain and low failure stress. The stress-strain curves for both materials are depicted in (Supporting material Fig. S1).

3.1. Volume fraction effect

The stress-strain responses of various volume fraction samples are shown in Fig. 3. Due to the high volume fraction of stiff material, 90% sample series fails in a similar way to 100% with low failure strain and high failure stress. In this case, the dominant amount of stiff material dictates the 90% series’ stress-strain response. For the other designs, we observe a combination of toughening mechanisms, driving a more progressive failure. In particular, there are successive crack deflections that can lead to a continuous energy release, contributing to an overall increase in the fracture toughness. Out of all the composite topologies, the 70% design has the highest failure strain and the 80% design has the highest failure stress. In Fig. 4(a,b) the red bars in the histograms show the toughness and strength of the series with different volume fractions of stiff material. 80% is the sample series with both the highest toughness and strength. We believe that the high performance of 80% material are due to its balance of soft and stiff elements. This design has a high amount of stiff material, which helps it to increase its stiffness and strength, but also enough amount of compliant material to allow for a nonlinear pattern, which makes its failure not a brittle one.

To understand the toughening mechanisms inherent in the designs, we can observe the failure patterns as reported in Fig. 3(c). For the 50% series, the crack does not propagate through the material in a straight path; rather, the crack is constantly deflected through the compliant phase when it encounters a material or geometry discontinuity. The same crack deflection mechanism observed in 50% also applies for 60% and 70% series, resulting in a zig-zag pattern. For the 80% design, there are fewer deflections, as the volume content of soft material is very limited to allow large deformation and deflections through the soft phase.

3.2. Mineral bridge effect

Various volume fractions with a fixed number of MBs (12) are tested in tension and stress-strain response with bridges is shown in Fig. 3(b). What is most evident from the stress-strain plot is the increase in strength and a decrease in failure strain for all the sample series, with respect to the topologies without MBs shown in Fig. 3(a). Roughly, from the stress-strain curve, the largest improvement in both toughness and strength is shown in the 70%-12mb series.

Fig. 3(d) shows the failure patterns for the various volume fractions with the addition of MBs. As can be shown in the figures, the addition of MBs affected the crack deflections in each case. For the 90% series, crack mostly just propagated through the specimen similarly to the case of homogeneous material (i.e. 100%), and finally branches, leading to a butterfly failure. As for 80% sample, adding the MBs causes the sample to be mostly dominated by a homogeneous stiff response, which is also evident from its stress-strain curve. However, when zoomed into the 80% sample with MBs, we can notice small deflections along the bridges, resulting in a saw-tooth path. Interestingly, 50% sample has many crack deflection pathways, constantly forcing the crack to change direction and allowing large energy dissipation, although the limited content of stiff material. From Fig. 3(c,d), it seems that MBs change the crack deflection to a more block-wise pattern rather than the zig-zag one observed in the case without MBs. This kind of failure pattern always leads to the increase in strength for all the composite topologies. In natural nacre, this block-wise crack propagation is also observed and shown in literature (Song et al., 2003) in transmission electron microscopy (TEM) micrographs revealing the mineral bridges hindering crack propagation in the matrix layer.

Fig. 4(a,b) shows histograms of toughness and strength of the different volume fractions, with and without the bridge feature. The green bars in the histograms are referred to the cases with 12 MBs. It can be seen that for 50%, 60%, and 70%, there is an improvement with MBs for toughness, but for the others (80% and 90%) there is no such improvement. Interestingly, strength is improved in all cases.

The change in toughness, (ΔToughness), and strength, (ΔStrength), for all volume fractions with and without MBs is summarized in Fig. 4. Also in this graph we refer to the cases with a fixed number of MBs, equal to 12. As seen in Fig. 4, overall, 70% has the largest mean change for both toughness and strength. This motivates our choice of 70% as the sample type to perform a systematic investigation on the effect of MBs on the mechanical behavior of nacre-like composites. An additional reasoning has to do with 70%’s failure mechanisms, as shown in Fig. 3(c). With its continuous deflections and its zig-zag shape, we believe that its failure has the most potential to be affected by the presence of MBs.

