Additive Manufacturing and Performance of Architectured Cement-Based Materials

Mohamadreza Moini  
*Purdue University*, mmoini@purdue.edu

Jan Olek  
*Purdue University*, olek@purdue.edu

Jeffrey P. Youngblood  
*Purdue University*, jpyoungb@purdue.edu

Bryan Magee  
*Ulster University at Newtownabbey*

Pablo D. Zavattieri  
*Purdue University*, zavattie@purdue.edu

Follow this and additional works at: https://docs.lib.purdue.edu/civeng

Part of the [Civil and Environmental Engineering Commons](https://docs.lib.purdue.edu/civeng)

Moini, Mohamadreza; Olek, Jan; Youngblood, Jeffrey P.; Magee, Bryan; and Zavattieri, Pablo D., "Additive Manufacturing and Performance of Architectured Cement-Based Materials" (2018). *Lyles School of Civil Engineering Faculty Publications*. Paper 27.  
https://docs.lib.purdue.edu/civeng/27

This document has been made available through Purdue e-Pubs, a service of the Purdue University Libraries. Please contact epubs@purdue.edu for additional information.
Dear Dr. Lenders,

We wish to submit the paper entitled “Additive Manufacturing and Performance of Architectured Cement-based Materials” for publication in the Advanced Materials. There is a quest to use additive manufacturing for 3D printing cementitious materials. However, due to the intrinsic limited strength, brittle behavior and presence of weak interfaces, this is a very challenging task. In this article, we examine the use of bioinspired architectures to create 3D printing cementitious materials with improved mechanical properties. In our work, we demonstrate that using bioinspired architectures with clever mechanisms that prevent catastrophic failure, we are able to increase the fracture energy by more than 150% with respect to its base material without sacrificing the strength of the base materials (similar to what we also find in natural materials).

We believe that this article fits into the scope of Advanced Materials as it brings important information about the role of architecture in materials. It shows controlled spread of damage through relatively weak interfaces, which is counter-intuitive in brittle materials. It also brings new insights into materials design. This is important considering that several current research efforts are actually trying to eliminate these interfaces. Please do not hesitate to contact me should you have any questions.

Sincerely,

Pablo Zavattieri
Purdue University

Do you or any of your co-authors have a conflict of interest to declare?

No. The authors declare no conflict of interest.
Abstract:
There is an increasing interest in hierarchical design and Additive Manufacturing (AM) of cement-based materials. However, the brittle behavior of these materials and the presence of interfaces from the additive manufacturing process represent the current major challenges. Our work focuses on harnessing the heterogeneous interfaces by employing clever designs from bio-inspired Bouligand architectured materials. In this paper, we aim to demonstrate some key mechanisms that can allow brittle hardened cement-based materials to gain flaw-tolerant properties. Mechanisms such as crack twisting at the interfaces have been previously observed in naturally-occurring or synthetic composite Bouligand architectures. In this paper, a heterogeneous interface with porous characteristics in 3D-printed solid hardened cement paste (hcp) architectures were characterized. We hypothesize that the presence of heterogeneous interface in 3D-printed hardened cement paste (hcp) elements, in conjunction with clever architectures, promote key damage mechanisms such as interfacial cracking and crack twisting that lead to damage delocalization. This delocalization can be energetically favorable and allow energy dissipation and promote toughening and flaw-tolerant properties. We found that these architectures can enhance the properties from the typical strength-porosity relationship, classically known for brittle hcp materials.
Additive Manufacturing and Performance of Architectured Cement-based Materials

Mohamadreza Moini, Jan Olek, Jeffrey Youngblood, Bryan Magee, Pablo D. Zavattieri*

M. Moini, Prof. J. Olek, Prof. P. D. Zavattieri

Lyles School of Civil Engineering, Purdue University at West Lafayette, Indiana 47907, USA

E-mail: zavattie@purdue.edu

Prof. J. Youngblood

School of Materials Engineering, Purdue University at West Lafayette, Indiana 47907, USA

Dr. Bryan Magee

Built Environment Research Institute, Ulster University at Newtownabbey, BT37 0QB, UK

Keywords: direct ink writing, architectured material, hardened cement paste, interface, mechanical response
Abstract

There is an increasing interest in hierarchical design and Additive Manufacturing (AM) of cement-based materials. However, the brittle behavior of these materials and the presence of interfaces from the additive manufacturing process represent the current major challenges. Contrary to the commonly adopted approach in AM of cement-based materials to eliminate the interfaces and to add reinforcements, our work focuses on harnessing the heterogeneous interfaces by employing clever designs from bio-inspired Bouligand architectured materials.

In this paper, we aim to demonstrate some key mechanisms that can allow brittle hardened cement-based materials to gain flaw-tolerant properties. Mechanisms such as crack twisting at the interfaces have been previously observed in naturally-occurring or synthetic composite Bouligand architectures. In this paper, a heterogeneous interface with porous characteristics in 3D-printed solid hardened cement paste (hcp) architectures were characterized. We hypothesize that the presence of heterogeneous interface in 3D-printed hardened cement paste (hcp) elements, in conjunction with clever architectures, promote key damage mechanisms such as interfacial cracking and crack twisting that lead to damage delocalization. This delocalization can be energetically favorable and allow energy dissipation and promote toughening and flaw-tolerant properties. These mechanisms can be controlled through AM and design of the architecture of hcp materials and can play a role in tuning, enhancing and diversifying the mechanisms that improve work of failure, strength, and inelastic deflection of the structure. The evidence is provided by multiaxial flexural tests comparing the architectured materials with cast specimens. We found that these architectures can enhance the properties from the typical strength-porosity relationship, classically known for brittle hcp
materials. In turns, these architectures exhibit interfacial damage mechanisms and
demonstrate improvements of the work of failure by more than 50% exhibiting the controlled
spread of damage without sacrificing strength.
There is a rising interest in hierarchical design and additive manufacturing (AM) of architected materials due to their ability to achieve unique and novel performance characteristics [1-8]. AM allows for engineering and fabrication of a vast array of metallic, ceramic, polymeric, composite, and hydrogel materials into complex solid and cellular structures and assists us in the understanding of the structure-property relationship [9-23]. It has been established that AM of metallic [9,10], polymeric [11,12,13], hydrogel [14], and ceramic [15] materials introduce microstructural heterogeneities such as porosity and interfaces which can result in anisotropy in the mechanical response of the elements. For instance, in case of ceramic and metallic materials, the resulting anisotropic mechanical properties are demonstrated to be similar, lower, or higher, compared to the conventionally cast counterparts and depending on the building directions, the type of applied AM techniques and mechanical property of interest [9-14]. Currently, there are two approaches towards enhancing the mechanical response of additively manufactured materials: a) elimination of detrimental heterogeneities such as porosities and interfaces present in fabricated metallic [9,10], ceramic [15], and hydrogel materials [14] via optimizing the printing parameters in order to achieve comparable performance to cast counterpart and; b) incorporation of multi-scale [13], hierarchical [16], and bioinspired [17] design principles over a broad range of architectures of fabricated materials from nano [18] to micro [19,20] in order to attain a facile approach to engineer the mechanical properties [19], significantly enhance the strength and tensile performance [13], load-bearing capacity, compliancy, and impact resistance [16], and overcome the brittleness and flaw-sensitivity limitations of these materials [18,20]. Similar to the trend in various additively manufactured materials [9-12,13,14], the presence of weak interface is
considered detrimental for the overall mechanical performance of additively manufactured cement-based materials, and current research efforts focus mostly on eliminating or strengthening the AM-induced interfaces as a mean to minimize their effect on the overall strength, bearing capacity and improve stress transfer across the interfaces in 3D-printed elements [25-30]. Contrary to this common approach that suggests elimination of the processing-induced interfaces in various materials [10,11,15], we present a facile approach that combines harnessing the heterogeneous interfaces with the design of the materials architecture that can promote damage mechanisms, achieve flaw tolerance and unique load-displacement response, and enhance the mechanical response in brittle cement-based materials. The focus of this work is on 3D-printing of brittle cement-based materials, in which the ability to control the internal architecture of the structure at the macroscopic level (i.e., mm scale) may play a significant role by enabling novel performance characteristics, such as a quasi-brittle mechanical behavior, fracture and damage tolerance, unique load-displacement response, and enhanced flexural strength. Materials with such enhanced properties may impact design approaches, processes, and products in several industries [31,32].

