FULL CRITICAL REVIEW

Architectured materials in engineering and biology: fabrication, structure, mechanics and performance

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Ever-increasing requirements for structural performance drive the research and the development of stronger, tougher and lighter materials. Specific microstructures, heterogeneities or hybrid compositions are now used in modern materials to generate high performance structures. Pushed to the extreme, these concepts lead to architectured materials, which contain highly controlled structures at length scales which are intermediate between the microscale and the size of the component. This review focuses on dense architectured materials made of building blocks of well-defined size and shape, arranged in two or three dimensions. These building blocks are stiff so their deformation remains small and within elastic limits, but their interfaces can channel cracks and undergo large deformations. These basic principles lead to building blocks which can slide, rotate, separate or interlock collectively, providing a wealth of tunable mechanisms. Nature is well ahead of engineers in making use of architectured materials. Materials such as bone, teeth or mollusc shells are made of stiff building blocks of well-defined sizes and shapes, bonded together by deformable bio-adhesives. These natural materials demonstrate how the interplay between building block properties, shape, size and arrangement together with non-linear behaviour at the interfaces generate unusual combinations of stiffness, strength and toughness. In this review we discuss the general principles underlying the structure and mechanics of engineering architectured materials and of biological and bio-inspired architectured materials. Recent progress and remaining issues in the modelling, design optimisation and fabrication of these materials are also presented. The discussion draws from examples in the engineering and natural worlds, emphasising not only how natural materials can help us improve existing architectured materials, but also how they can inspire entirely new structural materials with unusual and highly attractive combinations of properties.

Keywords: Architectured materials, Bio-inspiration, Biomimetic materials, Tunable materials, Topologically interlocked materials, Nacre, Bone, Tooth enamel

Introduction

Modern engineering applications demand ever-increasing structural performance, with materials which are stronger, tougher, lighter and multifunctional. Simple homogeneous materials cannot fulfil these requirements and therefore engineers have turned to hybrid materials, which combine materials with complementary and synergistic properties. The simple idea of combining two or more materials with distinct properties which complement each other leads to a rich design space where the combinations of materials, the geometry, size and arrangement of the different phases can be tailored to produce a vast range of properties. Most interestingly, hybrid materials offer the possibility of combining properties not possible to achieve in monolithic materials.[1] For example, tough materials are generally deformable and soft, while harder and stronger materials are brittle, so that strength and toughness* are generally conflicting.[2] By combining hard and soft ingredients in the right concentrations and architectures, hybrid materials can offer unique combinations of strength and toughness. The structural performance of hybrid materials (stiffness, strength, toughness) is governed by their mechanics of deformation and failure, which in turn is largely governed by their microstructure. Optimised performance can therefore be attained with tight control over the

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*The term 'toughness' used in this context refers to fracture toughness (unit: MPa.m$^{1/2}$) or work of fracture (unit: J/m^2). The energy absorbed by the material (area under the stress-strain curve) is referred to as 'Energy absorption' (unit: J/m^3).

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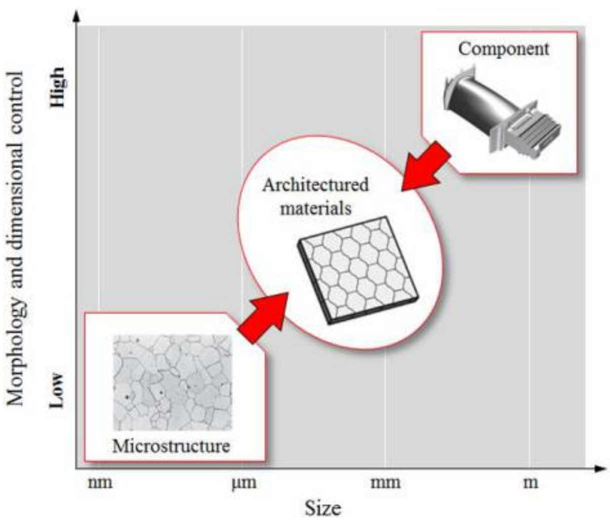
microstructure (size, topology, arrangement), an idea which can be exploited to the extreme in architectured materials. Periodic cellular materials or 'lattice materials' currently dominate the field of architectured materials.[3] These materials are made of slender solid elements and are mostly filled with void, so they offer useful combinations of structural properties and low weight. Another class of architectured materials is made of building blocks that completely fill space in periodic patterns, leaving little or no interstices. In contrast to lattice materials, these fully dense architectured materials have not been explored extensively and are the focus of this review. In the first section, a definition of architectured materials is discussed, followed by a few examples of engineering architectured materials. Biological materials and their similarities with man-made architectured materials are then discussed. General principles in terms of structure, mechanics of deformation and fracture are presented and discussed. Fabrication is then discussed, followed by the final section on future perspectives in dense architectured materials and bio-inspiration.

Architectured materials: general characteristics and examples

To introduce and define 'Architecture' in materials it is useful to consider Fig. 1, which shows different levels of structural elements with their characteristic length scales (i.e. the size of their main geometrical features) and the degree of control and geometrical fidelity that current fabrication techniques provide. At the largest length scale, the engineering component itself (here a turbine blade) ranges from one centimetre to a few metres in size. The geometry of the component and the choice of materials must be optimised simultaneously to fulfil a set of structural requirement(s). The material is then formed into its final shape, using one of the many fabrication techniques available to engineers, for example machining, casting or injection moulding. These techniques allow a very high control over the morphology and a high dimensional fidelity. Dimensional tolerances are small and reproducibility is high, which is critical because the component itself often serves as element in a larger machine or structure (truss members, shafts, turbine blades). In order to fulfil its functions, the component must therefore conform and fit other components reliably and consistently. The design and fabrication of mechanical components at these length scales have traditionally been the realm of mechanical engineers, structural engineers and civil engineers.



1 Architectured materials bridge the length scales of microstructures to the larger length scales at the component size (adapted from Refs. 4 and 5)

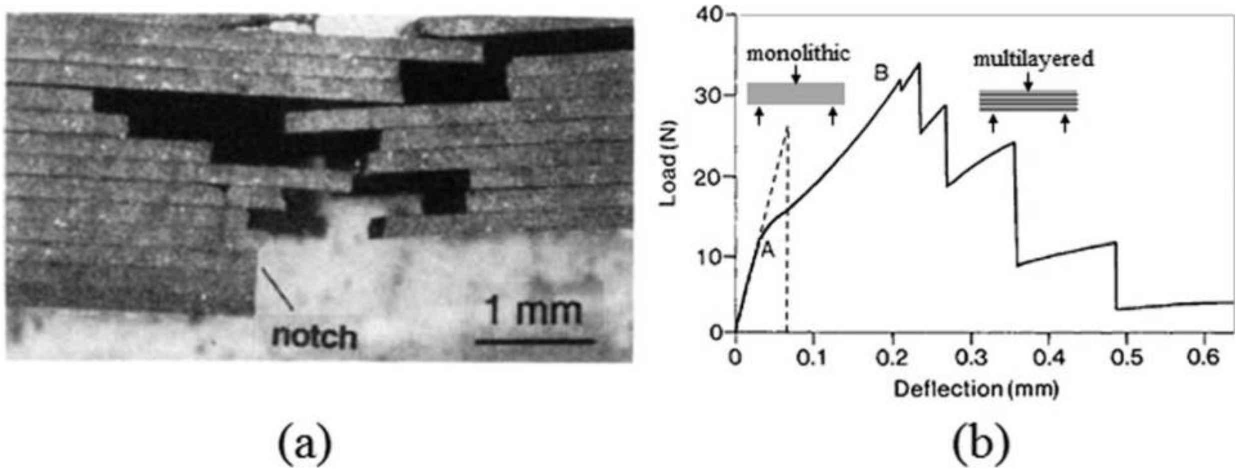
In contrast to large-scale components, the lower left corner of Fig. 1 is the domain of what is traditionally considered 'microstructure' and includes scales ranging from nanometres to hundreds of micrometres (the grain structure of a metal is shown as an example). At this length scale the chemical composition, the molecular structure or the granular structure of materials are designed and optimised to achieve specific combinations of material properties, but not necessarily for a specific function or end-application. The array of techniques available to adjust the microstructure and performance of materials is vast and includes chemical composition (alloying), heat treatments (annealing, quenching, sintering) and other mechanical processes such as cold drawing. The accuracy and fidelity at these small length scales is however limited by stochastic variations associated with crystallisation, polymerisation, spatial distributions of defects and impurities, local thermodynamic fluctuations and other chaotic processes. For example, the size of the grains in a metal can be manipulated to a great extent, but the final microstructure invariably displays a distribution of grain size with a large standard deviation. Microstructure design and optimisation has traditionally been the domain of chemists and materials scientists. As shown in Fig. 1, components and microstructure are diametrically opposed in terms of the length scales involved and in terms of morphological control. They are also different in terms of design philosophy: components are designed and made from available materials in order to fulfil a specific function, while materials are designed and made to achieve a set of properties to fulfil a general need, but not necessarily with a specific function in mind. Figure 1 also shows that there is a gap of length scales between microstructural scale and component scale. This gap represents a traditional divide between the fields of materials science and mechanical engineering. This 'separation of length scales' is also used to our advantage. For example, the mechanical behaviour of heterogeneous materials such as polycrystalline metals can be represented using homogenised properties, provided that the characteristic length scale of the heterogeneities (i.e. grains in metals) is significantly smaller than the size of the component.[6] However, current knowledge in multi-scale modelling and design[7] suggests that this traditional divide might disappear in modern materials. The proposition of architectured materials is to fill the gap between component and microstructure. Architectured materials have internal structures at length scales which are smaller than the size of the components, but which are larger than the length scales traditionally associated with the microstructures of materials (e.g. grain size, lattice constant). The corresponding range is typically in the 100 μm to 100 mm range. The fabrication methods at these intermediate length scales allow for high geometrical fidelity and high morphological control, and for this reason the term 'architecture' is preferred over the terms 'microstructure' or 'mesostructure'. In terms of length scale and morphological control, architectured materials therefore bridge component and microstructure. As such, they represent the opportunity to simultaneously design structural systems at all length scales in order to meet the requirements of specific functions. Structural periodicity is often used in architectured materials, and therefore their structure and mechanics are often described with unit cells. Periodic cellular materials or 'lattice materials' are typical examples of architectured materials made of thin solid elements (struts or plates). The architecture of the cells (geometry, strut thickness, morphology of the struts) largely governs the performance at the macroscale,[3] and some topologies have been shown to lead to highly unusual mechanical responses such as negative Poisson's ratio.[8] To achieve the required level of morphological control, an array of fabrication methods is available including stamping[9] or 3D printing.[10,11] In fully dense architectured materials, the architecture is generated by material heterogeneities, or by constructing the material with building blocks of intermediate size. Large structures such as arches, domes, stonewalls or tiled pavements fall within the category of dense architectured materials. These structures are made of building blocks with well-defined shapes and sizes which interact through gravity, through contact and often by additional cohesive forces provided by mortars. The building blocks can be made of clay, stone or concrete materials which are durable and very strong in compression but weak in tension. Structures such as arches or domes rely on specific architectures to offset tensile stresses arising from flexural loading. Relatively weak building blocks made of brittle materials such as unfired clay[12] can therefore be assembled into strong and durable structures. These traditions of construction techniques have a long history spanning from antiquity to renaissance,[13] leading to modern pavement systems[14] and other more advanced interlocking building blocks used in modern masonry.[15] Architecture is also used in modern engineering materials as shown in the two examples below.