We consider the nacre-like topology with 70% volume fraction of stiff bricks and we add the bridging features. To observe the impact of changing the amount of mineral bridging, we designed new series of samples systematically varying the number of bridges per brick (from 6 to 18). Fig. 4(d) shows the stress-strain response of the new series tested. It can be seen that with any addition of bridges, it improves upon the strength of the 70% sample. Additionally, another interesting thing to note is the strength for the various number of MBs is similar, with the highest strength samples being the 70% with 9 and 12 bridges.

In terms of the failure mechanisms for 70% sample, the addition of different numbers of MBs allowed for a more block-wise crack travel, similar to the other volume fraction cases with MBs. The failure mechanisms pictures of the samples are depicted in Table 2, for four representative cases: 60% and 70%, with and without bridges. It can be shown that in the beginning of loading for both cases, small micro-cracks starts to form in the soft phase of the entire sample, allowing continuous and progressive energy dissipations. On the other hand, the load is increasing, revealing that the entire sample is working together to withstand the load, rather than just at the crack tip. These mechanisms help to distribute the stress and increase material toughness.

Toughness and strength trends with varied number of MBs are shown in Fig. 5. The shear length factor (l S), defined as the platelet length, p, divided by shear length (SL) is non-dimensional and is proportional to the number of MBs. The number of MBs is also indicated on Fig. 5. It can be shown that for toughness the curve increases as mineral bridge increases, reaches a peak, and then starts to decrease. From the fitting curve,

$$T(l_s) = \alpha_T l_s^\beta_T + \gamma_T l_s + \delta_T$$

where $T(l_s)$ is the value of toughness in terms of the shear length factor ($l_s$) and $\alpha_T$, $\beta_T$, and $\gamma_T$ are fitting parameters. We want to note that this proposed equation is valid in a limited domain. Additionally, for strength, it starts to level off as mineral bridge increases. The maximum peak for toughness is reached around 9 MBs and 12 MBs when strength starts reaching a plateau. From the fitting curve,

$$S(l_s) = \alpha_S l_s^\beta_S + \gamma_S$$

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where $S(l_c)$ is the value of strength in terms of the shear length factor ($l_c$) and $\alpha_S$, $\beta_S$, and $\gamma_S$ are fitting parameters. From this analysis, it shows that there is an optimal ratio for MBs and can be determined from the non-dimensional shear length factor. This may inspire the interfacial design of synthetic materials.

### 3.3. Simulations

DIC is used to analyze the strain field experimentally. Moreover, after testing we perform FE simulations of two different topologies (with and without mineral bridges), to obtain a deeper understanding of the local and global effect of mineral bridging on the stress and strain fields. Strain fields obtained from FE simulations and from DIC of 70% sample and 70%-12mb are compared (Fig. 6). From the DIC images related to the case without mineral bridges (Fig. 6(a)), it can be seen that the nacre-like design helps to distribute the strain field, with high strains concentrated in a strip-like fashion around the crack tip region. A similar strain field is observed in the simulation. In the 70% sample, during loading, the large difference in strain and stress between the platelets and the matrix, leads the crack to follow a preferential path through the compliant phase, despite the energy “effort” owing to continuous deviations.

The strain field generated from experiment of sample 70%-12mb is shown in Fig. 6(b). It is difficult to discern by bare eyes the difference between the strain fields with and without MBs because of the limitations of speckle size compared with the length scale of the diameter of the MBs. The simulation strain field, however, allows the viewing of the fine features of the MBs in the design, making it possible to notice a clear effect of mineral bridges on the strain map. In Fig. 6(b), we can notice a smooth transition between the strain level in the soft and in the stiff component. The recurring presence of these stiff features interrupts the continuity of the matrix, altering the stress and strain fields and allowing for a more homogeneous distribution. This leads to a failure characterized by less deviations through the matrix. The final path is nonlinear, and characterized by a rough and jagged surface. However, the strain and the stress levels are higher in this sample series, allowing for a larger energy dissipation before failure (i.e. higher toughness modulus). Here the energy is dissipated by two main mechanisms: i)}
breakage of the stiff pillars (bridges) and ii) matrix failure by shear yielding and crazing. The latter slow the process of crack propagation through fibrillar bridges and micro-voids. This analysis helps us to understand the origin of the different failure modes occurring in the two sample series.

