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Mineral Nano-Interconnectivity Stiffens and Toughens Nacre-like Composite Materials

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Biological materials have evolved a wide range of complex structure-property relationships by organizing simple building blocks over multiple length scales.^[1] Nacre, a mineralized biological composite found in mollusk shells, has been a prime source of inspiration for creating composites with multiscale structural architectures. Despite being composed of intrinsically weak and brittle materials, mollusk shells display an unusual combination of strength, stiffness, and toughness, which is desirable for many structural applications.^[2-4] This results from the onset of several energy dissipation mechanisms operating at multiple length scales during the fracture process. At its finest organizational level, nacre is a nanocomposite of aragonite nanoparticles intercalated by biopolymers, which reduces the brittle nature of the mineral through local deformation of the organic phase and rotation of the nanoparticles.^[5,6] In turn, this mineral nanocomposite is further structured into micron-scale platelets divided by nanometric layers of biopolymers. The resulting "brick-and-mortar" architecture toughens the material by deflecting cracks that hit the platelet surface and by providing additional plastic deformation of the organic ductile phase. Controlling the spatial distribution and orientation of these mineral platelets and modulating their interconnectivity through mineral bridges,^[7] frictional contacts between nanoasperities^[8] and a strain hardening organic matrix^[9] appear to be key to nacre's toughening deformation mechanisms.

Manufacturing multiscale materials that exhibit nacre-like structural features requires the development of processing tools to simultaneously control the distribution, orientation, and contact strength between mineral building blocks. Implementing this hierarchical microstructure in a synthetic material should allow us to probe the underlying structure–function relationships and test our understanding of biological design principles. Furthermore, translating these concepts into engineering materials would offer new access to antagonistic combinations of properties unique to natural materials, such as high stiffness and toughness.^[4]

Most studies on nacre-like composites have focused on replicating the biological material's mineral density and brick-and-mortar microstructure of closely packed mineral

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DOI: 10.1002/adma.201605039

platelets intercalated by a polymer phase, either by controlling the alignment and distribution of preformed ceramic "bricks,"[10-16] or processing ceramic slurries to form platelet morphologies in situ.^[17,18] However, recent studies suggest that mineral nano-interconnectivity is also an important parameter to impart both high strength and toughness in these bioinspired materials.^[7,19,20] Composites exhibiting continuously interconnected ceramic bonds between platelets, mimicking the mineral bridges observed in the biological structure, are significantly stiffer and stronger than composites without.^[21] Such interconnected composites are typically produced by freeze-casting or magnetically assisted slip casting of nacrelike ceramic scaffolds, followed by infiltration with a polymer matrix.^[21] In freeze-cast SiC lamellar systems, for example, it has been shown that increasing the number of mineral bridges between lamella significantly enhances the flexural strength of the composite.^[21]

Although mineral interconnectivity has a demonstrable effect on the mechanical properties of lamellar composite materials when mineral layer thickness is in the range of $5-35 \ \mu m$,^[21] the effect of nano-interconnectivity between submicron mineral platelets, as observed in biological nacre, is not yet well understood. Mineral bridges have been observed in magnetically assisted slip cast scaffolds with submicron platelet thickness;^[15] however, the effect of bridge morphology at these finer length scales has not yet been fully exploited and studied. To improve our understanding of this important structural feature, synthetic nacre-like materials exhibiting different levels of interconnectivity within the inorganic phase need to be developed and thoroughly investigated.

Using magnetic assembly to align preformed heterogeneous ceramic bricks, we produce inorganic scaffolds, which are hot-pressed and infiltrated with an organic phase to generate a strong and tough composite that has a nacre-like brick-andmortar structure, interconnected with submicron interplatelet mineral bridges. The pioneering aspect of this work is the use of alumina platelets that are precoated with a ceramic layer (titania) that sinters at a lower temperature compared to the sintering temperature of the alumina platelets. Using precoated alumina platelets significantly minimize the processing time and material heterogeneity, which are commonly observed in fabrication processes that rely in cosedimentation of particles exhibiting different size and/or density. Partial sintering of the ceramic coating enables the in situ formation of mineral nano-interconnectivity between the alumina platelets. This results in denser scaffolds, larger fractions of mineral bridges, and larger fractions of platelet clusters of increasing size as the temperature applied in the hot-pressing process is increased.





Figure 1. Production of nacre-like composites by vacuum assisted magnetic alignment (VAMA). A) Rotating magnetic field aligns magnetized titaniacoated alumina platelets suspended in a liquid, while vacuum consolidates the aligned material into green bodies of bulk ceramic with a brick-andmortar microstructure. B) Green bodies are hot-pressed into sintered porous ceramic scaffolds. During this process, titania forms surface asperities and mineral bridges between platelets. C) Scaffolds are infiltrated with low-viscosity thermoset monomers by applying vacuum or isostatic pressure to form dense polymer–ceramic composites. D) Increased scaffold sintering temperature results in increased composite density.

