Graphene oxide bulk material reinforced by heterophase platelets with multiscale interface crosslinking

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Graphene oxide (GO) and reduced GO possess robust mechanical, electrical and chemical properties. Their nanocomposites have been extensively explored for applications in diverse fields. However, due to the high flexibility and weak interlayer interactions of GO nanosheets, the flexural mechanical properties of GO-based composites, especially in bulk materials, are largely constrained, which hinders their performance in practical applications. Here, inspired by the amorphous/crystalline feature of the heterophase within nacreous platelets, we present a centimetre-sized, GO-based bulk material consisting of building blocks of GO and amorphous/crystalline leaf-like MnO2, hexagon nanosheets adhered together with polymer-based crosslinkers. These building blocks are stacked and hot-pressed with further crosslinking between the layers to form a GO/MnO2-based layered (GML) bulk material. The resultant GML bulk material exhibits a flexural strength of 231.2 MPa. Moreover, the material exhibits sufficient fracture toughness and strong impact resistance while being light in weight. Experimental and numerical analyses indicate that the ordered heterophase structure and synergetic crosslinking interactions across multiscale interfaces lead to the superior mechanical properties of the material. These results are expected to provide insights into the design of structural materials and potential applications of high-performance GO-based bulk materials in aerospace, biomedicine and electronics.

Graphene oxide (GO) nanosheets have attracted increasing interest in the field of material science by virtue of their superior mechanical properties, sufficient biocompatibility, high aqueous dispersibility, diverse functionality and easy oxidative exfoliation from graphite1–5. Such advantages make GO nanosheets a promising nanofiller for mechanically superior macroscopic structures. GO- and reduced GO-based three-dimensional (3D) bulk assemblies as mechanical or functional parts have potentially widespread applications in aerospace, biomedicine and electronics6–8. However, self-standing GO-based structures directly prepared from dispersions or gels have largely been limited to high-performance long fibres9–12, thin films13–15, and lightweight foams16,17. In spite of a decade of research efforts, the preparation of GO-based bulk materials with superior mechanical performance, especially with improved flexural mechanical properties and multifunctionalization, is still a major challenge12,13,18,19. One of the main hurdles is the difficulty in creating strong and controllable micro- and nano-interfaces that act as critical bridges between GO nanosheets for strengthening, toughening and stiffening of the assembled bulk nanocomposites18,19.

Natural structures are frequently used as inspiration for structural material design. During the typical biomineralization process, living organisms control complex interfaces of organomineral components to create hierarchical, heterogeneous structures with intriguing mechanical performances18,19,20. A well-known example is the natural nacre, a product of molluscs that has a highly regular 3D ‘brick-and-mortar’ (BM) assembly of ordered aragonite platelets connected by a thin organic interlayer19,20. The design, aspect ratio and interface strength of aragonite platelets allow maximization of nacre strength19,20. Inspired by nacre structures, researchers have successfully prepared various types of nacre-like 3D bulk materials21–24. However, there remain valuable structural features that have not been considered or used in the creation of nacre-imitative 3D bulk materials. For example, it has been reported that the creation of a continuous amorphous/crystalline heterophase layer between hard mineral tissues can provide better interlayer adhesion and interaction in the composite material, analogous to interface polymers in some natural polymeric composites25. Despite its promise, such an approach has yet to be realized in artificial nacres19–24. MnO2 is often used as a highly efficient electrochemical material26. Recently, leaf-like MnO2, hexagon nanosheets with an amorphous/crystalline structural feature (A/C-LMH) have been demonstrated27. In this material, a ~0.6-nm-thick microporous, mesophyll-like amorphous monolayer with higher oxygen vacancies facilitates effective bonding with the oxygen-containing groups of GO nanosheets. A 2–4-nm-thick, vein-like crystalline skeleton supports the entire structure and ensures the formation of the stiff GO/MnO2 heterophase. Due to its excellent property, MnO2 is expected to be an ideal reinforcer in GO composites that can lead to sophisticated heterophase platelets.