Layered ceramics

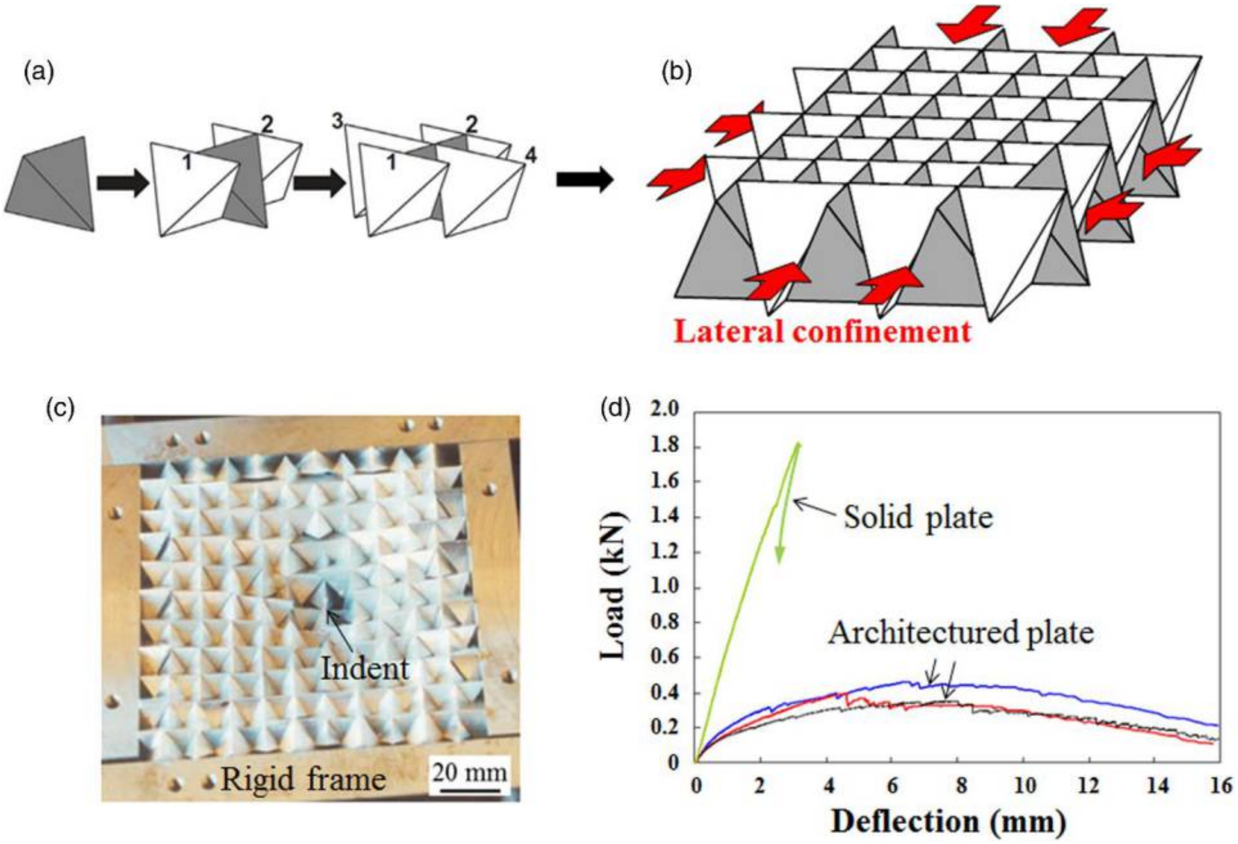
Although they were developed before the emergence of the term 'architectured materials', layered ceramics fall within this category. In layered ceramics the building blocks are individual layers of material, which are bonded by weaker interfaces. Layered ceramics are designed so that the interfaces between the layers intercept and deflect incoming cracks owing to flexural stresses. For example, the multilayered ceramic shown in Fig. 2*a* consists of thick *SiC* layers intercalated with thin graphite layers. This ceramic is as stiff as bulk *SiC*, but the weaker graphite layers can deflect flexural cracks and make this multilayered material a hundred times tougher than *SiC* (in energy terms[16]). Figure 2*b* shows the typical flexural load–deflection curves for monolithic and multilayered *SiC*. The monolithic form of *SiC* is inherently brittle, but its deformation and failure mechanisms are profoundly changed by the weak interfaces.[16] After a linear elastic region the notch-induced crack is deflected into a weaker layer (point A, Fig. 2*b*) and requires an increase in force for further propagation because of two effects: (i) the deflected crack is in mixed mode and (ii) while the crack propagates along the interfaces its driving force does not increase with crack length. Eventually the crack propagates through the layer (point B), accompanied with a sudden drop in force. The crack may be deflected at the next interface, and the process can repeat several times before the material completely fails. These multiple deflections produce a progressive failure and massive energy dissipation. Fracture toughness also significantly increases and, as a result, the flexural strength also increases (Fig. 2*b*) since the flexural strength of brittle materials is largely governed by their fracture toughness.[17] A natural extension of multilayered materials is segmented multilayered or tiled laminates, where each layer is made of individual tiles. These additional degrees of freedom in the design of laminates offer interesting possibilities where the material can be locally tuned to mitigate stress concentrations.[18]

Topologically interlocked materials

This type of architectured material is more sophisticated than multilayered materials, and is directly inspired from interlocking strategies developed in masonry. **Topologically interlocked materials** (TIMs)[5] have recently emerged as an attractive design solution for structural panels with damage tolerance, tunable stiffness and pseudo-ductile response, despite being built of brittle building blocks.[5,19–21] The building blocks are interlocked from their shape and arrangement, as shown in Fig. 3 for a TIM based on tetrahedral blocks. Each block is constrained by its four neighbours, which prevent its translation and rotation in any direction (Fig. 3*a*). This basic motif is repeated to form large panels of interlocked blocks (Fig. 3*b*) held together by a rigid frame, which serves as an external 'ligament'.[21,22] No adhesive is required, and the blocks interact through contact and friction only. The TIMs fabricated and tested to date were made of building blocks in the orders of tens of millimetres in size and fabricated using a variety of techniques: machined Al–Mg–Si alloy,[22] casting of polyester,[5] cement paste[15] or even ice,[23] 3D printing of ABS,[24] freeze gelation of ceramic slurries.[25] The assembly is generally performed manually, although automated systems with a robotic arm have also been used.[24] Experiments and modelling on TIM subjected to flexural loading have shown that architectured panels outperform the monolithic form of the material in terms of energy absorption, impact resistance and damage tolerance, but at the expense of flexural strength.[5,24] Fig. 3c shows the deformed shape of the panel resulting from a point force applied to the centre of the panel, normal to its surface. The panel displays large and permanent deformations generated by the collective sliding and rotation of the tetrahedral blocks rather than by their individual deformation.[19,21] The force–deflection curve (Fig. 3*d*) shows large deflection, pseudo-ductile behaviour and progressive failure, resulting in large energy absorption and hysteresis.[26] The key for the non-linear behaviour of TIMs is the sliding of the blocks on one another, accompanied by frictional forces. Interfaces with high coefficient of friction dissipate more energy locally, but high friction also delays the sliding of the blocks. Autruffe *et al.*[23] demonstrated that lower coefficients of friction lead to softer overall response, but also to the sliding of blocks over larger volumes, which translates in more energy dissipation for the



2 A relatively simple but highly effective architectured material:[16] *a* Multiple crack deflections in a SiC ceramic containing weaker graphite interfaces subjected to flexural loading; *b* corresponding load–deflection curve: compared to the monolithic form of SiC which is brittle, the layered ceramic exhibits non-linear processes associated with crack deflection and progressive failure. Deformation and failure mechanisms are profoundly changed by the weak interfaces