Despite recent works on processing [33-35], and characterization of mechanical performance [25-30] in 3D-printed cement-based materials, as well as earlier works on microstructural aspects of fracture properties of hcp [36-38], there are only limited studies that highlight control of the mechanical behavior through the architectural design of the materials [39,40]. Due to its intrinsic properties, the cast hardened cement paste (hcp) does not exhibit typical toughening mechanisms, e.g., crack branching, observed in other materials [41-44]. Correspondingly, cast cement paste behaves as brittle material and does not show non-linear post-peak load-
displacement behavior [45]. However, existing studies demonstrated that directionality of response, as enabled by controlling the internal architecture of the elements, can play a part in spreading of the damage, and may improve the overall inelastic response of composite materials, specifically brittle ceramics and compliant organic materials [46-53]. In this work, the mechanical response of 3D-printed cement paste elements with specific architectures, along with the associated damage mechanisms, have been investigated by examining the behavior of both, the individual filaments (i.e., layered deposited material) and the interfaces between the filaments.

Many of the internal architectures that can be fabricated via 3D-printing are not possible or are extremely challenging to achieve while using conventional casting methods. To illustrate this point, this paper presents several elements with various materials architecture achieved by 3D-printing of the ordinary portland cement paste using the direct-ink-writing (DIW) method. These architectures included: a compliant structure with honeycomb architecture (Figure 1a), a cellular sandwich panel prism with solid top and bottom layers (Figure 1b), a ‘Bouligand’ architecture with helicoidal alignment of filaments at pitch angles $\gamma = 2^\circ$ and $45^\circ$, (Figures 1c,d), 3D rendition of the design of Bouligand architecture with $\gamma = 45^\circ$ (Figure 1e), 3D rendition of the entire volume of Bouligand architecture with $\gamma = 45^\circ$ upon X-ray Micro-CT processing (Figure 1f).

When subjected to cycling loading, a compliant structure with honeycomb architecture (similar to that illustrated in Figure 1f) displayed bi-linear stress-strain behavior characterized by two discrete values of moduli of elasticity (see Figure S1 in Supporting Information).
The values of modulus of rupture (MOR) of printed solid prisms with various filament orientations (i.e., 0°, 45°, and 90° with respect to X-axis, Figure 2a) were determined using the three-point-bending (3PB) test (Figure 2b). A comparison of average values of specific MOR for printed and cast specimens (Figure 2c) reveals that they were not statistically different (i.e., at the 95% confidence level p ≥ 0.05 for all printed specimens when compared to cast specimens). This implies that the mechanical response of all three of the printed prisms was independent of the orientation of the filament, and the specimen processing method (i.e., printed vs. cast). Since there are some observable variations in crack patterns of specimens with different filament orientations (Figures 2d-m), the lack of statistically discernible changes in the values of specific MOR (despite the presence of such differences in work of failure (WOF) values of printed and cast specimens shown in Figure 3c) may simply imply that the 3PB test is not capable of adequately capturing the microscopic level fracture response. However, the 3PB test can be used to characterize the strength of the materials (i.e., tensile strength of the individual filaments) and the interfacial strength. The strength of the materials reaches a plateau as the thickness of both cast, and the 3D-printed prisms with 0° filament orientations increases from 1 mm (i.e., 1 layer) to 12 mm (i.e., 12 layers) and is demonstrated in Supporting Information (Figure S2). The strength of the materials is estimated with the average value of this plateau (Figure S2). The interfacial strength was estimated via 3PB test of prims with 12 mm thickness and 90° filament orientation. The interfacial strength was found to be statistically similar to materials strength.
Previous research indicated that 3D-printed cement-based elements exhibited zones of weakness at the interfaces between individual filaments [25-30], a phenomenon not commonly observed in conventionally cast hcp. The heterogeneous characteristics of the interfacial regions (IRs) in the 3D-printed solid prism (with 0° filament orientation) were characterized using X-ray micro-computed tomography (Micro-CT) and demonstrated in Supporting Information (Figure S3a,b). The heterogeneous IRs demonstrated a porous characteristic in the solid 3D-printed prism. The influence of these pronounced interfaces on the overall crack paths, and on the associated micro-cracking, has been observed to be unique for each of the 0° and 45° prisms used in this study. Specifically, the crack paths in specimens with these two architectures intercepted the filaments (Figures 2d,e) whereas the crack path was parallel to the filament in the prisms with the third type of architecture (i.e., the one with 90° filament orientation). When the first two types of prisms (i.e., 0° and 45° filament orientations) were examined microscopically, the crack path was observed to be partially deflected to the heterogeneous interface along the layered filaments (i.e., it was parallel to the X direction). This partial deflection resulted in somewhat staggered crack pattern (Figures 2d,e,g,h).

Furthermore, examination of Figures 2j,k revealed the development of microcracking along the interface between two filaments (i.e., in the X-Y plane) at the same locations where partial deflections of the crack path were observed. Micro-CT characterization of a prism with 0° filament orientation in two magnifications further elucidated the presence of micro-cracking at the interfacial regions near the fractured plane and is provided in Supporting Information (Figure S4). In contrast, not such microcracking was observed along the X-Y plane interfaces of the prisms with 90° filament orientation (Figure 2i). This particular prism failed due to the...
formation of a single, predominantly unidirectional crack along the interfaces in the X-Z plane (Figure 2i).

Overall, the microscopical comparison of crack paths in these three prism architectures indicates the presence of heterogeneous interfaces in the 3D-printed elements and the micro-CT examination of the prism with 0° filament orientation revealed the heterogeneous and porous characteristics of the interfacial regions (IRs) as provided in Figure S3a,b. However, these observations also suggest that the crack paths in 3D-printed elements could be controlled by varying the orientation of the filaments. If such damage mechanisms are combined with architectures that promote local hardening by guiding cracks and promoting multiple site nucleation, then delocalization can be attained \cite{57}. In other words, the implication of “engineering” the architecture of the 3D-printed elements enables mitigation of catastrophic failure that was not attainable in cast elements.

The Bouligand architectures utilized here have been previously reported to introduce damage mechanisms and increase the toughness and energy absorption capacity \cite{54-57}. These architectures have found applications in engineering materials and offer enhanced fracture properties by enabling crack propagation in a stepwise pattern, crack redirection, branching, and prevention of catastrophic failure in various biological organisms such as lobster, crab, and mantis shrimp \cite{54-59}. Previous research has shown that these Bouligand architectures, found in the endocuticles of arthropods (such as mantis shrimp), tend to grow cracks in twisted patterns following the direction of the fiber \cite{54}. These twisting patterns have been
found to be responsible for increasing toughness\textsuperscript{[56]} and promote the spread of the damage\textsuperscript{[57]}. In naturally occurring fibrous Bouligand architectures, a competition between interfacial failure (i.e., the separation between fibers) and solid failure (i.e., fiber fracture) of materials, is anticipated to be a trade-off between small and large pitch angles\textsuperscript{[54-59]}. While small pitch angles facilitate the crack to grow through the interface, they also allow local softening\textsuperscript{[54-59]}. However, this interfacial failure can be controlled by providing a crack path that leads to local hardening (e.g., such as crack twisting). This enables delocalization and spread of the damage to neighboring regions. In contrast, large pitch angles may lead to crack growth through the solid materials (e.g., biomineral in case of arthropods) and hinder the twisting or spread of the crack at the interface. These competing mechanisms can be controlled with the pitch angle as a design variable (among other material properties). This competition is demonstrated in this paper by focusing on the analysis of the specimens with small pitch angle (e.g., $\gamma = 8^\circ$) and the large pitch angles (e.g., $\gamma = 45^\circ$ and $90^\circ$).