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Here we report a centimetre-sized GO/MnO$_2$-based layered (GML) bulk material that imitates nacreous amorphous/crystalline heterophase platelets and features high-density crosslinking interfaces at multiple scales. Specifically, we achieved this by assembling microscale building blocks in a straightforward bottom-up fashion. These building blocks are composed of nanoscale A/C-LMH/GO heterophase reinforcing units glued by polymer-based crosslinkers. The resultant GML bulk material displayed sufficient fracture toughness and strong impact resistance, and achieved higher flexural mechanical performance (strength, 218.4 ± 11.2 MPa) than nearly all GO-based bulk composites reported to date. We also conducted multilevel simulations explaining the enhanced strength and toughness properties of our material.

### Design, assembly and characterization

To imitate the structural features of natural nacre (Supplementary Fig. 1), we designed a GML bulk material in five steps by following a bottom-up assembly process (Fig. 1). (1) As a reinforcing phase, A/C-LMH nanosheets with superior mechanical properties (nanoindent Young's modulus ($E_n$) = 80.3 ± 13.2 GPa and hardness ($H$) = 3.2 ± 0.9 GPa) are inserted into the interlamination of GO nanosheets in the layered nanocomposite films. Subsequently, additives are incorporated into the surface and interface of the A/C-LMH/GO heterophase to form a nanoscale A/C-LMH/GO reinforcing structural unit via in situ complex crosslinking. This microscale building block extends across the overall nanocomposite film. (2) Thin mixed borate/SA crosslinking interlayers are incorporated between adjacent nanocomposite films in a stacking-up process. The resulting macroscopic 3D multiscale crosslinking network undergoes a hot-pressing process to create the GML bulk material. Integration of the molecular-scale A/C-LMH/GO heterophase, nanoscale crosslinking interfaces and microscale film–film interfaces can be precisely optimized by controlling the contents of different constituents and the assembly technology.

Fig. 1 | Schematic illustration of the design and assembly of GML bulk material featuring amorphous/crystalline heterophase platelets and multiscale crosslinked interfaces. a, A/C-LMH nanosheets are deposited on the surface of the GO nanosheet, forming a nanoscale A/C-LMH/GO heterophase by non-covalent interactions at amorphous and crystalline regions (H, white; C, grey; O, red; Mn, blue). Subsequently, additives are incorporated into the surface and interface of the A/C-LMH/GO heterophase to form a nanoscale A/C-LMH/GO reinforcing structural unit via in situ complex crosslinking. This microscale building block extends across the overall nanocomposite film. b, Thin mixed borate/SA crosslinking interlayers are incorporated between adjacent nanocomposite films in a stacking-up process. The resulting macroscopic 3D multiscale crosslinking network undergoes a hot-pressing process to create the GML bulk material. Integration of the molecular-scale A/C-LMH/GO heterophase, nanoscale crosslinking interfaces and microscale film–film interfaces can be precisely optimized by controlling the contents of different constituents and the assembly technology.
As seen in Fig. 2b and Supplementary Fig. 9, the 2D SAXS pattern of these layered films shows two strong diffuse spots in the equatorial direction, corresponding to azimuthal angles (θ) at 90 and 270°, respectively. The calculated Herman's orientation factors (f) of these layered nanocomposite films are all lower than that of the GO film (0.86). This is especially true for the GO/MnO$_2$/SA/rSF film, which exhibits the lowest orientation factor (f = 0.58), indicating an orderly interlaced distribution of GO nanosheets within the layered film. Scanning electron microscopy (SEM) images show a densely stacked, ‘wavy’ lamellar arrangement within the nanocomposite
films (Fig. 2c and Supplementary Fig. 10). X-ray diffraction patterns demonstrated a broadening of the interlayer space of the GO nanosheets, which is evidence of intercalation of the mixed additives into the gallery space of the nanosheets (Supplementary Fig. 11). SEM images and mappings of several key elements, as detected by energy-dispersive spectrometry (EDS), demonstrated that many A/C-LMH nanosheets were randomly embedded in the intercalation of the GO nanosheet, establishing a staggered stacking heterophase (Fig. 2d,e). At a finer scale, atomic force microscope (AFM) images confirmed that ~1-nm-thick A/C-LMH nanosheets had been randomly adsorbed on individual GO nanosheets (Fig. 2i and Supplementary Fig. 12a,e). The estimated areal ratio of GO to A/C-LMH is 4.6, establishing the heterogeneous A/C-LMH/GO heterophase unit. The successful adsorption of a biopolymer-based nanocomposite films can also be observed (Fig. 2j,k and Supplementary Fig. 12b–d,f–h), which indicates successful formation of the synergetic heterophase structural unit.