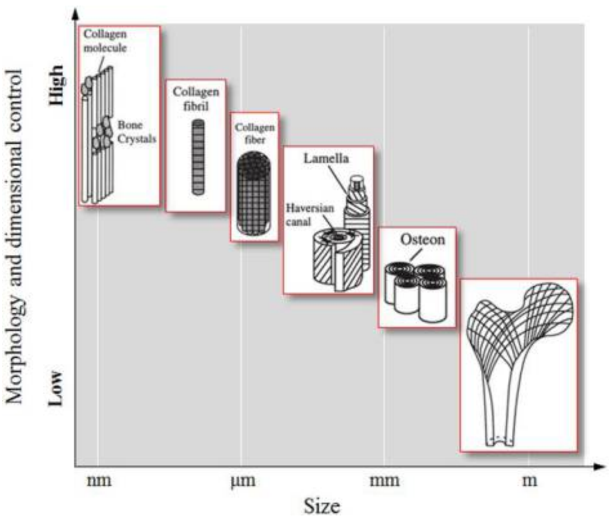


3 Example of a topologically interlocked material (TIM): *a* Basic interlocking unit: the central (greyed) tetrahedral block is surrounded and confined in all directions by four adjacent (white) tetrahedral blocks; *b* Assembly of tetrahedral blocks into a panel with lateral confinement; *c* actual picture of a panel made of a TIM after a puncture test, showing large, pseudo-ductile deformations; *d* typical mechanical response (adapted from Refs. 19, 21 and 24)

entire panel. These attributes make TIMs attractive as impact-resistant materials[27] or acoustic insulation materials.[28] A monolithic plate made of a brittle material fails catastrophically, with long cracks ruining its structural integrity and functionality. In contrast, failure in TIM architectured panels only involves one or a few blocks, which are destroyed or pushed out of the panel. The rest of the panel remaining largely intact and functional,[5,21] and only the damaged blocks may need to be replaced.[29] Interestingly, TIM architectured panels can also be disassembled and re-assembled with little losses in structural performance,[24] offering interesting perspectives in re-manufacturability.

The stiffness, strength and toughness of TIMs can be tuned by changing the size and/or arrangements of the blocks to fulfil the requirements of specific applications.

Other types of blocks with non-planar interlocking surfaces and which can be assembled in panels[5] or in three-dimensional materials.[15,30] Many other shapes are of course possible, giving rise to interesting topological optimisation problems. This huge design space has yet to be fully explored. A variety of models have recently emerged to explore the effects of morphology and materials properties on the overall response of TIMs, with the objective to guide the design and optimisation of these materials. Three-dimensional finite element models have successfully been used to model TIMs made of a relatively small number of blocks,[21,31] but the large number of contact surfaces rapidly makes finite element simulations computationally prohibitive for larger systems. As an alternative, more efficient methods such as thrust line analysis[21,32] or discrete element modelling[31] have been used successfully. Despite the simplifications these models rely on, they can be remarkably accurate,[21,31,32] and can therefore be used to optimise the size and number of the building blocks,[31,32] the coefficient of friction between the blocks,[26,31,32] or the pre-stress provided by the external ligament.[26,31]



4 The hierarchical structure of natural bone: distinct structural features are present over at least six levels of hierarchy (adapted from Ref. 41). The transitions across length scales are continuous and there is no clear distinction between microstructure and component

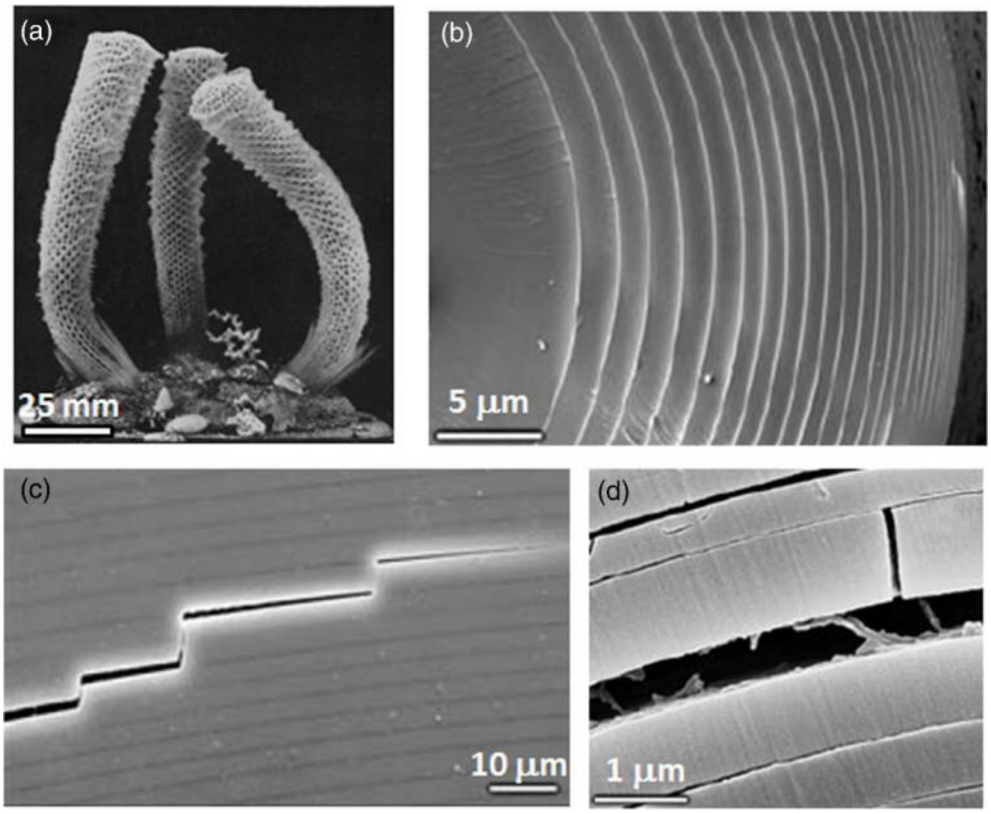
Architectured materials in nature

Nature is well ahead of engineers in making use of architectured materials. The exquisite micro-architectures found in natural materials have been refined over millions of years of evolution, and produce remarkably high structural performance. In particular, hard biological materials such as bone, teeth or mollusc shells achieve outstanding mechanical properties despite their relatively weak constituents.[33–38] These materials can also combine properties which are usually conflicting, such as stiffness and toughness. There are striking similitudes between engineered architectured materials and biological architectured materials.[39] Natural materials are also made of stiff building blocks of well-defined sizes and shapes, bonded together by much softer and more deformable matrices. In terms of microstructural features, biological materials are richer than synthetic materials, since their architecture is organised over several length scales in a hierarchical fashion. The architecture of bone, shown as an example in Fig. 4, can be compared and contrasted to Fig. 1. Bone possesses 6–7 levels of structural hierarchy spanning from the nanometres to the size of the entire bone.[40,41] In biological materials, morphological control is high at the smallest length scales. Proteins and other biological 'universal building blocks' are produced through natural processes which are tightly controlled and inherently repeatable,[42] which can be at least partially explained by optimised mechanisms at the nanoscale. For example, tropocollagen molecules have a length of 280 nm, which maximises load transfer between molecules and energy absorption.[43] The main proteins in spider silk have a very narrow distribution of molecular weight compared to synthetic polymers,[42] which grants the silk with high toughness.[44] When these building blocks assemble to generate larger structures, fluctuations and variations appear and accumulate up to the macroscale, which becomes the realm of biomechanics with its characteristic variations in tissue size and properties.

Unusual combinations of stiffness and toughness make bone, teeth or mollusc shells attractive as models for the development of new materials. Stiffness is provided by the high mineral content of these materials, while toughness is generated by intricate toughening mechanisms governed by architectures and interfaces.[45,46] Crack bridging is a common mechanism in these materials,[47–49] and large amounts of energy are dissipated through visco-plasticity at the interfaces between building blocks.[50,51] Theoretical models have suggested that the hierarchical structures of natural materials increase their properties via mechanisms operating over multiple length scales.[52–54] In particular, the nanoscopic size of the hard inclusions they contain imparts them to extremely high strength.[55] Examples include the nanosize of hydroxyapatite crystals in bone,[55] the β-sheet nanocrystals of proteins in spider silk,[56] the cellulose nanocrystals in plant[57] or of the nanofibres of the mineral goethite in limpet teeth.[58] However, small size does not produce toughness at the macroscale, and as seen in the examples given below, the most powerful toughening mechanisms appear to operate predominantly at 'architectural' length scales that are intermediate between the microscale and the macroscale.

Nature's layered materials: glass sponge spicules

Figure 5 shows the structure of a glass sponge, a marine animal that anchors itself in large oceanic depths. The skeleton of this sponge (Fig. 5*a*) is made of silica glass, which confers the sponge with high stiffness and useful optical properties.[59] Glass is inherently brittle, and nature's answer to this limitation is to arrange the material into ~100 μm diameter spicules which contain weaker interfaces arranged concentrically (Fig. 5*b*). The glass layers are composed of nanograins presumably surrounded by a molecular-thick organic network,[60] but it is not clear whether this nanostructure improves strength. The prominent feature of this material is its multilayered architecture. Cracks propagating in this material are deflected multiple times over the weak interfaces (Fig. 5*c*), making the spicules about four times stronger than bulk silica glass[61] and about



5 One of nature's layered materials: the spicules of the glass sponge. The glass rods have a multilayered architecture which can deflect cracks and produce toughness. Proteins are found at the interfaces between the glass layers (adapted from Ref. 60)