To further investigate the structure-performance relationships, elements with several Bouligand architectures were 3D-printed by varying pitch angles ($\gamma = 8^\circ$, $15^\circ$, $30^\circ$, $45^\circ$, $90^\circ$) and infill percentages (60\% and 100\%, i.e., cellular and solid). The Ball-on-three-Ball mechanical testing (B3B) was performed on these elements for determination of specific strength (MOR), specific work of failure (WOF), and documenting load-displacement behavior.
The results presented in Figure 3a illustrate that maximum load deflections of elements with Bouligand architectures were consistently higher than the maximum load deflections of the cast elements. Specifically, the observed increases in the maximum load deflections were 5%, 25% and 50% for architectures with $\gamma = 8^\circ$ (60% infill), $\gamma = 45^\circ$ (60% infill), and $\gamma = 8^\circ$ (solid, i.e., 100% infill), respectively. It should also be noted that these Bouligand architectures have achieved higher deflection while having relative densities (i.e., the density of each specimen relative to the average of the conventional cast solid) lower than cast specimens.

As discussed in the prisms study above, the presence of the heterogeneous interface and the deflection of the crack path into the interface and presence of micro-cracks in the interfaces are also of particular importance for the printed disc structures. The heterogeneous characteristics of the IRs in the 3D-printed solid Bouligand architecture specimens (with $\gamma = 8^\circ$) were characterized using X-ray micro-CT and are provided in Supporting Information (Figure S3c,d and Video S10). The heterogeneous IRs demonstrated a porous characteristic in 3D-printed solid Bouligand architecture similar to those found in solid prism with $0^\circ$ filament orientation. The identified porous IR found in the microstructure of 3D-printed materials (in both solid prism and solid Bouligand architecture, Figure S3), can enable the spread of the damage in the solid structure by localization of micro-cracks. In cellular structures, fracture of sacrificial links between filaments without sacrificing the integrity of the structure can provide the spread of the damage in the structure and tolerance to fracture. The damage and fracture of filaments at pre- and post-peak is additionally captured in the studied Bouligand architectures. The screenshot of the acoustic recording of the fracture
during testing for $\gamma = 45^o$ and the cast is also illustrated in Figure 3a. The screenshot of the acoustic recordings qualitatively describes the propagation of multiple cracks prior- and post-peak in the Bouligand structure. The major peaks of the acoustic graph match the local maximum loads. This detected damage propagation is distinguished when compared to fracture of cast cement in a brittle manner (Figure 3a).

In terms of strength, the majority of Bouligand structures ($\gamma = 15^o$, 30$^o$, 45$^o$, 90$^o$), other than $\gamma = 8^o$ with 60% infill, are statistically similar in average specific MOR when compared to cast structures (Figure 3b). This equivalent performance includes the solid specimen with the small pitch angle with $\gamma = 8^o$ with 100% infill.

The WOF is assessed for all Bouligand architectures, and an increase in WOF is observed as $\gamma$ increased from $8^o$ to $90^o$ for 60% infill structures (Figure 3c). The observed pattern is consistent with previous studies on composite materials with the Bouligand architecture, suggesting increased WOF with the increase in rotation angle [55-57]. Figure 3c describes how $\gamma$ or infill percentage can play a role in the fracture properties of materials. The solid structures with $\gamma = 8^o$ demonstrated elevated WOF compared to its identical $\gamma$ at lower density (60% infill). The solid structures with $\gamma = 8^o$ show a counter-clockwise orientation of the fractured plane following the right-hand pattern in consecutive layers (positive counter-clockwise $\gamma$) indicating subtle twisting in the fracture plane across the height of the specimen.

The fracture properties of Bouligand architectures studied here indicates the ability to control the WOF by controlling the pitch angle and relative density in brittle materials. The detailed comparison of specific MOR and WOF between Bouligand architectures and monolithic cast
hcp counterparts is provided in Supporting Information (Figure S5). It was demonstrated that most cases (where $\geq 15^\circ$) of Bouligand architectures could maintain specific MOR compared to cast elements, while statistically significant enhancement in WOF of both solid ($= \gamma \ 8^\circ$) and cellular ($= \gamma \ 90^\circ, \ 45^\circ$) architectures was observed compared to cast elements.

The performance of Bouligand structures in terms of MOR with respect to their relative density is assessed for various $\gamma$ and compared to conventionally porous solid cast counterparts over a broad range of porosity (Figure 3d). Apparent from Figure 3d, and benchmarked against theoretical curve and values of MOR for hardened cast cellular hcp [60], is the emergence of a distinct group of printed Bouligand architectures with $\gamma = 15^\circ \ to \ 90^\circ$ (outlined in blue in Figure 3d) that consistently out-performs conventionally cast specimens across the relative density range considered (0.5-0.65). When the average values of MOR for the Bouligand architectures with $= \gamma \ 15^\circ, \ 30^\circ \ 45^\circ, \ 90^\circ$ (as outlined in blue in Figure 3d) were compared with the porous cast specimens (i.e., porous cast of similar relative density range, between 0.50 to 0.65 as shown in Figure 3d), a statistically significant enhancement in favor of Bouligand architecture specimens was found. When a similar comparison is performed between Bouligand architecture specimens with $= \gamma \ 8^\circ$ and porous cast specimens, no statistically significant loss of Specific MOR was found. The comparisons of MOR in Figure 3d demonstrates that Bouligand architectures can have at least similar (in case of $= \gamma \ 8^\circ$) or significantly improved (in cases of $= \gamma \ 15^\circ, \ 30^\circ \ 45^\circ, \ 90^\circ$) MOR compared to their porous cast hcp counterparts within the same range of density. This presents clear indication that significantly improved performance is attainable in most cases by 3D-printed Bouligand
architectures relative to the conventionally cast specimen with equivalent density, reflecting
the unique ability of elements architecture to enhance the mechanical properties. (Figures 3d). It must be noted that naturally-occurring architectured materials typically exhibit improved
toughening, in many cases an order of magnitude higher, compared to monolithic counterparts [61-64]. Nature materials achieve this improvement, without significantly sacrificing other
mechanical properties such as strength and stiffness [61-64]. The mechanisms that lead to this
improvement have been attributed to the composite effect of minerals with soft materials
combined with the hierarchical architecture that results in triggering controlled failure through
the interface and delocalization of crack [61,63]. In turn, this delocalization leads to improved
energy dissipation over large volumes that contributes to the toughness of the materials [63]. In
our work, the enhanced improvements in the mechanical properties demonstrate that some of
these mechanisms can be reproduced by controlling the architecture and incorporating the
heterogeneous interface in the 3D-printed architectured hcp materials. However, the size of
specimens here compared to the features of the architecture (e.g., the size of the filament
height and width) may be relatively small for capturing a similar increase in toughness with
respect to the monolithic hcp specimens. The mechanical response of the Bouligand
architecture specimens studied here suggest that an increase in toughness is attainable and the
architecture can assist in achieving similar mechanisms that is previously reported in this
architecture [54-57,59]. However, obtaining such increase in toughness will occur as more spread
of the damage and delocalization of crack is expected to take place in specimens of larger
volumes.
Bouligand architectures are further studied for identification of the fracture patterns, crack paths, and micro-cracks using optical microscopy (Figure 4). A variety of fracture paths and crack patterns are exhibited at the bottoms (Figures 4a.1-c.1) and cross-sections of Bouligand architectures (Figures 4a.2-c.2). In specimens with large pitch angles such as $\gamma = 45^\circ$ (with 60% infill, the crack path appears to shear the filaments (Figure 4c2), whereas it advances at the interfaces between adjacent filaments in specimens with small pitch angle $\gamma = 8^\circ$ (in both cases 60% and 100% infill, Figures 4a.2,b.3). The crack path, for the $\gamma = 45^\circ$, resulted in shear failure in the filaments typical in Bouligand structures with large pitch angles.