Ultraviolet-visible spectra (Supplementary Fig. 13) revealed that, after incorporation of additives into the GO system, the peak position of the characteristic absorption of the GO nanosheet shifted slightly toward a lower wavelength. This effect can be attributed to the reduced domain size of π–π conjugated electrons as a result of increases in functional groups and defect sites in GO nanosheets27. Fourier-transform infrared spectroscopy (Supplementary Fig. 14) of the composite films shows that the peak centred at 1,630 cm⁻¹ (C=C stretching vibration of GO) shifted to lower frequencies, while the intensity of the peak at 975 cm⁻¹ (C=O stretching vibration of GO) became very weak or even disappeared28. Raman spectra obtained by uniaxial tensile test (f). Error bars represent s.d. of the measured properties; n = 5 for each specimen. | Fig. 3 | Mechanical properties of layered nanocomposite films. a, Sample preparation scheme for one-directional (z) probing of nanoindentation contact response and uniaxial tensile test. Colour coding indicates different types of sample. b, Nanindent Young’s modulus (Eₜ) (b) and hardness (H) (c) measured by static nanoindentation test. d–f, Ultimate stress (σₚ) (d), work of toughness (W) (e) and maximum Young’s modulus (Eₚₚ) obtained by uniaxial tensile test (f). Error bars represent s.d. of the measured properties; n = 5 for each specimen. g, h, Plots of μ versus W (g) and H versus Eₚₚ (h) of nanocomposite films.

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lower than that of a pure GO film\(^{29}\). Furthermore, we observed a decreased C1s component of the oxygen-containing functional groups of GO in X-ray photoelectron spectroscopy spectra and an increased value in average zeta potential analysis (Supplementary Table 2)\(^{30,31}\). Based on the above results, we concluded that the order of bonding ability of additives with GO was GO > A/C-LMH > SA > rSF. SA > A/C-LMH/rSF > SA > A/C-LMH > rSF.

In the second stage, a number of quaternary nanocomposite films of equal size (6 × 6 cm\(^2\)) and ideal thickness (~20 μm) were glued together using thin layers (~1 μm) of mixed borate/SA solution brush-coated on the surface of each film. The resulting laminates had a total of 50–180 layers (Supplementary Fig. 18a,b). The thin glue layers were used to integrate borate/SA crosslinking interactions into the interfaces between adjacent films via the combined effects of non-covalent/covalent bonds. During the assembly, these films coated by borate/SA layers were carefully aligned to form a highly ordered 3D BM structure. After pre-compression and drying, the bulk material was subsequently soaked in a mixed borate/SA solution to further interconnect the multiscale interfaces (including nanoscale A/C-LMH/GO interfaces and microscale film–film interfaces) by in situ crosslinkage of SA with borate ions. Next, a hot-pressing process was used to minimize defects and fill voids between assembled lamellae and complete densification of the processed materials. Finally, a brown GML bulk material with a width of 5.0 × 5.0 cm\(^2\), thickness of 3.0 mm and density of 1.85 g cm\(^{-3}\) was successfully prepared, as shown in Fig. 2l. It comprised approximately 69.4 wt% GO, 23.3 wt% MnO\(_2\), 6.5 wt% SA, 0.5 wt% rSF and 0.3 wt% borate (Supplementary Tables 3 and 4). Its fracture surface was strikingly similar to that of natural *Cristaria plicata* nacre (Fig. 2m,n). In addition, a densely layered bulk structure can be observed in the material cross-section shown in Supplementary Fig. 19, suggesting that the isolated reinforcing units in adjacent...
films were interconnected with each other through bridging compositions. For comparison, we also prepared three other representative 3D specimens, including pure GO bulk, pure SA bulk and no-borate/SA immersing samples (Supplementary Fig. 18c,d).