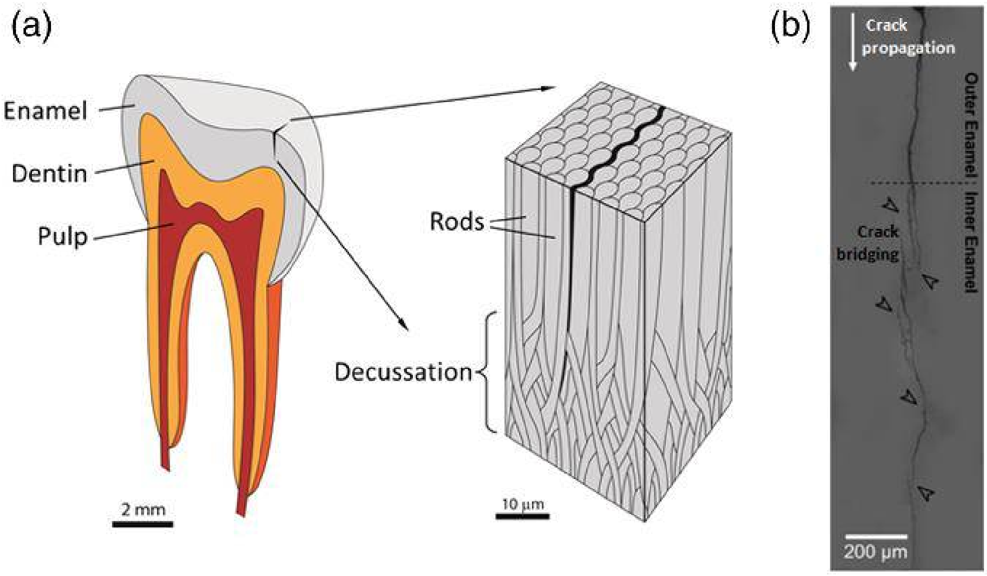
2.5 times tougher.[62] Crack deflection along weak interfaces therefore appears to be a prominent toughening mechanism in glass sponge spicules, a mechanism which is identical to what is sought in the *SiC*-graphite multilayered ceramic described above. As in synthetic multilayered materials, crack deflection in spicules also implies that the protein-rich interfaces between the glass layers are significantly weaker than the glass layers (the definition for what 'weaker' means in terms of crack deflection along interfaces is discussed further down in this article). Detailed data on the properties of the proteins in glass sponge is currently not available, but imaging reveals that they can sustain large deformations, as shown by the ligaments they form within the interfaces as the layers separate[60] (Fig. 5*d*). This mechanism is only present in a hydrated environment, water acting as plasticiser for the protein layers.[63] This feature provides an additional energy dissipation mechanism which is absent in the brittle interfaces of synthetic multilayered ceramics.

Tooth enamel

Enamel is the outermost layer of mammalian teeth (Fig. 6*a*). It is the tissue with the highest mineral content in the body of mammals, which confers this material with the extreme hardness required for mastication, predation or defence. Enamel is composed of long rods about 5 µm in diameter saturated with the mineral hydroxyapatite, and separated by a thin layer of protein (sheath). As in the case of glass sponge spicules, the sheaths represent weak interfaces which offer an easier path of propagation for cracks. Near the surface of the tooth the rods are perpendicular to the surface, so that the cracks which may emanate from the surface from excessive contact stresses or from impacts are 'channelled' along the rods, towards deeper regions in the enamel layer. Channelling of cracks away from the surface is beneficial because it prevents chipping of the tooth surface. In the inner part of enamel, the rods crisscross in more complex architectures (decussation), so that crack propagation in this region involves crack deflection and crack bridging (Fig. 6*b*). The rise in toughness resulting from these mechanisms is significant[64–66] so that cracks can be arrested and stabilised in the decussation region. These cracks can remain stable over many years, and can resist repeated loading of the teeth (these cracks are the so called craze lines). The cracks may propagate further from extreme stresses, but they will then meet additional lines of defence at the dentino-enamel junction and eventually at the dentine itself.[67] Enamel and its fracture mechanisms can be interpreted in the context of architectured materials: stiff building blocks of well-controlled cross-sections and shape are arranged in a quasi-periodic pattern to form a material. The blocks themselves contain a smaller structure (rods are made of nanocrystallites of hydroxyapatite) which do not appear to contribute significantly to the toughening mechanisms. The interfaces between the building blocks are weaker than the building blocks, which makes initial crack propagation easy. The interfaces channel the cracks into regions where propagation is more difficult, and powerful toughening mechanisms (crack deflection and crack bridging) operate.

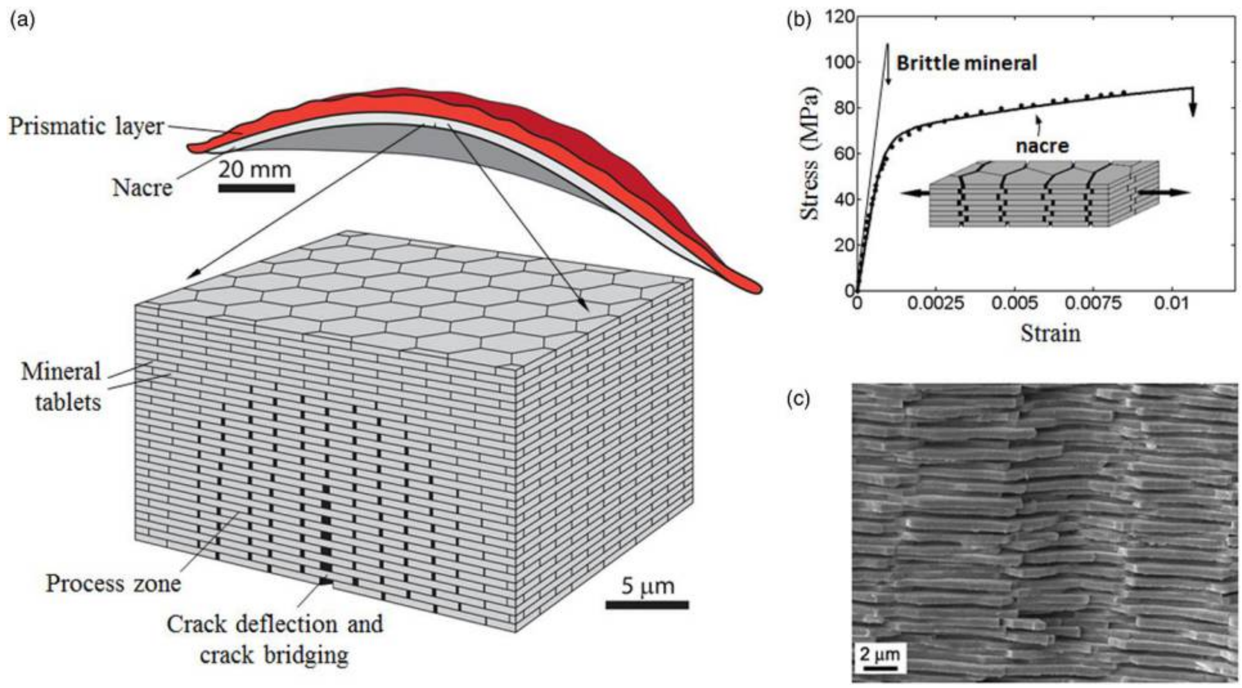
Nacre

Nacre is a highly mineralised tissue found in the inner layer of many species of mollusc shells (oysters, mussels



6 **A natural material with complex architecture: tooth enamel *a* overview of a mammalian tooth and micro-architecture of enamel (adapted from Ref. 68); *b* scanning electron micrograph of a crack propagating in the decussation region showing crack bridging (adapted from Ref. 48)**

or abalone). Nacre is made of microscopic polygonal tablets (~5 to 15 µm in diameter, ~0.5 µm thick) of the mineral aragonite.[69] These building blocks are arranged in a three-dimensional brick wall (Fig. 7*a*) bonded by softer interfaces of proteins and polysaccharides. The tablets are themselves made of nano-structured grains,[70] which may not directly contribute to the toughening mechanisms in this material. The softer interfaces are very thin (30–40 nm) so that the tablets make most of the volume of nacre, and the mineral content is high (~95% vol.). High mineral content makes nacre both stiff and hard, which is a critical functional requirement for a protective shell. Nacre can, however, also absorb a relatively high amount of deformation when it is stressed along the direction of the tablets. When loaded in this manner (which can occur when the shell undergoes flexural stresses), the tablets slide on one another over large volumes (Fig. 7*b*). This mechanism generates relatively large deformations at the macroscale. The strain at failure for nacre in tension can reach about 1%, which is two orders of magnitude more deformation than aragonite. Eventually the material fails along the



7 **Nacre from mollusc shell *a* overview of the structure of nacre with the main toughening mechanisms (adapted from Ref. 68); *b* tensile stress-strain curves for nacre and for pure aragonite. In nacre the sliding of the tablets on one another is the primary deformation mechanism which generates large strains. *c* scanning electron micrograph of a fracture surface in nacre, showing the mineral tablets arranged in a brick wall fashion (adapted from Ref. 51)**

interfaces, the pullout of the tablets prevailing as the main deformation and toughening mechanism[51,69,71] (Fig. 7*c*). The sliding of the tablets on one another is mediated by the thin organic layers, which must be hydrated to produce the adequate deformations.[51] Nanoscale bridges across the interfaces[72] and nanoasperities on the surface of the tablets[71] also contribute to the sliding resistance of the tablets.

A crack propagating in nacre will meet several barriers generated by the architecture of this material. First, the crack is deflected along the interfaces and circumvents the tablets. Multiple crack deflections generate long regions of crack bridging (Fig. 7*a*). The high stresses in the vicinity of the crack tip also trigger the sliding of tablets over large volumes, which leaves a wake of inelastically deformed material behind the crack tip (Fig. 7*a*). Crack bridging and process zone toughening combined can generate an overall toughness which is far superior to the toughness of both the mineral and the interfaces.[49] A slight waviness of the tablets is sufficient to generate progressive locking and the propagation of tablet sliding over large volumes.[51] Nacre is another example of a natural material which displays the characteristics of an architectured material: building blocks with intermediate length scales arranged in a quasi-periodic fashion in a three-dimensional architecture. The deformation and fracture behaviour of nacre are governed by collective mechanisms between the tablets, which in turn are governed by the mechanics of crack channelling and controlled deformation at the interfaces.