Although, the filaments in the layers parallel to the main failure plane remained intact (in layer 1- bottom and layer 5, Figures 4c.2). In contrast with the large pitch angle architecture ($\gamma = 45^\circ$, Figures 4c.3), the horizontal propagation of the crack paths at the interfaces is observed at the small pitch angle ($\gamma = 8^\circ$) structures with 60% infill (between layers 4 and 5) as demonstrated in Figures 4b.3,b.4. In the solid structures with small pitch angle ($\gamma = 8^\circ$), the micro-cracks propagate at the interface (between layers 6 and 7) and between layers 2 and 3 near the crack divergence points at the cross-section viewed in Figure 4a.3. Advancement of the micro-crack at the interface in the solid specimens with $\gamma = 8^\circ$ is further accompanied by observation of multiple parallel micro-cracking throughout the top (Figures 4a.4) and bottom layers (Figures 4a.5,a.6). Also, a staggered fractured pattern is observed in the main failure plane (Figure 4a.2,a.8). Micro-CT characterization of a solid Bouligand architecture with $\gamma = 8^\circ$, further elucidated presence of the crack advancement and micro-cracking at the IRs and that the heterogenous IRs can facilitate damage mechanisms as provided in Figure S6 and
Videos S12 to S14 in Supporting Information). The two damage mechanisms (i.e., horizontal propagation of the crack path and micro-crack propagation at the interface) at the small pitch angles are of great interest as they can promote controlled crack growth and local hardening. In contrast, Micro-CT characterization of a cellular Bouligand architecture with large pitch angle \( \gamma = 45^\circ \) demonstrated the shear failure of the filaments at this large pitch angle (Figure S7a,b, and Videos S15-S18). The contrast between damage mechanism in this large pitch angle is further elucidated in Figure S7c,d comparing it with the solid Bouligand architecture with large pitch angle \( \gamma = 45^\circ \). The shear failure of the filaments at large pitch angles are in accordance with previous researches on damage mechanisms in composite Bouligand architectures that present solid failures at such large pitch angles \([54-57]\). The higher WOF for solid structures with \( \gamma = 8^\circ \) seemed higher than that the conventionally cast discs (Figure 3c), may be attributed to the allowance of toughening and damage mechanisms such as observed micro-cracking advancement at the heterogeneous interfaces.

Micro-cracking in other arrangements in the bridging links between the filaments in Bouligand architectures is recognized in \( \gamma = 30^\circ \) structures. Multiple parallel micro-cracks near the fractured plane of the specimens are observed at the bottom layers 1, 2 and 3 (Figures 4d.1,d.2). These parallel micro-cracks are spaced equally from the fracture edge in the very bottom layer (Figure 4d.1) and appear twisting in the subsequent bottom layers 2 and 3 at the bridging links (Figure 4d.2).

A similar sinusoidal fractured pattern is observed in the Bouligand architecture with small pitch angle \( \gamma = 8^\circ \) with both 60% infill and 100% infill (Figures 4a.7,b.5). It is noteworthy
that in the 60% infill case, the micro-crack advancement is also observed at the interface (Figure 4b.6).

Overall, in Bouligand architectures, the crack deflection at the interface are commonly observed in smaller pitch angles ($\gamma = 8^\circ$ with 60% infill and 100% solid, Figures 4b.3,b.4,a.1). The micro-crack advancement at the interface is also observed in small pitch angle (Figures 5a.3-a.6,b.5) indicating heterogeneous properties at the interface. The presence of this heterogeneous interface, not only allows to control the crack path to follow the interface but also can initiate numerous micro-cracking advancement. Acknowledging this possibility, control of the architecture (via control of the pitch angle) and the properties of the interface can be combined to promote crack initiation and interfacial damage mechanisms and allow controlled crack growth and an increased threshold to crack initiation, initiation toughness, and WOF (Figure 3c).

As reported earlier, Bouligand architectures are known to present competing interfacial and solid damage mechanisms corresponding to small and large pitch angles, respectively \[56,57\]. The small pitch angles allow for crack growth at the interface and control of the crack path, where large pitch angles facilitate crack advancement through the solid material. The damage mechanisms for small pitch angle ($\gamma = 8^\circ$) here, in both solid (100% infill) and cellular (60% infill) Bouligand architectures, demonstrate that the interfaces promote damage mechanism such as crack advancement at the interface and micro-cracking as shown in Figure a2-a8 and Figure b3-6, respectively, as well as Figure S7c,d. In contrast, the damage mechanisms in large pitch angles ($\gamma = 90^\circ$ and 45$^\circ$), demonstrates a dominant crack growth through the solid
filaments as demonstrated in Figure c2,3 and Figure S7a,b. The mechanisms demonstrated in solid and cellular Bouligand architectures with a small pitch angle of 8°, can allow for achieving flaw-tolerant behavior in a larger volume. We surmise that an optimum architecture could be obtained with a Bouligand structure with moderate pitch angles. Such angles will be large enough to promote local hardening in the material, and therefore, allow multiple site crack nucleation, and small enough to avoid advancement of one dominant crack through the filaments.

The fracture behavior of hcp commonly exhibits brittle and unstable crack propagation [30]. Overall, in 3D-printed prisms with 0° and 45° filament orientations, horizontal deflection of crack is demonstrated and redirected at the interface, followed by advancement of micro-cracks at the interface between filaments (Figures 2g,h, Figure S4). This crack deflection and the subsequent micro-crack induction, suggests the possibility of the increased spread of the damage in the design of these architectured materials. In 90° prisms, no micro-crack or crack deflection at the interface is observed. However, a remarkable observation, in this case, is that the main crack occurs at the interface between the filaments in the mid-span of the specimens through the entire cross-section (Figures 2i). The demonstrated interface between layers can be utilized in an architecture in which the micro-cracks can be advanced in multi-layers and allow for a fracture toughening mechanism [47,48].

More broadly, in both types of solid prisms and Bouligand architectures studied in this work, micro-crack advancement along the interface is observed. In most cases, the initiated micro-cracks in solid prisms (Figure 2g,h, Figure S4) and solid Bouligand structures (Figures 4a,3-
a.6, Figure S6) spread to the edges of the specimen. Moreover, these interfacial micro-cracks are straight on a macroscopic scale, and follow the architectural pattern of the interfaces, both in prisms (Figures 2g,h, Figure S3a,b) and Bouligand architectures (Figure S3c,d). Typical fracture features of brittle hcp initiated from Knoop dent and is discussed to have a macroscopic scale (merely 0.5 to 5 mm for a 3-kg indentation load) and extend straight along the dent, followed by forward and backward crack branches on the order of 10s of microns and a common termination in a short fork form \([41]\). In contrast, in 3D-printed hcp we demonstrate that the properties of the interface between the filaments can be designed to act as a crack trap leading to prompt multiple site nucleation across filaments, and eventually define the overall response of the 3D-printed architectured hcp materials under loading.

The periodic crack patterns found in bridging elements near the failure plane in the 30° Bouligand architecture signifies that architecture of the material can allow for induction of cracks through sacrificial links without compromising the integrity of the structure. The failure of the sacrificial links does not necessarily decrease the strength (Figure 3b). However, it can contribute to the spread the damage due to the improved initiation toughness \([48]\). Such architectures, despite the brittle nature of their base materials, can undertake localized damage triggered by sacrificial links (Figures 4d.1,d.2) and yet be able to tolerate micro-cracks in each link. These micro-cracks can contribute to overall inelastic deformation and toughening of the material without abrupt macroscopic failure of the structure. Further understanding of such critical architectural parameters and interfacial properties can result in the design of flaw-tolerant brittle architectured materials.
In summary, the results demonstrate damage mechanisms that can allow brittle hcp materials to obtain flaw-tolerant properties. These damage mechanisms include crack growth at the interfaces, and interfacial microcracking. Other mechanisms, such as crack twisting, previously reported in naturally-occurring materials and synthetic Bouligand architecture [47,48], are a product of the interplay between interface properties and architecture. It was found that the presence of heterogeneous interface in 3D-printed hcp elements, facilitates damage mechanisms such as interfacial cracking and micro-cracking and the delocalization of the damage. This delocalization can be energetically favorable and allow energy dissipation and promote toughening and flaw-tolerance properties. These mechanisms can be controlled via AM and design of the architecture of hcp materials and can play a role in tuning the damage mechanisms and enhancing work of failure, strength and overall inelastic response of brittle materials. It was found that Bouligand architectures demonstrate elevated improvement from the typical strength-porosity relationship, classically known for brittle hcp materials. In turns, the Bouligand architectures showed improvements of the work of failure by more than 50% exhibiting the controlled spread of damage without sacrificing the strength.