4. Discussion

The analysis reported here shows that solely increasing the number of MBs will add much benefit to the performance in terms of strength, but not in terms of toughness. Indeed, increasing the number of bridges will increase the toughness until a certain threshold, beyond which the toughness decays (Fig. 5). The bridging threshold corresponds to a critical number of bridges (about nine), above which the material becomes more brittle. This is probably due to a limited shear length domain, which constrains the deformations to a restricted region, affecting the energy dissipation and the failure mode. This phenomenon is reminiscent of the cross-linking mechanism in thermosetting polymers. Cross-linking generally improves the properties of thermosets and rubbers (mechanical strength, stiffness, and rigidity of polymer microbeads). However, increasing the crosslinking degree above a certain threshold may cause the polymer embrittlement. From a phenomenological point of view, this corresponds to the fact that the polymer chains in between two consecutive cross-links have a limited deformation domain (to allow the chain disentanglement and the polymer chain sliding and stretching).

All data is gathered in an Ashby chart (Fig. 7), comparing strength and toughness with two distinct families shown. The first family is shown to solely explicate the volume fraction effects on composite performance. From the first family, it can be shown that 80% achieved the best combination of strength and toughness. When combining volume fraction and mineral bridge effects, it can be shown that 70% volume fraction has the best combination of strength and toughness. This effect is shown in the second family. Additionally, the second family shows that with the addition of MBs, all volume fraction samples improve in strength, which is consistent with literature (Song et al., 2003). The second family shown discusses the effects of MBs with a fixed volume fraction of 70%. With that, an optimal number of MBs is found to be approximately 9 bridges, with its best combination of strength and toughness. This effect is shown in the second family. Additionally, the second family shows that with the addition of MBs, all volume fraction samples improve in strength, which is consistent with literature (Song et al., 2003). The second family shown discusses the effects of MBs with a fixed volume fraction of 70%. With that, an optimal number of MBs is found to be approximately 9 bridges, with its best combination of strength and toughness. This effect is shown in the second family. Additionally, the second family shows that with the addition of MBs, all volume fraction samples improve in strength, which is consistent with literature (Song et al., 2003). The second family shown discusses the effects of MBs with a fixed volume fraction of 70%. With that, an optimal number of MBs is found to be approximately 9 bridges, with its best combination of strength and toughness. This effect is shown in the second family. Additionally, the second family shows that with the addition of MBs, all volume fraction samples improve in strength, which is consistent with literature (Song et al., 2003). The second family shown discusses the effects of MBs with a fixed volume fraction of 70%. With that, an optimal number of MBs is found to be approximately 9 bridges, with its best combination of strength and toughness.
are clearly also important features evident in natural nacre (Shin et al., 2016). One current limitation of additive manufacturing is that 3D printers that can print with nanoscale resolution cannot print objects at the macroscale, and vice versa. As additive manufacturing advances, however, smaller features can most likely be printed together with larger features to capture the other structural features in natural materials and they can be systematically studied with the approaches proposed in this work. Another interesting follow-up to this work includes using an algorithm driven approach to find the optimal number of MBs to add for future nacre-inspired composite designs.

5. Conclusions

Nacre's microstructural features, such as MBs, play an important role in enhancing its mechanical properties. Some researchers, as a result, implemented nacre's mineral bridge features in de novo materials, but a systematic approach in doing so is missing in the literature. Here, the use of additive manufacturing has allowed us to perform a systematic analysis by designing, manufacturing, and testing samples with varied structural features (e.g. mineral fraction and MBs). In terms of stiff mineral volume fraction, results reveal the importance of the stiff phase in carrying the load and the soft phase in transferring the load through the platelet by shear, allowing for larger deformation under mechanical loading and for toughness enhancement through the activation of several mechanisms. Results also reveal the crucial role of the addition of MBs in terms of improving mechanical properties such as toughness and strength. The mimicking of this feature allows us to implement new toughening mechanisms, changing crack deflection to a more block-wise pattern rather than the zig-zag one observed in cases without MBs. Additionally, we notice a major effect of design rather than volume fraction on improving the properties of strength and toughness, meaning the stiffness is led by the brick-phase, while the design drives the strength-toughness relationship. Simulation work shows that the recurring presence of these stiff MB features interrupts the continuity of the matrix, altering the stress and strain fields and allowing for a more homogeneous distribution. Given the critical role of design revealed in this study, it has been envisioned that future optimization driven generation of bio-inspired engineered materials can bolster the search for new functional advanced materials.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.jmbbm.2017.05.007.

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