Other examples of high-performance natural materials

Nature provides an abundance of other examples of high-performance natural materials with micro-architecture. A large number of mollusc shells also display cross-lamellar structures,[73] which consists of calcium carbonate building blocks arranged over three distinct layers and bonded by thin proteinaceous interfaces. The outer layers guide flexural cracks into tunnelling cracks, which are arrested in the middle layer which has a cross-ply structure to deflect cracks and generate bridging.[46] The interplay between the architecture of the mineral blocks and the weak interfaces trigger unique toughness mechanisms, which make the work of fracture of conch shell more than four orders of magnitude higher than pure calcium carbonate.[74] Fibrous structural materials are abundant in nature and provide more examples of high-performance structural materials. In these materials the building blocks consist of long fibres made of collagen, chitin or cellulose. In the simplest arrangement, the fibres are aligned along one direction, for tissues that are specialised in carrying uniaxial tensile forces (e.g. tendons and ligaments[75]). In cross-plies, the fibres are laid in plies of alternating fibre angles. Cross-plies are found in tissues requiring tensile strength and stiffness along several directions, as in teleost fish scales.[76,77] The Bouligand structure is a more complex arrangement found in arthropod shells (cuticles). In this form of twisted plywood, the fibres are laid in the plane of the shell, but their orientations change gradually across the thickness. This structure imparts the cuticles with attractive tensile, flexural and impact properties.[78–80] As the architecture of the fibres becomes complex and multidirectional, the properties of the material become more isotropic.[81] Natural fibres can also arrange in helicoids to form hollow tubular building units, as seen in bone osteons[40,41] or wood cells.[82] Fibrous materials demonstrate how various properties can be achieved by varying the architecture of the fibres. The interface between the fibres (sometimes referred to as the matrix) is also critical to maintaining cohesion of the fibrous tissue. In collagenous tissues, proteins such as proteoglycans, osteocalcin and osteopontin[83] play a critical role, displaying large deformations thanks to unfolding mechanisms at the molecular scale. In plants, the cohesion of the fibres is largely controlled by hydrogen bonds which can break and re-form dynamically as external loads are applied, giving rise to 'Velcro like' mechanisms at the interfaces and large macroscale deformations.[84]

Complex hierarchical materials such as bone[40,41] or wood[84,85] integrate different structural motifs (staggered arrangement, cross-ply, helical fibres) over several length scales. In bone at the nanoscale, mineralised collagen fibrils are aligned along one direction, and their gliding on one another provides a mechanism for large deformations[86] which can also contribute to macroscopic toughness. This staggered structure and its associated mechanism is similar to nacre and offers unique combinations of stiffness, strength and toughness.[87,88] Crossplies of collagen are also found in bone, notably in the walls of osteons. While small-scale features and mechanisms are important in bone, experiments demonstrated that fracture is mainly dominated by larger scale crack deflection and pullout of osteons.[40,41]

There are also numerous examples of larger scale natural structures which fit the definition of architectured materials, as pointed by Khandelwal *et al.*[21] and Dunlop *et al.*:[39] the spine of vertebrate is composed of a series of building blocks (the vertebrae) interconnected by ligaments, the shell of a turtle can be considered as an assembly of planar plates with intricate interfaces.[89] Arthropods have segmented armour systems to allow simultaneous flexibility and resistance to puncture.[90] Scaled skins in fish or snakes and osteoderms in alligators or armadillos are composed of stiff segments which interact collectively to generate attractive combinations of resistance to penetration and flexibility.[91,92] While these systems would be traditionally considered structures, it is useful to interpret them as architectured materials in the context of bio-inspiration. As pointed by Meyers *et al.*,[93] in natural materials there is no distinction between the concepts of 'structure' and 'material'.

Architectured materials in nature and in engineering: general principles

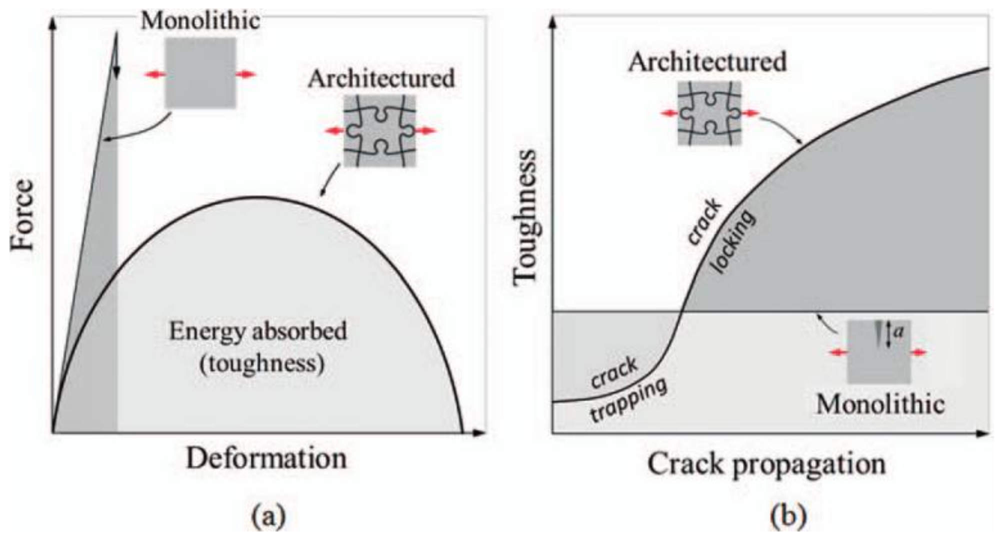
The examination of engineered and natural architectured materials reveals common characteristics in terms of structure, mechanics and performance. It is useful to identify these characteristics and to pinpoint their similarities and differences because this knowledge can serve as a basis for the development of new materials.

Building blocks and interfaces

In engineered and natural architectured materials, the building blocks are made of stiff and hard materials: rigid polymers, metals, engineering ceramics or biominerals. The material of the building blocks has its own microstructure, which is significantly smaller than the size of the blocks: granular structure for aluminium blocks, nanograins for nacre tablets and nanocrystallites for enamel rods. The deformation of individual blocks remains small and within the limits of linear elasticity, even in the case of large deformations and extreme loadings. In natural materials, the mineral building blocks contain traces of proteins segregated at the boundaries of the nanograins.[70] These proteins may confer the mineral an additional strength[94] but they do not seem to significantly change the elastic properties of the mineral.[95] In other cases the building blocks are themselves made of complex mineral–protein architectures as it is the case for bone osteons. The shape and arrangements of the building blocks vary from simple multilayered to layered-segmented to more complex three-dimensional arrangements. In engineered architectured materials the size and shape of the building blocks are highly uniform, with periodic arrangements of building blocks in two or three dimensions. The architecture of natural materials is not as uniform, but it shows a high degree of regularity and periodicity. TIMs are made entirely of interlocked blocks with no materials at the interfaces, and only rely on contact and friction for interactions. In natural materials, there is a thin (tens of nanometres) interface of proteins and/or polysaccharides between the blocks. The mineral concentration is very high: ~95% vol. for nacre[69] and tooth enamel[48] or even higher for the multilayered glass sponge spicules.[60] In bone, the interface between osteons and the bone matrix (which is also composed of osteons in mature cortical bone) is also very thin (cement line). In dense architectured materials, the building blocks almost fill the entire volume of the materials, with little or no interfaces between the blocks.

Deformation mechanisms

Figure 8a shows a generic force–deformation curve for a brittle monolithic material and for an architectured material based on the same constituent. In architectured materials individual blocks do not deform significantly. Instead, large deformations are generated by the collective motion of the blocks relative to each other, in a fashion similar to grain boundary sliding in polycrystalline metals.[96] The mechanical response is therefore largely governed by the structure, composition and mechanics of the interfaces.[23,97–100] Nature provides intricate examples of interfaces and sutures made of interlocking elements which can stiffen at high loads.[89,101] The sliding or opening of the blocks along their interfaces is governed by fracture mechanics, contact mechanics, friction or viscoplastic deformation of the materials at the interfaces. Importantly, these processes are non-linear and dissipate mechanical energy (area under the force–deformation curve). Some of the proteins found at the interfaces in natural materials can indeed display pronounced viscous behaviour in hydrated conditions[102] accompanied with large deformations generated by the breakage of sacrificial bonds such hydrogen bonds or organo-metallic bonds at the molecular scale.[99,100] The propagation of these non-linear mechanisms over large volumes and the translation of attractive micro-mechanisms into macroscale performance require hardening mechanisms at the interfaces. Hardening can be provided by the jamming of the building blocks as they move relative to one another, the geometrical interference between building blocks being absorbed by elastic deformation of the blocks. This 'geometric hardening' operates in TIMs and in nacre. In TIMs there is no intrinsic cohesion between the blocks, and the interlocking is achieved by containing the blocks with an external rigid frame (an external 'ligament'). In other more complex architectures, interlocking can be achieved by balancing the compressive locking stresses which occur in the sliding regions by tensile stress in other regions. These powerful self-equilibrated mechanisms are found in nacre,[51] turtle shells[89] and other natural sutures.[103] Hardening may also be achieved by the material present at the interface, which can itself display strain hardening behaviour. Recently, experiments and models have also suggested that strain rate hardening at the interfaces between blocks could also be a powerful mechanism to delay localisation.[104] These mechanisms are not exclusive: geometric hardening, interface strain hardening and interface strain rate



8 Key concepts in architectured materials: *a* Deformation: interfaces in architectured materials profoundly change the way inherently brittle materials deform. In particular, large deformations and energy absorption become possible; *b* Fracture: cracks are trapped onto weaker interfaces, where they are channelled into toughening configurations

hardening may be combined, although such combinations have yet to be systematically harnessed in engineered architectured materials.