While competing damage mechanisms are known between interfacial and solid failure in Bouligand architectures, it was found that in Bouligand architecture hcp material, small pitch angles (8°) facilitate interfacial crack growth through the interface and promote interfacial micro-cracking, where larger pitch angles (90° and 45°) demonstrates a dominant crack growth through the solid filaments (Figure S7).

The heterogeneous characteristics of the interfacial regions in the solid 3D-printed prism and Bouligand architecture specimens was characterized using micro-CT and provide in
Supporting Information (Figure S3). It was demonstrated that the presence of a porous IRs could promote damage mechanisms such as crack advancement and micro-cracking in these regions. These mechanisms can allow crack initiation and controlled crack growth, followed by local hardening mechanism (e.g., crack twisting).

We have demonstrated that AM and control of the architecture of the structure, can uncover novel behaviors of cement-based materials. These behaviors, observed in compliant design (Figure S1), prisms and Bouligand architectures, demonstrate new capacities to engineering performance of cement-based materials. Architectures such as compliant design demonstrated bilinear stress-strain behavior, not attainable in cast elements, and provides the ability to customize stress-strain behavior as applicable. In prisms, using architecture to control the crack path and allow advancement of multi micro-cracking (and spread of the damage) using a fracture toughening mechanism is conceivable.

Processing-induced weak interfaces are commonly considered defects in AM of cementitious materials and are avoided. In Bouligand architectures, we demonstrated that such heterogeneities interfaces exist and are not necessarily detrimental to the overall performance, but also can provide mechanisms that can lead to novel responses such as an increased deflection in load-displacement, enhanced WOF, and a variety of damage mechanisms. It must be noted that the enhanced properties certainly depend on the ability of the material to spread the damage over larger volumes. Indeed, the mechanisms analyzed in this work can be applied to other specimen sizes and can be used in the architectural design of brittle materials.

To further explore opportunities provided by architected cement paste materials, a fundamental understanding on the intertwined relationships between processing-induced
heterogeneities, interfacial strength, ink properties (cement hydration, rheology, chemistry, and formulation), architectural parameters (such as pitch angle and infill percentage), and microstructural characteristics of the intra-filaments and interfaces must be developed to fine tune the performance of resulting elements. Further understanding of the architectural parameters and interfacial properties, can result in the design of flaw-tolerant architectured materials with a brittle base such as hardened cement paste.

Experimental Section

Cementitious Ink Formulation: An iterative trial and error ink design procedure is used to identify cement inks suitable for the DIW process. The ink with proper flow properties that can overcome processing challenges such as flocculation, bleeding, and can result in suitable shape holding is designed. The final ink used constituted the sub 150 µm fraction of commercially available Type I cement (Buzzi Unicem USA) in accordance with ASTM C150 [65], deionized water, and both high range water reducing admixture (HRWRA-MasterGlenium 7700) and viscosity modifying admixtures (VMA-MasterMatrix 362) in accordance with ASTM C494 [66] and the findings of previous study [67]. For each 250 g of cement, the mix comprised 65.2, 1.1 and 3 g of deionized water, HRWRA, and VMA, respectively.

Mixing Procedure: A Twister Evolution Venturi vacuum mixer is used in three steps to mix and eliminate entrapped air. Admixtures are added and dispersed in water and mixed with cement at 400 rpm for 25 s, at 400 rpm for 90 seconds at 70% vacuum and then finally at
400rpm at 100% vacuum. This procedure was applied in preparing the cement paste ink for
3D-printed and cast specimen.

**Ink Rheology:** Rheological properties of the ink are characterized using a Malvern Bohlin
Gemini HR rheometer with 40 mm parallel plates (with the serrated surface to minimize the
slippage during the tests). A solvent trap was used to avoid evaporation during the test. The
rheological protocol used, and the yield stress and viscosity versus shear rates are presented in
the Supporting Information (**Figure S8**). The shear rate at the nozzle is calculated in
Supporting Information, and the corresponding viscosity of the ink is estimated and provided
at this rate (**Figure S8b**).

**3D-Printing:** A bespoke system is developed by merging a 3D printer typically used for
printing thermoplastics (Ultimaker 2 Extended+) with a stepper motor-driven extrusion
system (Structur3d Discov3ry Paste Extruder) capable of applying desirable extrusion rates to
mounted 75 mL ink-charged syringes. The 3D printer hardware is modified by mounting a
lightweight aluminum nozzle holder on the gantry for nozzle placement. The printer and
extrusion system are merged through standard luer locks and polyethylene tubing. Slicer-
generated g-code command included X,Y, Z point cloud coordinates and E (extrusion), and F
(printing speed) axis movement commands specific to each design. A nozzle with an internal
diameter of 1.36 mm, a layer thickness of 1 mm, and a printing speed of 250 mm min⁻¹ is used
throughout. The resulting filaments have a nominal width of 1.63 mm and a height of 1 mm.
The nominal width is calculated by multiplying internal nozzle diameter by a factor of 1.20 to
account for die-swell effect. Specimens are transferred to a curing chamber with a relative
humidity of 93 ± 1 % (using potassium nitrate) at 25 °C immediately after printing or casting.

The specimens were cast and printed in the lab environment at 18 ± 3 °C and 45 ± 5 % relative humidity. During casting, the paste was carefully poured into the mold to ensure no additional entrapped air is introduced during casting.

Characterization: Flexural strength and modulus-of-rupture (MOR), is used to characterize the mechanical properties via uniaxial three-point bending (3PB) testing of prism specimens and multi-axial ball-on-three-ball (B3B) testing of disc-shaped specimens. For 3PB testing, prisms are designed to have final dimensions of 12 x 12 x 40 mm, with surfaces being ground flat prior to testing to ensure acceptable tolerances and good contact with test support plates [68]. MOR is calculated based on the measured dimensions of each specimen. B3B testing is adopted given its high sensitivity to internal defects and insensitivity to outer and surface imperfections [69,70]. A load is applied via a central ball on the top face of round, disc-shaped specimen of 55 mm diameter and 8 mm thickness supported underneath by three equally sized, equidistantly spaced balls placed on a circle of diameter of 50 mm [71]. Bouligand structure discs are aligned to ensure that bottom filament orientation is aligned with the maximum stress field. A stereo microphone device (Zoom iQ6) with customizable stereo width is used to capture crack noise.

Force and displacement for both tests are measured using a 10 kN capacity test rig (MTS insight 10). All reported data is an average of at least two specimen results. Specimen relative density is calculated from measured mass and volume of each specimen divided by the average mass of conventionally cast ‘solid’ specimens. Specific MOR is calculated by
dividing the MOR value for each specimen by its relative density. WOF is calculated by integrating the entire areas under load-displacement curves. Although the first crack occurs at the first drop in the load-displacement curve, the work for the failure is requires to be quantified based on the entire area under the load-displacement curve. Two theoretical relationships between porosity and strength for brittle materials are presented in Figure 4 and describe the strength-porosity relationship of lightweight cellular structures based on the strength of a control specimen with zero porosity \[^{60,67,72,73}\]. All specimens are tested at the age of 3 days (72±2 hours). Aluminum powder and variations of water/cement ratios are used to cast lightweight cellular specimens.