**Analysis of mechanical properties**

To evaluate the effectiveness of the heterophase reinforcing structure at multiscale interfaces the mechanical properties of the nanocomposite films and sheets were first studied, as shown in Fig. 3.
Supplementary Figs. 20–22 and Table 1. In Fig. 3bc, the binary nanocomposite film (GO/MnO₂) displayed better micromechanical performance than pure GO and other binary competitors (such as GO/rSF and GO/SA); the Eₛ and H of GO/MnO₂ were measured at 11.4 ± 1.0 and 1.2 ± 0.2 GPa, respectively, which is approximately 83.9 and 100.0% higher than those of the pure GO film. The Eₛ and H of the optimal quaternary GO/MnO₂/SA/rSF nanocomposite film were 16.3 ± 2.0 and 1.4 ± 0.2 GPa, respectively, higher than those of the unary film and other nanocomposite films (Supplementary Fig. 20). Furthermore, tensile tests revealed that the GO/MnO₂ film achieved better tensile property than that of the pure GO and GO/crystalline-MnO₂ films; the tensile property of the GO/MnO₂/SA/rSF film was superior to that of the other nanocomposite films (Fig. 3d–f), due to a unique integration of high tensile strength (σ₁ = 368.1 ± 9.9 MPa) and toughness (Wₜ = 13.8 ± 2.6 MJ m⁻²). Compared with unary films, the maximum Young’s modulus (Eₛ) of the GO/MnO₂/SA/rSF film was significantly enhanced, by up to 9.5 ± 1.5 GPa (Fig. 3f). The performance of the GO/MnO₂/SA/ rSF nanocomposite film at both micro- and macromechanical levels (Fig. 3gh) realized the ideal building block for the GML bulk assembly. This was also confirmed by the results of a scratching test (Supplementary Fig. 21). By analysing the fracture cross-section of typical nanocomposite films (Supplementary Fig. 22), we confirmed that the A/C–LMH/GO heterophase can be readily crosslinked by biopolymer-based additives. This crosslinking further enhanced the load-bearing capability of the A/C–LMH/GO reinforcing unit and formed the densely stacked layer within these nanocomposite films. Interestingly, we found that the order of the mechanical properties of the nanoscale heterophase reinforcing units is consistent with that of the synergistic bonding abilities of GO nanosheets with different types of additive.

We further measured the flexural mechanical property of the as-fabricated GML bulk materials by a three-point bending test in comparison with other bulk materials (Fig. 4a–c and Supplementary Fig. 23). The flexural strength of the GML bulk material was 218.4 ± 11.2 MPa (specific strength up to 118.1 ± 6.1 MPa per Mg m⁻³), which was 11 times higher than that of the pure GO bulk sample (17.4 ± 3.4 MPa) and two times higher than that of the pure SA bulk sample (78.5 ± 16.2 MPa) and that of the no-borate/SA immersing bulk sample (72.3 ± 3.1 MPa). Our GML bulk material demonstrated the highest yield strength among GO-based bulk nanocomposites reported to date. As shown in Fig. 4b, a combination of high strength (218.4 ± 11.2 MPa) and improved Young’s modulus (7.3 ± 0.3 GPa) was achieved after laminations of those quaternary films were mediated by the mixed borate/SA networks. We also measured fracture toughness for crack initiation, K╻C, as a measure of resistance to crack initiation. The result for the GML bulk material (0.87 ± 0.03 MPa m¹/²) was lower than that of natural nacre (3–10 MPa m¹/²) but higher than those of pure GO bulk, SA bulk and the no-borate/SA immersing specimens. The fracture toughness for stable crack propagation, K╻C, of the GML bulk material (5.4 ± 0.4 MPa m¹/²) was comparable to that of natural C. Plicata nacre (~5.9 MPa m¹/²) and exceeds that of other as-fabricated bulk materials, as shown in Fig. 4c.