Fracture mechanisms

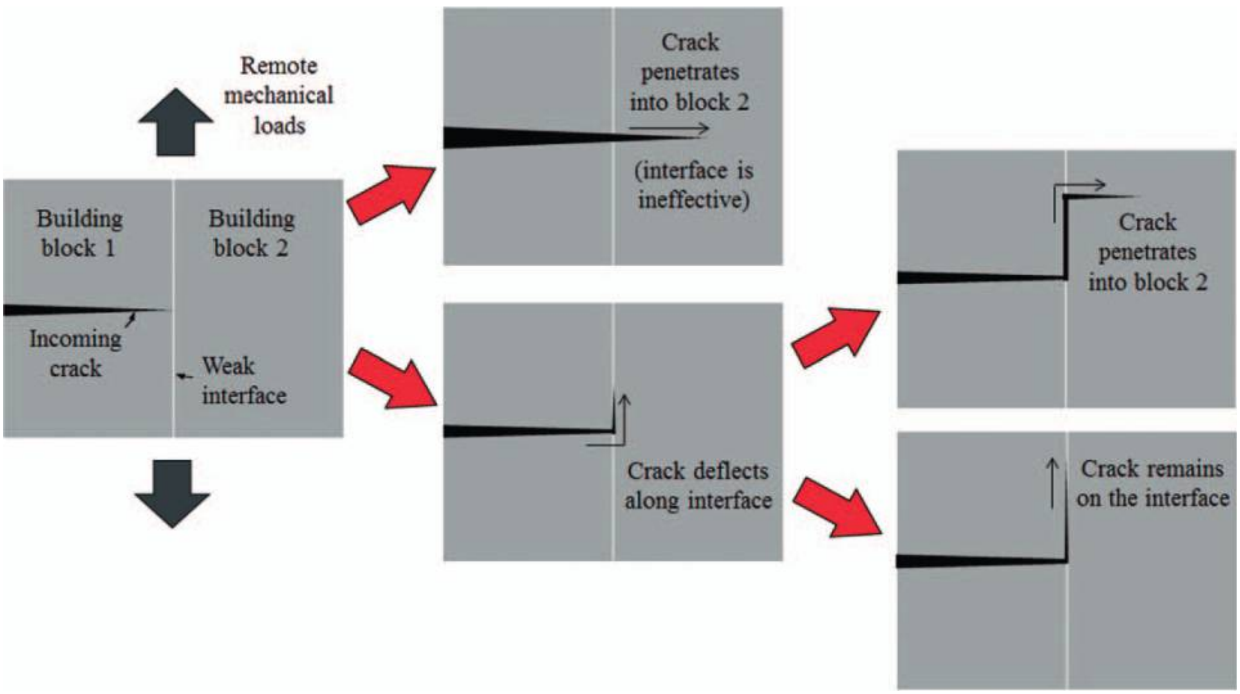
The deformation mechanisms described above also give rise to powerful toughening mechanisms. A critical requirement to trigger these mechanisms is that the crack must follow the interfaces instead of propagating through the building blocks. Once the cracks are 'trapped' into the weaker interfaces, they can trigger a second line of toughening mechanisms which can involve crack deflection, interlocking, friction, pullout or a combination of these mechanisms. As the crack progresses along the interfaces, the architecture of the material therefore forces the cracks into configuration where further propagation is more difficult. As a result, the overall toughness of the materials can rise to levels which can be significantly greater than the monolithic materials (Fig. 8*b*).[49] In order to achieve the deformation and fracture mechanisms shown in Fig. 8, the interfaces must deflect and channel propagating cracks, and also confine shear deformation between building blocks. Tailoring the interface is therefore paramount to the optimisation of architectured materials: the interfaces must be weak enough to deflect cracks, yet strong enough to provide cohesion between blocks and overall strength. The mechanics of interaction of propagating cracks with weak interfaces within a brittle material can be traced back to the work by Cook and Gordon,[105] Cook and Erdogan[106] and He and Hutchinson.[107] Fig. 9 shows possible scenarios for a propagating crack intersecting a weaker interface. If the interface is brittle, relatively simple models are available to predict whether a crack will be deflected along the interface or will penetrate into a layer. The condition for the deflection of a crack coming from an arbitrary angle into a brittle interface between two isotropic elastic materials was given by He and Hutchinson.[107] For the simpler case where the layers are made of an identical material and where the angle of incidence of the crack is 90° (Fig. 9), the condition for deflection is simply[107]

$$G_C^{(i)} \leq \frac{1}{4} G_C^{(b)}$$

Where $G_C^{(i)}$ and $G_C^{(b)}$ are the critical strain energy release rates of the interface and building blocks, respectively. Provided that the crack is initially deflected, it must also remain on the interface as long as possible, which leads to additional constraints on the interfaces and on the surface defects on the building blocks.[107,108] These design guidelines have been successfully applied to the optimisation of multilayered ceramics.[109]

There are, however, many architectured materials where the interfaces are not governed by brittle fracture. In TIMs, for example, the mechanisms at the interfaces are contact and friction. In biological materials, the interfaces are governed by the 'ductile' failure of the biopolymers they contain. For these interfaces the condition for crack deflection becomes more complex. For frictional interfaces the condition for crack deflection is a function of the friction coefficient and of pre-stresses.[110] For ductile interfaces, deflection becomes a function of the shear strength of the interface.[110] While these conditions apply to individual interfaces or to multilayered materials, they can also be extended to more complex architectures, as recently done for nacre-like materials.[111]

Mechanistic models and experiments[16,110]demonstrated that for the crack to be deflected and remain on the interfaces these interfaces must be sufficiently weak in terms of fracture toughness, yield strength or contact/friction, depending whether the interface is brittle, ductile or dominated by contact forces, respectively. Surface cracks on the building blocks may



9 Possible scenarios for the interaction of a crack with a weaker interface at 90° from the crack line. The crack remaining on the interface as much as possible is a condition for mechanical performance in architectured materials

prevent interfacial cracks and therefore these types of defects should be minimised. Meanwhile, the interfaces must be sufficiently strong to transfer stresses between the stiff layers and to ensure the cohesion of the layers. These conflicting requirements gives rise to a rich set of interesting design and optimisation problems.

Natural materials are constructed for specific functions, and studying their mechanics and performance cannot be dissociated from their function.[112] Likewise, architectured materials must be designed for a specific function. For example, layered ceramics are optimised to generate energy absorption and toughness in flexural loading.[16] Layered ceramics would not perform as well in uniaxial tension, for which other architectures are probably more appropriate. Likewise, arches and dome are designed to carry weight, but may not perform as well against horizontal loads. A comprehensive library of architectural design for specific loading conditions is yet to be established, and here again natural materials can serve as models and inspiration.

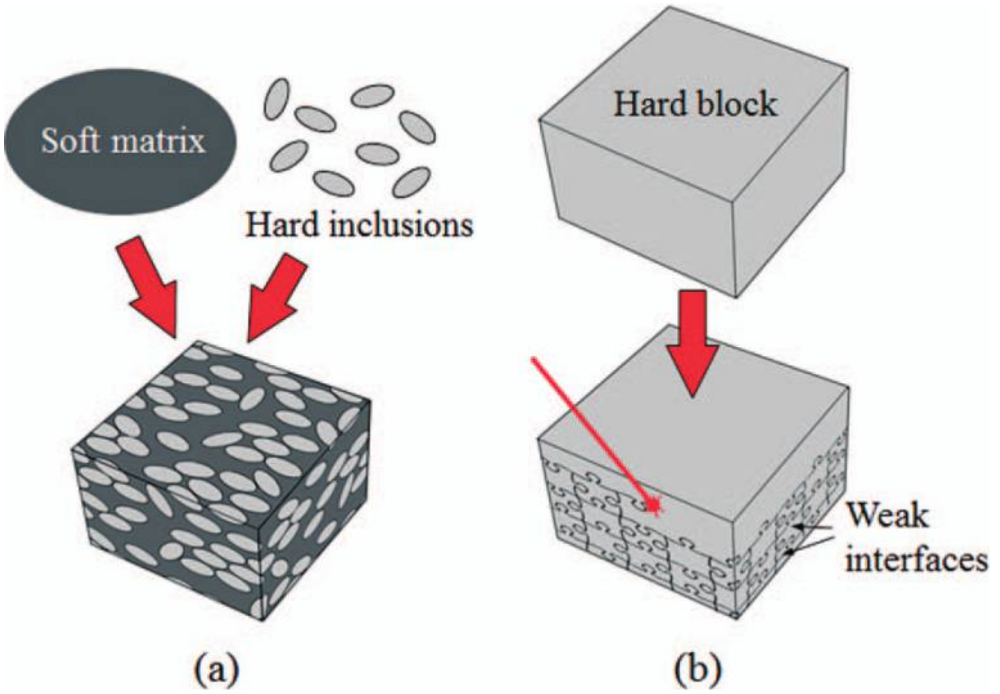
Bio-inspired materials and architectured materials

The mechanical performance of architectured materials relies on finely tuned mechanisms of deformation and fracture, and these mechanisms, in turn, rely on highly controlled architectures. Natural materials, as seen in the examples above, also display complex three-dimensional architectures with high uniformity and periodicity. Because of their high mechanical performance, they are increasingly serving as inspiration for the development of novel bio-inspired materials.[34,36–38,113,114] However, despite several decades of research in bio-inspired materials, duplicating the sophisticated features observed in structural natural materials still presents formidable challenges. The quest for engineering materials with complex bio-inspired architecture has prompted the development of innovative methods, some of which are discussed in the coming sections.

Bottom-up fabrication approach

The bottom-up fabrication strategy, which consists of assembling disordered ingredient into ordered microstructures (Fig. 10*a*), has dominated the area of bio-inspired materials. Many of these fabrication methods aimed to mimic nacre, which has been the prominent model for bio-inspired materials. The simplest fabrication method consists in simply mixing micro or nano-size platelet-like hard inclusion with softer matrices, and to order these inclusions into nacre-like brick-and-mortar structures. In order to arrange these inclusions, a variety of approaches were developed including self-assembly,[115] centrifugation, shearing cylinder, spinning plate or sedimentation[116] or layer-by-layer deposition.[117] However none of these methods has so far produced materials with the regularity and spatial periodicity found in natural nacre. More recent techniques include assembly at air–water interfaces[118] freeze-casting[119,120] and orientation of microscopic platelets using magnetic fields.[121] While these newer methods produce microstructures with higher structural order, the structures of these materials are still inferior to the highly regular structure of natural nacre, and still cannot approach its extremely high volume concentration of stiff building blocks.