X-ray micro-CT characterization: An X-ray microscope (XRM), Zeiss Xradia 510 Versa which allows for an increase in the resolution of scans through dual-stage magnification process was utilized. In the first stage (i.e., 0.4X scan), the field of view (FOV), desirable to scan the entire volume of the specimens was established via geometric magnification process, which involved setting distances between the source, detector, and specimen (as in conventional micro-CTs) \[^{76,77}\]. In a second stage (4X scan), additional optical magnification was enabled at the detector system through objective lenses. The detector is equipped with scintillator and objective lens which converts X-rays to light rays and thus allows for optical magnification and higher resolution. The 0.4X scans were performed for a solid Bouligand architecture with \( \gamma = 8^\circ \), a solid prism specimen with 0° filament orientation, and a cellular Bouligand architecture specimen with \( \gamma = 8^\circ \) which allowed a large FOV and thus facilitated to scan the entire specimens (55.1 \( \mu \)m, 37.2 \( \mu \)m, and 46.8 \( \mu \)m pixel size, respectively). For the
solid prism, this was followed by a 4X scan, allowing higher resolution (4.42 µm pixel size) at the region of interest near the main crack (ROI). The beam energies of 150 KeV, 140 KeV, 90 KeV, 100 KeV, the powers of 10 W, 10 W, 8 W, and 9 W, and exposure times of 4 s, 2 s, 4 s, and 14 s were used for 0.4X scans of the solid Bouligand architecture with $\gamma = 8^\circ$ and $45^\circ$, and the 0.4X and 4X scans of the solid prism specimens with $0^\circ$ filament, respectively.

Dragonfly software was used for post-processing of the data.

Supporting Information

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

Acknowledgments

The authors gratefully acknowledge generous support from the National Science Foundation (CMMI 1562927) of this research. The authors would also like to thank the BASF chemicals company for providing materials.

References


Figure 1. Various 3D printed architectures of hardened cement paste (hcp) elements: a) Compliant structure with honeycomb architecture, b) cellular sandwich panel prism with solid top and bottom layers, c-d) Bouligand architecture with, respectively, pitch angles \( \gamma = 2^\circ \) and \( 45^\circ \), e) 3D rendition of the design of Bouligand architecture with \( \gamma = 45^\circ \) and, f) 3D rendition of the entire volume of Bouligand architecture with \( \gamma = 45^\circ \) in X-ray micro-CT. All scale bars are 10.0 mm long.
Figure 2. Mechanical response of 3D printed solid prisms with various architectures tested in 3PB: a) Schematic of the top face (X-Z plane) of the specimens showing orientation of the filaments, b) Schematic of the 3PB test, c) Specific modulus of rupture of 3D printed and cast elements, d-f) Post-failure images of specimens with 0°, 45° and 90° filament orientation illustrating crack paths (as viewed along Z axis), g-i) Crack paths on the bottom face of specimens (as viewed along the Y axis), j-k) micro-cracks along the interfaces in prisms with 0° and 45° filament orientations (viewed in X-Y plane, along Z axis) and, i) uncracked interfaces in prism 90° with filament orientation (viewed in the X-Y plane along the Z-axis). Unless indicated, all scale bars are 1.50 mm long.
Figure 3. Mechanical response of Bouligand architecture using ball-on-three-balls test. a) Load-displacement for printed and cast disc specimens, including screenshot of acoustic spectrum recorded during testing; b) Specific modulus of rupture, c) Specific work of failure, and d) Modulus of rupture (MOR) versus relative density for Bouligand architectures with varying pitch angles ($8^\circ, 15^\circ, 30^\circ, 45^\circ, 90^\circ$) and percentages of infill (60% and 100%) compared to MOR of cast control discs; e-g) Views of bottom faces of discs with different Bouligand architectures, h) Schematic of Bouligand architecture with helicoidal alignment of filaments.
Supporting Information: Additive Manufacturing and Performance of Architectured Cement-based Materials

Compliant Architecture (Figure S1)

A honeycomb architecture with close cell (Figure S1a) and open cell (compliant) design (Figure S1b) is demonstrated. The compliant structure can demonstrate bilinear stress-strain behavior, including a primary linear strain recovery ($E_1$) at strains below which the layered filaments make contact (cycles 1-5 in Figure S1c1) and a secondary linear response above strains ($E_2$) at which the filament’s contact take place (cycles 6 in Figure S1c1). As can be seen, the jointless compliant structure shown exhibits two discrete moduli ($E_1$, $E_2$) depending on whether the filaments have made contact (Figure S1d,e) or not (Figure S1f,g). In contrast, the closed cell honeycomb architecture (HC) and cast element exhibit only one value of modulus (Figure S1c2). This dual response can be customized as applicable with a suitable design of the architecture, the spacing between filaments, and material property. The cast element represents a strain at failure of about 0.008. This is in the general range reported for typical hardened cement paste \cite{42}. In complaint structure, in addition to the bi-linear response, a strain (as high as 0.025 in the bi-linear region) much higher than the strain at failure commonly observed for cast hardened cement paste (0.005 to 0.008) \cite{42} is exhibited.
**Figure S1.** a) Closed cell honeycomb structure, b) Compliant structure with honeycomb architecture, c1) Bilinear stress-strain behavior of compliant structure (b), including five primary linear strain recovery (Cycles 1-5) and secondary response (Cycle 6) before and after filament’s contact, c2) Comparison of moduli of elasticity ($E_1, E_2$) of compliant structure (b2) with closed cell honeycomb (a) and cast, d) Compliant structure in cyclic loading (cycles 1-5) in which filaments do not make contact and, f) Compliant structure (in cycle 6) where filaments make contact. All scale bars are 10 mm long.
Characterization of Material Strength (i.e., filament strength) and Interfacial Strength (Figure S2)

The strength of a single filament and the interfacial strength was estimated using 3-Point-Bending (3PB) test on prism printed and cast specimen. To obtain material tensile strength, an experiment with specimens of varying thickness was designed. Cast specimen with 10 mm width and 1, 2, 5, and 12 mm thickness were made and tested in 3PB, and the specific MOR was obtained (as outlined in grey in Figure S2). Similarly, printed specimen with 10 mm width and 1, 2, 5, and 12 mm thickness (corresponding to 1, 2, 5, and 12 layers) and 0° filament orientation were fabricated and tested in 3PB, and the specific MOR was obtained (as outlined in blue in Figure S2). As the thickness of specimens increases, this specific MOR as reported in Figure S2a reaches a plateau for the specimens with a thickness greater than 5 mm. As the bottom layers remain in tension, the average tensile strength of a single filament is assumed to be the average strength of the prisms at the plateau.

To obtain interfacial strength, prisms with 10 mm width, 12 mm thickness and 90° filament orientation was fabricated. The specimens were tested in 3PB, and specific MOR was obtained. An evident cleavage, parallel to the filaments (as shown in Figure S2e in XY plane), was observed in the fractured prisms with 90° filament orientation. The interfacial strength is assumed to be the average strength of the element with 90° filament orientation.

The average value for interfacial strength as estimated from the 12 mm thick prism with 90° filament orientation is found to be 246.4 ± 49.1. The average filament strength as estimated from the 12 mm thick prism with 0° filament orientation and the cast is found to be 317.2 ± 95.5 and 243.1 ±73.6, respectively (as outlined in green rectangle in Figure S2a. It must be noted that the specimens with 12 mm layer height and 0° and 90° filament orientations in Figure S2 are also presented in Figure 2a, and is deployed here to provide the interfacial strength and filament strength.

Although the estimated average value of interfacial strength is lower that the tensile strength of the materials, when the estimated strength of the filament and the interface are compared, no statistically significant difference was found.
Figure S2. a) Specific MOR vs. prism thickness for cast specimen (schematically shown in grey (b)), printed prism with 0° filament orientation specimens (schematically shown in blue (c)); and the Specific MOR of the prism with 90° filament orientation specimens (schematically shown in red (d)). Dash lines present limits corresponding to the minimum and maximum values of error bars in cast (grey) and printed prisms with 0° (in blue).
Micro-CT Characterization of the interface in Solid Bouligand Architectures (with $\gamma = 8^\circ$ and 100% infill) and in Solid Prism (with 0° filament orientation, Figure S3)

To investigate the characteristics of the interface, the microstructure of solid hardened cement paste Bouligand architecture disc with $\gamma = 8^\circ$ (Figure S3a,b) and solid prism specimen with 0° filament orientation (Figure S3c,d) was characterized using micro-CT. In micro-CT images of hcp, darker intensities represent pores filled with air or water, with greyscale intensities corresponding to hydrated cement paste products [76].