We then investigated indentation impressions on the GML bulk material by SEM and optical microscopy (Fig. 4d and Supplementary Figs. 24 and 25) and compared the results with those of geologic GO bulk material to understand the former’s resistance to localized damage. The damage area (Aₚ = 9.503 ± 0.1 µm²) on the GML bulk sample was smaller than that of the GO bulk sample (Aₚ = 16.286 ± 0.1 µm²). For the GML bulk case, small cracks and other signs of damage were observed in post-indentations, correlated with the indentation curves (Supplementary Fig. 25). Cracking inhibition or delay at sharp contacts in some biomaterials under conditions of high stress can be due to the capability of these materials to endure localized shear deformation. This mechanism results in contact stress redistribution under the contact point, generally leading to the formation of a notable residual stress field. To estimate the residual stress produced in those areas, we measured shifts in the D band of GO around the indents in these samples by high-resolution Raman microspectroscopy (Fig. 4d, middle). The residual stress field in the GML bulk sample was almost three times larger than that in the GO bulk sample (Fig. 4d, right). This result further demonstrated that a high fraction of indentation energy was released by cracking in the geologic GO, thus leaving a smaller residual stress field. A larger yielding zone developed around the contact point in the GML bulk sample, establishing a complex residual stress field where a large amount of contact energy was absorbed with less cracking. Similarly, in situ observation of the 3D GML bulk specimen under a single-edge notched-bending test showed that the main crack propagated along a complex path at the interfaces of these stacked laminates (Fig. 4e and Supplementary Fig. 26). The large zig-zag crack deflection, branching and microcrack bridging at the crack tip (Fig. 4f,g) all indicated effective extrinsic toughening mechanisms that increased crack resistance.

We finally performed molecular dynamics (MD) and finite element (FE) simulations to verify the above mechanisms, as shown in Fig. 5a–d, Supplementary Figs. 27–30, Tables 5 and 6 and Supplementary Videos 1–3. MD simulation showed that the amorphous-MnO₂/GO interface strength was much stronger than that for the crystalline-MnO₂/GO interface (Fig. 5a,b), suggesting a stronger binding capability of amorphous-MnO₂ and GO. FE simulation demonstrated that the main loading was borne by the hard heterophase nanosheets while typical microcracks propagated along the heterogeneous interface in the heterophase reinforcing structure unit (Fig. 5c, top). Owing to the BM structural design, the hard heterophase nanosheets played an important role in resistance to deformation and fracture, and the strong interface between hard and soft phases can effectively facilitate load transfer by shear deformation. In the microscale model (Fig. 5c, bottom), FE simulation results were similar to those observed for the GML bulk sample: the main loading was borne by the lamellae and distinct cracks were deflected along the interlayer between lamellae (Fig. 4e-g and Supplementary Fig. 26). The in silico flexural stress–strain curve of the microscale lamellar structure matched the experimental curve of the GML bulk, and the simulated flexural strength of the nanoscale heterophase structure was higher than that of the microscale lamellar structure (Fig. 5d).

From the above analyses, the ordered A/C–LMH/GO heterophase unit combined with polymer-based crosslinkers at molecular-nanoscale levels provides an intrinsic strengthening and toughening mechanism, enhancing the mechanical properties of the nanocomposite film. At the microscale level, the strong and highly aligned interlayer between mechanically optimized lamellae is beneficial for effective loading transfer within the whole system, improving the holistic mechanical performance.

Impact resistance and comparison of mechanical performance

This strong and tough 3D GML bulk material holds excellent promise for impact energy absorption. To demonstrate this potential, a split Hopkinson pressure bar (SHPB) experiment was carried out, as shown in Fig. 5e and Supplementary Fig. 31a. The impact resistance of the GML bulk material was higher than that of other as-fabricated bulk materials. For example, at driving pressures of 55,000, 45,000 and 35,000 Pa, the compression stress of the GML bulk material reached ~240.0 MPa, ~187.0 MPa and ~120.0 MPa, respectively, and the energy absorption of compression was ~51.5 MJ m⁻³, ~36.4 MJ m⁻³ and ~23.0 MJ m⁻³, respectively. At a driving pressure of 55,000 Pa, the impact resistance of the GML bulk sample (~51.5 MJ m⁻³) was over four times that of pure GO bulk material and over two times that of the pure SA and the no-borate/
SA immerging specimens. As shown in Supplementary Fig 3ib, the stress–strain curves of the GML bulk material reflect a higher impact modulus during the whole impact process than that of other as-fabricated bulk materials. The curves of the GML bulk material also illustrate a larger wave-like increase compared with those of the no-borate/SA immerging bulk sample, which are distinct from the quasi-linear increase in the pure GO bulk sample and the large plastic platform of the pure SA bulk sample. The above results demonstrate the excellent impact energy absorption property of our GML bulk material, suggesting its potential applications in armoury materials.