We are indeed still limited by our fabrication technologies which cannot compete, to this day, with the complex bio-fabrication processes mastered by nature.[122] A possible approach to circumvent the limitations of small-scale fabrication is to produce structures at a larger scale, within the range of length scales of architectured materials. Larger building blocks also represent larger obstacles for cracks, which in general lead to higher fracture toughness.[123,124] In TIMs the building blocks are in the orders of tens of millimetres in size, which are fabricated using traditional methods (casting, machining), laser sintering[125] or 3D printing.[21] Large-scale bio-inspired materials have also been recently developed using similar approaches. For example, Meyer reported a large-scale nacre-like material made of thin plates of aluminium oxide bonded with a highly deformable adhesive.[126] This material was assembled manually, so that the thickness, width and arrangement of the tablets could be highly controlled. More recently, Livanov *et al.*[127] developed a multilayered alumina/polymer (PMMA and PVA) multilayered material which was one order of magnitude tougher than bulk alumina, thanks to the energy dissipation at the interfaces and to interlocking of the broken layers. Following the same approach of manual assembly of bio-inspired architectured materials, a nacre-like large-scale material fabricated from machined PMMA blocks was reported[128] (Fig. 10*b*). The blocks had the wavy characteristic of the tablets in nacre and were held together by miniature bolts, which served as external ligaments to hold the tablets together. This material could duplicate the mechanics of geometrical hardening observed in natural nacre, and the interaction between the blocks was governed by dry friction as in TIMs. Interestingly, the strength of the material could also be pre-programmed in the material by adjusting the pretension in the bolts. Another recent example of a large-scale assembled architectured materials is provided by Karambelas *et al.*,[129] who co-extruded and assembled ceramic components into conch-like cross-ply architectured beams. As in the natural conch shell, the cross-ply structure of the ceramic could deflect cracks, generate crack bridging and significantly increase toughness at the macroscale.[129] 3D printing is a natural choice for the fabrication of large-scale bio-inspired materials.[130] This relatively new technique enables high spatial fidelity, flexibility and high throughput, and it has proven to be a powerful tool to explore the mechanics of bio-inspired architectured materials.[131,132] Espinosa *et al.*[37,131,132] used ABS through a fused deposition modelling (FDM) rapid prototyping technique to fabricate a two-dimensional nacre-like material where the tablets were held in place by small bridges of ABS. The tablets were then infiltrated with a flexibilised epoxy, and some of the geometrical hardening observed in natural nacre could be duplicated. Dimas *et al.*[131,132] also used 3D printing to make nacre-like and bone-like architectured materials, by printing two distinct materials simultaneously. A stiff acrylic polymer was used for the tablets and a softer, more deformation urethane was used as the interfaces.[131] The building blocks in these 3D printed materials are in the order of millimetres size because the thickness of the interfaces between the



10 Two broad categories for the fabrication or architectured materials: *a* in the bottom-up approach, ingredients are assembled into architectures and *b* in the top-down approach, material is removed from a hard block to generate architectures

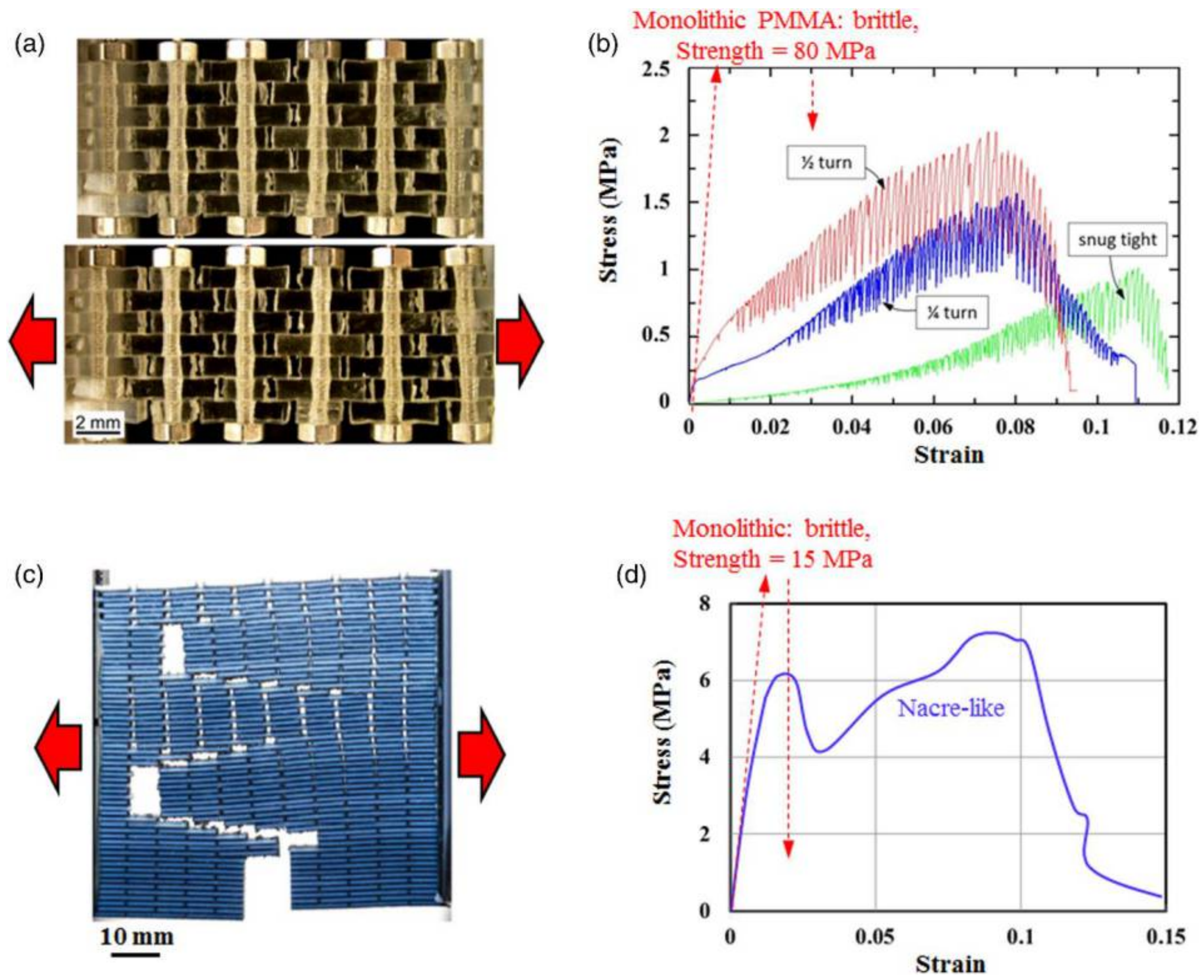
blocks (200–300 μm) must be larger than the spatial resolution of the printer. These materials, developed in parallel with numerical models, demonstrated the ability of soft interfaces to channel cracks and generate powerful toughening mechanisms and flaw tolerance. 3D printing was also recently used to generate intricate bio-inspired sutures and explore the effect of fractal hierarchy on mechanical performance.[133]

Top-down fabrication approach

In contrast to the bottom-up approach where ingredients are assembled to form materials, the top-down approach (Fig. 10*b*) consists of carving architectures within the bulk of monolithic materials. Figure 11 shows two examples of such approach. Chen *et al.* used photolithographic microfabrication methods to carve interfaces within silicon[134] (Fig. 11*a*). Three 2.5 μm thick polysilicon layers were deposited, and between each deposition step the layers were carved with ±45° trenches using photolithographic processes. The trenches were then filled with a deformable photoresist polymer. The process resulted in a cross-ply micro-architectured material mimicking the cross-ply architecture of the *Strombus gigas* shell.[46] In contrast to polysilicon which is brittle, mechanical tests on the architectured silicon showed progressive and 'graceful' failure. Imaging revealed multiple deformation and toughening mechanisms including delamination and crack bridging, which were identified as powerful toughening mechanisms in the natural *Strombus gigas* shell.[46] The architecture of this multilayered polysilicon material therefore completely changed the deformation and fracture mechanisms of silicon, and in this case amplified its toughness by a factor of 36.[134] Another more recent example of an architectured material made by a top-down strategy is the laser-engraved bio-inspired glass of Mirkhalaf *et al.*[68] In this approach, three-dimensional laser engraving was used to carve weak interfaces within the bulk of glass. The toughness of the interfaces could be tuned by adjusting the engraving parameters. In particular, sufficiently weak interfaces were shown to deflect and channel cracks, which can be used to control the path of crack propagation in glass. The laser-engraving method also allows the fabrication of complex two- or three-dimensional architectures of weak interfaces which can be designed to build toughness in glass (or any other material which is transparent to laser light). For example, Fig. 12*a* shows multiple jigsaw-like features which were carved within a thin glass sample.[68] Upon applying tensile stress, a crack initially propagates along one of these interfaces, which occurs at relatively low stress. However, when the faces of the crack separate the interlocking features generate geometric hardening, resulting in increased stress and also in the sequential failure of the other interfaces. The material eventually fails progressively by pullout of the jigsaw features, dissipating a large amount of energy by dry friction at the interfaces. The interfaces can also be infiltrated with elastomeric polymers, further enhancing the mechanical performance of the interfaces.[68] These two examples show how weak interfaces and architecture can be used to overcome the inherent brittleness of ceramics or glasses, following the concepts illustrated in Fig. 8. To achieve these mechanisms the architecture of the material must be finely tuned, which requires fabrication methods with very high structural fidelity. Although top-down approaches are currently limited to transparent materials or to thin opaque materials, top-down fabrication provides a new fabrication paradigm and an interesting alternative to bottom-up approaches.