The horizontal slices (C1,T1) shown in cross-sectional (H9) view in Figure S3c, corresponds to the ‘core’ (i.e., through the interface) and ‘interfacial regions’ (IRs) of the filaments as indicated in plan view (Figure S6d) for the solid Bouligand architecture with $\gamma = 8^\circ$. Similarly, The horizontal slices (C2,T2) shown in cross-sectional (H8) view in Figure S6a, corresponds to the core (i.e., through the interface) and interfacial regions (IRs) of the filaments as indicated in plan view (Figure S6b) for the solid Bouligand architecture with $\gamma = 8^\circ$. Analysis of Figures S6b,d indicates that porosity (appearing in these figures as darker regions within the hardened cementitious matrix as indicated by arrows) are only present in the images representing slices (T1, T2) through the interface (i.e., they are absent from images representing slices through the cores, C1 and C2). The typical horizontal slices of C1, C2, T1, T2 demonstrate the homogeneous characteristics of the microstructure along the cores (C1, C2), compared to the heterogeneous characteristics of the microstructure along the IRs where interfacial porosity is present (T1, T2).

The observation interfacial porosity is typical in IRs and the cores in both prism and disc elements and was made possible due to the differences in the gray level intensities between the signals from the core sections and interfaces of the filaments in the micro-CT. Application of micro-CT characterization technique for 3D-printed solid Bouligand architecture and prism demonstrates the presence of the processing-induced interfacial heterogeneities and that it can follow the architectural pattern. While these heterogeneities can give rise in anisotropic properties and mechanical response of architectured hcp elements, they are utilized in this paper, to
allow the spread of the damage through this heterogeneous network of IRs. Fine-tuning of the interfacial strength via optimization of processing and printing parameters, environmental conditions can allow better control of the mechanical response of the elements. The equivalent strength of the hcp filament and the interface found in Figure S2 can be of considerable prominence. The interfacial strength, due to its equivalence to filaments strength would not sacrifice the overall strength of the element and therefore allows 3D-printed prisms to obtain similar MOR compared to cast counterparts as discussed in Figure 2a.
Figure S3. X-ray micro CT image of the microstructure of the core (i.e. through the center) and interfacial regions (collected during 4X scan) of a solid prism with 0° filament orientation in, a) cross-sectional view and, b) plan view and, a solid Bouligand architecture with $\gamma = 8^\circ$ in, c) cross-sectional view and, d) plan view; and All scale bars are 10 mm long.
Micro-CT Characterization of the Prism (with 0° filament orientation, Figure S4)

To investigate the role of the interface in damage mechanisms, the microstructural of a solid hardened cement paste prism with 0° filament orientation (Figure S4a,b1,b2,c,d) was characterized using micro-CT (in both 0.4X and 4X scan), and damage in the prism was assessed. The 3D rendition of the interior of the solid prism in 0.4X scan of the entire prism and the volume of the region of interest (ROI) near the main crack of the prism in the 4X scan is illustrated in Figure 4Sa.1 and Figure 4Sa.2, respectively.

Micro-cracking at the interfacial regions in the cross-section of the prism (H6) near the main crack (as shown in Figure S4b1) is illustrated in Figure S4b2 in a 0.4X CT. As outlined in the dashed white rectangle and pointed out with arrows, the micro-cracking demonstrated from the tip of the main crack through the interface and is propagated along the horizontal and vertical IRs.

The Micro-CT of the ROI in the 4X scan reveals further information about propagation of micro-cracks along the IRs (Figure S4c,d). The slice (H7) shown in Figure S4d, corresponds to the cross-section of the ROI in XZ plane (Figure S54). The hairline micro-cracking at the IRs (appearing thin hairline dark regions) was observed to be present near a micro-crack and to propagate at the horizontal and vertical IRs as shown by the arrows in Figure S4c.
Figure S4. X-ray micro-CT images of the microstructure of post-fracture solid prim specimen with 0° filament orientation collected during 0.4X scan: a.1) 3D rendition of the entire volume of specimen in 0.4X scan and corresponding volume of the region of interest (ROI) in the 4X scan, a.2) 3D rendition of the entire volume of specimen including the cylindrical region of interest (ROI) for 4X scan, b.1) 2D image of the cross-section in YZ plane in 0.4X scan, b.2) 2D image of the cross-section in XY plane in 0.4X scan, c) 2D images in the XZ plane in 4X scan and, d) 2D images in the XY plane in 4X scan. Unless indicated, all scale bars are 1 mm.
Comparison of Strength and Work of failure (WOF) between Bouligand Architecture and Cast Specimens (Figure S5)

The mechanical properties (MOR and WOF) of solid and cellular Bouligand architectures versus cast counterparts presented in Figure 2c, is further elucidated in Figure S5a,b. In terms of work of fracture, when the average WOF of cellular Bouligand architectures specimens of pitch angles $\gamma = 90^\circ$, $45^\circ$, and solid Bouligand architectures specimens of $\gamma = 8^\circ$ (as outlined in the light blue in Figure S5a) were compared with that of solid cast specimens (as outlined in the light grey in Figure S5a), a statistically significant enhancement of the Bouligand architectures was found. This significant enhancement indicates that both solid ($\gamma = 8^\circ$) and cellular ($\gamma = 90^\circ$, $45^\circ$) architectures can provide significantly enhanced work of failure compared to cast elements.

In terms of strength, when the average Specific MOR of Bouligand architectures specimens with various pitch angles including $\gamma = 15^\circ$, $30^\circ$ $45^\circ$, $90^\circ$ (i.e., cases where $\gamma \geq 15^\circ$ as outlined in the light blue in Figure S5b) were compared with that of solid cast specimens (as outlined in the light grey in Figure S5b), no statistically significant loss of Specific MOR was found. This demonstrates that most cases of Bouligand architectures (where $\gamma \geq 15^\circ$) could maintain specific MOR compared to cast elements.

Although larger pitch angles do not exhibit interfacial damage mechanisms and rather show cracking through the filament, the enhanced WOF in cellular cases where $\gamma \geq 45^\circ$ and solid case with $\gamma = 8^\circ$, demonstrates that larger pitch angles allow for solid failure in the filaments and on itself can provide higher fracture properties as a promising architectured structure. The comparison of strength and work of failure between Bouligand architectures and monolithic cast hcp specimen provides supporting evidence that architectured hcp can provide significant enhancement without compromising the strength. We surmise that low pitch angles, that allow crack propagation along the interfaces leading to twisting crack patterns, will be more efficient for larger specimens where delocalization can be promoted.
Figure S5. a) Specific WOF vs. Specific MOR and, b) WOF vs. MOR of the cast specimens (outlined in grey), Bouligand architecture specimens with varying pitch angles $\gamma = 8^\circ$ (solid), $15^\circ, 30^\circ, 45^\circ, 90^\circ$ (outlined in blue), and solid Bouligand architecture specimens with 60% infill and pitch angles $\gamma = 8^\circ$ (outlined in green)
Micro-CT Characterization of Solid Bouligand Architecture (with $\gamma = 8^\circ$ and 100% infill, Figure S6)

To investigate the role of the interface in damage mechanisms, the microstructure of a solid hardened cement paste Bouligand architecture disc (Figure S6a,b,c,d) was characterized using micro-CT (in 0.4X magnification) and the interfacial damage mechanisms were investigated. These mechanisms are illustrated in Figure S6b,c,d for XY, XZ, YZ planes and in Figure S6a for 3D rendition of the interior of the solid Bouligand architecture. In micro-CT images of fractured hcp, cracks, micro-cracks and voids correspond to darker greyscale intensities [76].