Figure 5f shows that the specific toughness (K/cρ) and specific strength (s/cρ) of the GML bulk material are higher than those of a wide range of polymer materials (for example, poly(methyl methacrylate) (PMMA), polystyrene (PS) and polyurethane (PU)), as well as many natural nacre-inspired bulk materials (for example, clay/polyvinyl acetate (PVA)\textsuperscript{32}, Al\textsubscript{2}O\textsubscript{3}/GO\textsuperscript{30} and Al\textsubscript{2}O\textsubscript{3}/polyetherimide (PEI)\textsuperscript{31} (Supplementary Table 7)) and some natural materials\textsuperscript{31}. The GML bulk material’s specific toughness and strength are also comparable to those of natural nacre\textsuperscript{17} and other unique bulk composites such as MTM/PVA/resol\textsuperscript{31}. By virtue of the impressive (specific) flexural strength, fracture toughness, resistance to impact, light weight, large size and accessible preparation processes of our 3D GML bulk material, we envision a potentially wide range of structural and functional applications in the future.

In summary, we prepared a centimetre-sized GML bulk material featuring a strong flexural strength among reported GO-based bulk materials. This was achieved by incorporation of heterophase platelets and multiscale interface crosslinking interactions. The resulting material performance originated from an optimal balance of different interfacial interactions. First, the A/C-LMH nanosheet bonds with the GO nanosheet to form a strong heterophase interfacial interaction at the molecular level, endowing the heterophase structural unit with intrinsic high strength, enhanced stiffness and toughness. Second, polymer-based crosslinkers further reinforce the nanoscale interfacial interactions between heterophase units, which can subsequently absorb larger amounts of mechanical energy to hinder crack initiation when loaded. Third, optimization of microscale film–film interfaces by the mixed crosslinkers enhanced microscale load transfer capability by enabling larger crack deflection and interlayer shearing. We realize that these detailed structure–property relationships still need further work due to the complexity of the composition of the material. This increased mechanical energy absorption provides the material with extrinsic toughness, excellent impact resistance and damage tolerance. We expect that the material developed in this work, and the concept of heterophase platelets for biomimetic 3D bulk composites, represent an important step in the design of engineered structural materials for widespread applications in aerospace, biomedicine and electronics.

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Methods

Fabrication of GML bulk and no-borate/SA immersing bulk materials. To assemble the GML bulk material, the prepared GO/MnO2/SA/rSi nanocomposite films were cut into pieces of equal size (6.0 × 6.0 cm2) and brush-coated with a thin layer (h = 1.0 μm) of SA solution on the surface. These films were then laminated together to form laminates with 50–180 layers; the laminates were rolled using a glass rod and transferred into a home-made aluminium alloy mould (Supplementary Fig. 18a). We then applied a pre-hot-pressing step with a pressure of 15 MPa at 40 °C for 24 h to obtain the no-borate/SA immersing bulk material. Next, this bulk material was immersed in a mixed borate/SA solution (0.3 wt% SA and 10 mg ml−1 borate) for 2 h. Finally, we applied a hot-pressing step with a pressure of 25 MPa at 50 °C for 48 h to obtain the GML bulk material with a thickness of approximately 0.5–3.0 mm.