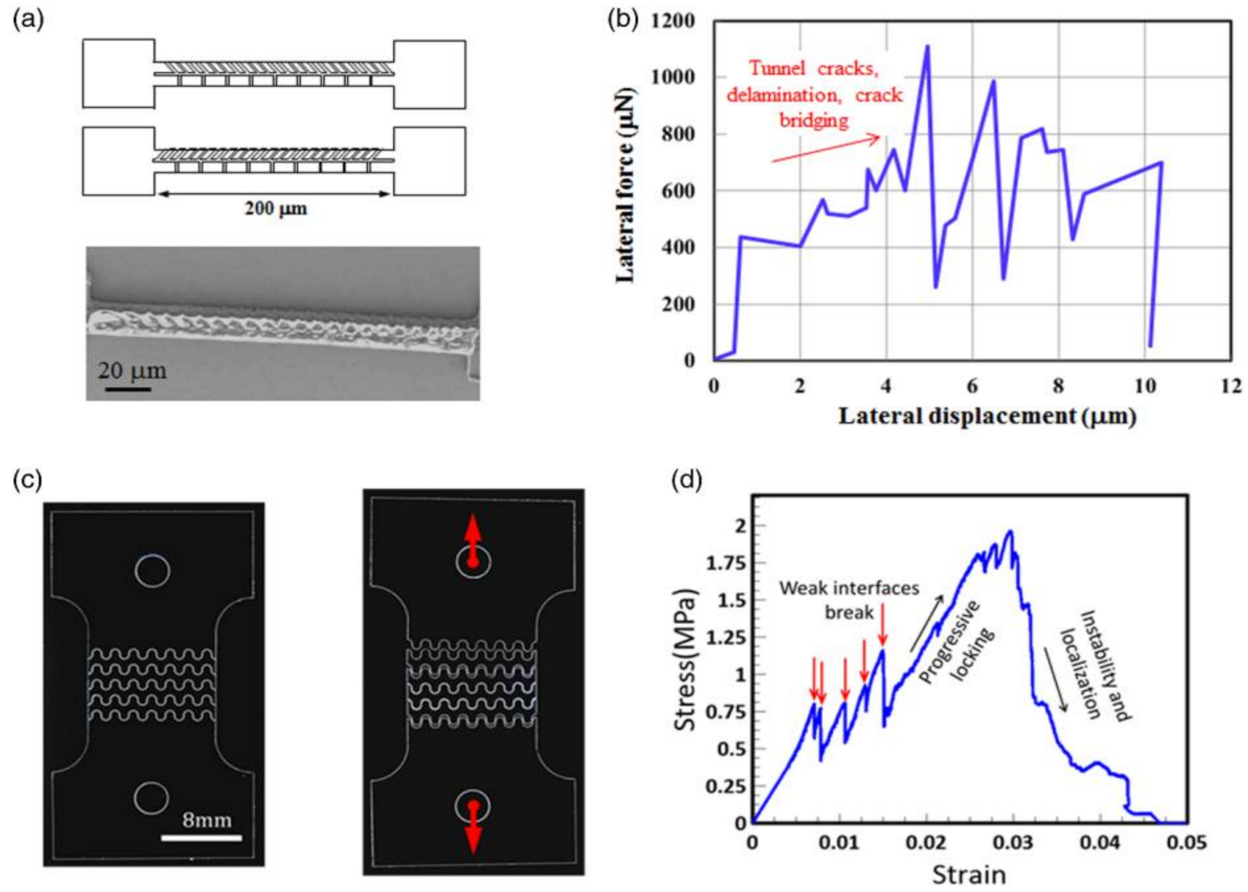
Conclusions and outlook

Architecture in materials is an emerging and promising strategy where structures are introduced at intermediate length scales and with high degree of morphological fidelity.



11 Two examples of bio-inspired architectured materials built from a bottom-up approach: *a* Nacre-like PMMA wavy tablets assembled with pre-stressed bolts; *b* corresponding tensile stress–strain curves at different bolt pre-stresses;[128] *c* 3D printed nacre-like notched composite with *d* corresponding stress–strain curves in tension.[131]

Dense architectured materials are made of stiff and hard building blocks of well-controlled shape and which are arranged in two or three dimensions. In dense architectured materials building blocks provide stiffness and hardness, and the interfaces provide toughness. The interfaces between building blocks play a critical role: they must deflect and channel propagating cracks and confine deformations, and they dissipate mechanical energy through non-linear mechanisms The examples of engineered and natural architectured materials discussed in this article illustrate how this strategy can lead to materials with unusual and attractive combinations of structural properties. A powerful concept in architectured materials is the ability to programme the mechanical response of the material (toughness, strength, strain at failure),[125] which promises interesting engineering perspectives. Nature can suggest new architectures such as nacre-like or conch shell-like materials, as well as specific mechanisms such as geometrically induced[135] or strain rate hardening at the interfaces[104] which have just begun to be exploited in bio-inspired architectured materials. In order to duplicate the soft interfaces found in natural materials, recent materials with bio-inspired architectures incorporated engineering polymers at the interface to generate additional strength and energy dissipation.[104,127,131,132,136] There is clearly an opportunity to exploit the interplay between architecture and the properties of these polymers. Other features such as residual stresses[137,138] or periodically varying modulus[139] have been shown to be powerful toughening mechanisms in multilayers engineering and biological materials, but they are yet to be implemented in more complex three-dimensional architectures. The development of new architectured materials also involves fascinating problems related to the tessellation of planes and the packing of space with building blocks of regular shape,[140–143] which may display complex interlocking features.[144] As in natural materials where structure, performance and function are indissociable,[112] the architecture of engineering materials must be designed and tailored for specific functions and loading configurations. Methodologies are now emerging to integrate architecture and design optimisation[145,146] but more tools for topology optimisation and integrated design will be required in the future. Interesting directions include topology optimisation,[147] multi-material design procedures[148] and evolutionary structural design algorithms.[149] These optimisation tools will require predictive capabilities and models, which for the cases of biological and architectured materials present special challenges. Architectured materials do not suit themselves to homogenisation, and therefore finite element models have focused on the explicit representation of the architecture representative volume element-based approach, yielding useful insights into the



12 Two examples of bio-inspired architectured materials built using a top-down approach: *a* Conch shell-like polysilicon–photoresist composite obtained from photolithography and deposition, *b* corresponding performance in flexion;[134] *c* Laser-engraved glass with jigsaw-like weak interfaces and *d* corresponding tensile stress–strain curve.[68] In both case, architecture turns brittle materials (in this case polysilicon and glass) into deformable and tough materials

mechanisms of biological materials,[51] or into two-dimensional topology optimisation.[88] Finite elements, however, become computationally prohibitive for large volumes of materials subjected to complex loading conditions. More effective approaches based on thrust line analysis[21,150] or discrete element methods[31] are highly promising for the modelling and optimisation of architectured materials.

Fabrication is also a significant challenge for architectured materials, because their mechanics and performance rely on high morphological fidelity. Topologically interlocked materials have so far been manually assembled from relatively large building blocks and into flat panels, although non-planar TIMs are also possible.[30] Rapid prototyping has also been successfully used to fabricate complex architectures and to demonstrate specific mechanisms experimentally.[131–133] Rapid prototyping has so far been used for relatively large structures made of polymers, but this technique could also be employed with other classes of materials and at smaller length scales. Examples include inkjet deposition of multilayered materials,[151] 3D inkjet printing of colloidal gels[152] and ceramics,[153] or small-scale deposition of glass.[154] Another fabrication strategy is self-assembly, which is usually performed with molecules and to form supramolecular nanostructures.[155] This approach can, however, also be used to assemble larger microscopic objects in the sub-micrometre range[156] or even larger.[157–160] Self-assembly is not limited to the assembly simple components; it can also be used to fabricate structures which have complex geometries.[158,159] This article also discussed the top-down approach as a highly promising strategy to 'carve' architectures within monolithic materials. Top-down methods such as photolithography, electron beam lithography or laser engraving have already been used to produce complex 2D and 3D metamaterials for photonics application.[161] So far there has only been a few examples where top-down methods were used to fabricate bio-inspired structural architectured materials.[68,134,136] Top-down methods are attractive because very hard and stiff materials such as ceramic or glasses can serve as base materials (although only the surface or a small depth from the surface can be machine for opaque materials). Top-down methods are also very accurate and can produce intricate architectures in two or three dimensions with a very high degree of morphological control. Finally this method can produce materials with extremely high volume content of stiff materials, since it is based on carving thin interfaces. As the array of high-fidelity bottom-up and top-down fabrication methods is expanding, they will enable additional features to be included, such as functionally graded architectures.[48,62] Smaller architectural features will also be possible, to possibly be incorporated within structural hierarchies to generate systems with superior properties.[53,54,133,162] However, as demonstrated in engineering and biological materials,[123,124] large architectural features at the mesoscale or even millimetre scale will remain critical to high toughness, since they represent larger obstacles to crack propagation.

In addition to useful combinations of structural properties, architectured materials offer multiple advantages over their monolithic counterparts. Architectured materials are damage tolerant,[5,22] they can be remanufactured[24] and reconfigured.[163,164] They also suit themselves to multifunctionalities[165] including electronic properties,[166] acoustic insulation,[167] active and responsive materials,[168,169] morphing[170] and actuated materials.[171,172] Self-assembly of modular blocks and self-organisation lend themselves to longer term goals where material and structures can autonomously adapt their construction to the requirements of specific functions, or to changes in loading conditions. This 'morphogenetic engineering'[173] goes back to similarities with natural materials and systems, which have been following this strategy for millions of years.

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