The slices (H1 to H5 in XZ plane in Figure S6c, and K1 to K5 in YZ plane in Figure S6d) shown in the XY plane in Figure S6b, corresponds to the cross-section of the solid Bouligand architecture with $\gamma = 8^\circ$ in XZ (Figure S6c) and YZ planes (Figure S6d), respectively. Micro-cracking at the IRs (appearing darker regions near the main crack) was observed between the layers 6 and 7 (H1, to H3, K1 to K5), layers 4 and 5 (H2 to H5), and layers 3 and 4 (H4, H5) as depicted in Figure S6c,d and pointed out by arrows. This micro-cracking is typically spread in both directions throughout the IRs. Moreover, crack advancement at the interfacial regions (appearing dark regions with broader width than micro-cracks) was observed between layers 3 and 4 (H4, H5, K1 to K3) and layers 4 and 5 (K4) as depicted in Figure S6c,d, and the orange layer numbers. The cracking advancement through the interface was resulted in crack staggering (as shown in Figure S6a.2) and accompanied by micro-cracking at the interface. It is surmised that the characteristics of porous IRs (as discussed in Figure S3c,d), favors the growth along the interfaces. Although an equivalent interfacial and materials strength was found (Figure S2), the micro-cracking and crack advancement through the interface can be attributed to its porous characteristics and lower strength and toughness at a smaller scale (i.e. that macroscopic scale). The spread of the damage observed in this Bouligand element here using micro-CT (similar to those observed in Figure 4a3-a8 using optical microscopy), alludes on the role of the interface in control of the crack growth. In turns, Bouligand architectures will lead to crack twisting. When the crack front aligns towards the plane perpendicular to the load direction, due to local twisting, a local hardening effect can take place which precludes further growth of the crack, and therefore
promotes initiation and growth in other neighboring sites. This delocalization helps the spread of the damage in larger volumes and can lead to flaw-tolerant behaviors.

Figure S6. X-ray micro-CT images of the microstructure of post-fracture solid Bouligand architecture with $\gamma = 8^\circ$ specimen collected during 4X scan: a) 3D rendition of the entire volume of specimen, b) 2D image of the cross-
section in layer seven in XY plane, c) 2D images in the XZ plane d) 2D images in the YZ plane. Unless indicated, all scale bars are 10 mm long.
Determination of Extrusion Rate of Cementitious Ink

The shear rate of the cementitious ink during extrusion at the tip of the nozzle was determined using following equation \cite{74,75}:

\[ \dot{\gamma} = \frac{4Q}{\pi r^3} \]  

(S1)

Where \( Q \) is the volumetric flow rate during extrusion at the tip of the nozzle with internal radius \( r \) equal to 0.68 mm. The value of flow rate was determined by measuring the mass of extruded materials over a specified time period and calculating the volumetric flow rate based on the density of extruded paste. The paste was extruded over 15 minutes and the mass of was measured as 8.86 g. The density of the extruded paste was separately determined as 2.28 ±0.06 g cm\(^{-3}\). The flow rate is calculated as 4.62 mm\(^3\) s\(^{-1}\). The strain rates during extrusion were then calculated based on equation 1, resulting in \( \dot{\gamma} \) equal to 18.70 s\(^{-1}\). The corresponding viscosity of the cementitious ink at this shear rate can be determined at this sheared.

![Figure S7. a) Shear stress and, b) viscosity as function of shear rate of the cementitious ink](image)

Figure S7. a) Shear stress and, b) viscosity as function of shear rate of the cementitious ink
Comparison of Competing Mechanisms in Bouligand architectures with small (\(\gamma = 8^\circ\)) and large (\(\gamma = 45^\circ\)) pitch angles demonstrated in 3D rendition upon Micro-CT processing (Figure S7)

The Micro-CT characterization of a cellular Bouligand architecture with large pitch angle \(\gamma = 45^\circ\) is compared with that of small solid pitch angle (\(\gamma = 8^\circ\)) in order to evaluate the damage mechanisms in small and large pitch angles (Figure S8, Videos S15-S18). The shear failure of the filaments at this large pitch angle (Figure S7a,b, and Videos S15-S18) demonstrates the crack propagation through the filament. In contrast (as discussed in Figure S6), the interfacial damage mechanisms are present at the small pitch angle (\(\gamma = 8^\circ\)) and crack twisting was allowed (Figure S7c,d). Comparison of the small and large pitch angles demonstrate the capacity of small pitch angle to promote damage and flaw-tolerant behavior.

**Ink Rheological Properties: Yield Stress and Viscosity (Figure S8)**

The rheological behavior of cementitious ink is shown in Figure S8. Stress and viscosity were obtained as a function of shear rate by measuring shear stress for controlled shear rates in ascending order at a fixed temperature of 23.6 °C (Figure S8a,b). Shear rates were increased logarithmically from 1 s\(^{-1}\) to 140 s\(^{-1}\). A water trap was used to minimize drying of the suspension during testing. The samples were pre-sheared each time at 50 s\(^{-1}\) for 30 s and followed by a 10 s resting time during which no shear was applied. Three replicate tests were performed. The obtained stress and shear rate were fitted to Bingham model as follow to estimate the yield stress:

\[
\tau = \tau_0 + \mu \dot{\gamma}
\]  

(S2)

where \(\tau\), \(\tau_0\), \(\mu\) and \(\dot{\gamma}\) are shear stress (Pa), yield stress (Pa), viscosity (Pa.s), and shear rate (s\(^{-1}\)).

The average static yield stress of 143.0 Pa was found based on the fitted linear Bingham model. The viscosity of the ink corresponding to the shear rate of 18.70 s\(^{-1}\) (calculated based on Equation 1) was determined by interpolating the data corresponding to Figure S8b. An average viscosity of 15.9 Pa.s was found.
**Figure S8.** X-ray micro-CT images of the microstructure of post-fracture Bouligand architectures collected during 4X scan: a,b) 3D rendition of the entire volume of specimen with 60% infill and $\gamma = 45^\circ$ demonstrating crack path through the filaments; c,d) 3D rendition of the entire volume of specimen 100% infill and $\gamma = 8^\circ$ demonstrating crack twisting through the cross section. Dash black arrows represent the crack path at the top and solid black arrows represent crack path at the bottom of the specimen.
**Videos 1 to 18:**

**Video 1-4:** Bouligand architecture with 15°, 30°, 45°, 90° pitch angle

15°: [https://youtu.be/2nu2tPTiTvQ](https://youtu.be/2nu2tPTiTvQ)

30°: [https://youtu.be/6UuSuF4Eiz0](https://youtu.be/6UuSuF4Eiz0)

45°: [https://youtu.be/VwkH_8jyGBQ](https://youtu.be/VwkH_8jyGBQ)

90°: [https://youtu.be/0nTWdgNsxeU](https://youtu.be/0nTWdgNsxeU)

**Video 5,6:** Two typical compliant structure

[https://youtu.be/M2_U4e5p9TI](https://youtu.be/M2_U4e5p9TI)


**Video 7-9:** Sandwich panel beams with closed top and bottom face

[https://youtu.be/ahOkzXWCzSY](https://youtu.be/ahOkzXWCzSY)

[https://youtu.be/gjx-aQ9oEj4](https://youtu.be/gjx-aQ9oEj4)

[https://youtu.be/q4qNOJmoIKk](https://youtu.be/q4qNOJmoIKk)

**Video 10:** Grid structure

[https://youtu.be/8DW6l7EfkP4](https://youtu.be/8DW6l7EfkP4)

**Video 11:** 3D rendition of solid Bouligand architecture with 8° pitch angle upon micro-CT processing

[https://youtu.be/nWq6YUegEKc](https://youtu.be/nWq6YUegEKc)

**Video 12:** XY view of the 2D slices of solid Bouligand architecture with 8° pitch angle upon micro-CT processing

[https://youtu.be/X8gBezIEfXw](https://youtu.be/X8gBezIEfXw)

**Video 13:** XZ view of the 2D slices of solid Bouligand architecture with 8° pitch angle upon micro-CT processing
Video 14: YZ view of the 2D slices of solid Bouligand architecture with 8° pitch angle upon micro-CT processing

Video 15: 3D rendition of the Cellular Bouligand architecture with 45° pitch angle upon micro-CT processing

Video 16: XY view of the 2D slices of solid Bouligand architecture with 45° pitch angle upon micro-CT processing

Video 17: XZ view of the 2D slices of cellular Bouligand architecture with 45° pitch angle upon micro-CT processing

Video 18: YZ view of the 2D slices of cellular Bouligand architecture with 45° pitch angle upon micro-CT processing