Flexural mechanical tests. We performed three-point bending tests with a Shimadzu AGS-X Tester. The specimens were carefully cut into samples of thickness d = 0.5–1.0 mm, width b = 2 mm and length l = 15 mm, then polished with sandpaper to remove flaws on the edges. A support span of 7.5 mm, a loading point size (radius of hemispheric) of 3.2 mm and a bending displacement rate of 2 μm s−1 were used in the three-point bending tests. For single-edge, notched-bend (SENB) tests, the specimens (d = 1 mm, b = 2 mm) were notched to about 50% of their width with a 150-μm-thick diamond and then sharpened by repeated gentle sliding of the razor blade. The final notch radius was ~30 μm. SENB tests were performed at a constant displacement rate of 2 μm s−1. The in situ, three-point bending tests on bulk samples (d = 1 mm, b = 2 mm) were performed in a Deben microtest tensile stage within a FEI Quanta 250 FEG environmental scanning electron microscope. Loading was applied under displacement control at a rate of 0.02 mm min−1. The applied loading direction for all three-point bending tests was perpendicular to the 2D building block surface.

Mechanical calculations.

(1) Calculation of stress σ and strain ε:

According to the ASTM D790-03 standard, we calculated stress and strain using the three-point bending force–displacement curves as follows15:

\[ \sigma = \frac{3FS}{2bd^2} \]  

and

\[ \varepsilon = \frac{6Dd}{S} \]

where F is the force, D is the displacement and S is the length of the support span. b and d represent the width and thickness of the specimen, respectively. Fracture strength and fracture strain were calculated using F and D at failure.

(2) Measurement of Young’s modulus, E:

Young’s modulus, E, was calculated from the slope of the linear portion of the three-point bending stress–strain curves.

(3) Measurement of fracture toughness:

Fracture toughness for crack initiation, \( K_{ic} \), was calculated with the following equations21:

\[ K_{ic} = \frac{P_{c}S}{BW^2}f\left(\frac{a}{W}\right) \]  

and

\[ f\left(\frac{a}{W}\right) = \frac{3}{2}\left(\frac{a}{W}\right)^{1/2} \left[ 1.99 - \left(\frac{a}{W}\right) \left(1 - \frac{a}{W}\right) \right] \left(2.15 - 3.9\left(\frac{a}{W}\right) + \left(\frac{a}{W}\right)^2\right) \]  

where \( P_{c} \) is the maximum load in the single-edge, notched-bend tests, S is the support span, B is the thickness of the specimen, W is the width of the specimen and a is the notch depth. Fracture toughness, \( K_{ic} \), was calculated from the elastic and plastic contributions by J-integral calculation, consistent with previously reported methods for estimation of the properties of bone and other composites21,22:

\[ J = I_{el} + I_{pl} \]  

where \( I_{el} \) is the elastic contribution on the basis of linear elastic fracture mechanics, and

\[ I_{pl} = \frac{K_{pl}^2}{E'} \]  

where the plastic contribution, \( I_{pl} \), can be calculated with the following equation:

\[ I_{pl} = \frac{2Ap}{B(W - a)} \]  

where \( Ap \) is the plastic area underneath the load–displacement curve. J values can be transformed into K values by the following equation:

\[ K_{pl} = \left(E'\right)^{1/2} \]

in which \( E' = E(1 - v^2) \); E is Young’s modulus and v is the Poisson ratio. Since the variation in E influences \( K_{ic} \) in a fairly limited way, here \( E' \) can be replaced by E.

Data availability

All data supporting the findings of this study are available within the paper and its Supplementary Information. Other supporting data are available from the corresponding authors upon request.

Code availability

The codes or algorithms used to analyse the data reported in this study are available from the corresponding authors upon request.

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Author contributions

L.G., L.D., X.D., K.C. and X.T. conceived the project and designed experiments. K.C., X.T. and J.H. performed in situ tensile tests. L.D. and C.C. carried out FE simulation. X.T. and B.J. characterized all samples. X.T., J.H. and K.C. performed mechanical testing. K.C., X.T. and J.H. performed in situ tensile tests. L.D. and C.C. carried out FE simulation. X.T. and C.C. compiled the videos. L.G., K.C., X.T., L.D., C.C., X.D., Y.W., B.J., T.-H.X., Y.W. and K.G. drafted the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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