Combined, these effects produce nacre-like materials with a combination of superior stiffness, strength, and toughness values, which exceeds previous literature reports for plateletreinforced polymer composites. Upon further densification, a limit is reached, at which extensive clustering and bridging between platelets prevents the onset of toughening mechanisms such as crack deflection and platelet pull-out.

To explore how different levels of nano-interconnectivity within the inorganic phase impact the mechanical properties of a brick-and-mortar structure, we have developed a process to quickly produce large, bulk nacre-like ceramic scaffolds. Our nacre-like composites are prepared using a three-step workflow: (1) magnetic alignment and vacuum-assisted assembly of diluted ceramic slurries followed by drying, (2) sintering under pressure, and (3) monomer infiltration. First, rotating magnetic fields align magnetized inorganic microplatelets in an aqueous suspension and subsequent vacuum filtration fixes the particles' orientation as it consolidates them into a green body (Figure 1A). Typical samples discussed here contain 20 g of mineral solids and are 46 mm in diameter. It takes just 25 min to go from a fluid suspension to a cohesive green body ready to be fired (see the Experimental Section for details). Although filtration processes are limited in thickness to a few centimeters, this process can be scaled to much larger diameters without further increase in the processing time. In the second step, the green bodies are hot-pressed to partially sinter the platelet interfaces, generating porous ceramic scaffolds with mineral nano-interconnectivity (Figure 1B). These sintered scaffolds are then infiltrated with a low viscosity monomer, which is polymerized into a continuous organic matrix (Figure 1C).

To modulate the strength of the mineral contacts at the platelet–platelet interfaces, we employ commercially available alumina microplatelets, which have been precoated with a continuous thin film of densely packed titania nanoparticles. This two-phase alumina–titania system, where a more temperaturestable oxide phase is coated with an inorganic layer that is more



prone to sintering, allows us to easily modulate the interface through control of the sintering temperature. As the scaffolds sinter during hot-pressing, these titania particles Ostwald ripen into larger surface asperities, and form in situ mineral bridges at contact points between platelets. This occurs at temperatures well below the 1100 °C minimum that we have found necessary to form necks between pure alumina platelets (data not shown). Sintered contacts between bare alumina platelets are very difficult to control; there is a very narrow temperature/ pressure window within which the brick-and-mortar architecture transitions from a nacre-like scaffold morphology with too-small alumina contacts to a porous alumina monolith with contacts so large that the desired morphology is lost. However, as the strength of titania (≈200 MPa) is about half the strength of alumina (≈400 MPa), this approach opens a wider processing window where the interface should still be weaker than the main phase.^[22] We find external pressure applied during sintering is key to the formation of robust mineral contacts in this system. Pressureless sintering produces vacuum assisted magnetic alignment (VAMA) scaffolds that are far less dense than hot-pressed samples and have little mechanical integrity, regardless of the sintering temperature or dwell time used (data not shown). Hot-pressing results in a high density of interfacial contact points between the aligned platelets, producing denser scaffolds (Figure 1D) with tunable microstructure that resembles the packing of the desired brick-and-mortar structure (**Figure 2**A).

Evolution of the titania phase morphology and connectivity was systematically evaluated after sintering under constant pressure and variable temperature conditions and a useful processing window is observed between ≈800 and 1100 °C (Figure 2A). Only negligible sintering occurs below this range. Above 800 °C, titania particles grow and become large enough to make contact with facing platelets. At higher temperatures, particles continue to grow beyond the initial contact point, causing more mineral bridges to form and the initial contacts to



Figure 2. Evolution of surface morphology and platelet architecture and quantification by image analysis. A) Increased formation of nanoasperities, mineral bridges, and clusters of continuously sintered platelets are observed with increasing sintering temperature under an applied pressure of 10 MPa. B) The fraction of titania asperities forming mineral bridges approach a limit defined by the geometric overlap between platelets. C) The size distribution of platelet clusters reflects the increasing microscale inhomogeneity of the composite material. Symbols indicate average values, whereas gray zone shows the 90% width of the size distribution. The intensity of the color circles in the leftmost images in (B) and (C) is directly related to their radius, from purple to orange when the radius increases.

spread. Above 900 °C, the titania phase spreads to fill all contact areas between faces. Image analysis was used to quantify these microstructural changes (see Figure 2B,C and the Supporting Information for detail).

When scaffolds are sintered at higher temperatures, we observe a significant increase in three interdependent structural parameters: titania bridge forming fraction, mineral density, and the size and distribution of platelet clusters. At higher temperatures, the titania phase begins to soften, causing the coating to spread under the applied external pressure and resulting in a marked increase in the titania bridge forming fraction, which jumps from 4 to 61% within the temperature range 800–900 °C before it eventually saturates at 1100 °C. The saturation value of \approx 68% is in agreement with the geometric limit determined by the available overlap areas between adjacent platelets. Since titania sintering reduces the average distance between platelets and likely facilitates platelet sliding and packing, we observe an increase in the overall composite density when the scaffold is sintered at higher temperatures (Figure 1D).

While the macroscale distribution of particles is quite even within the scaffold, this is not necessarily the case at the microscale (Figure 3C). The VAMA process creates layered structures



Figure 3. Mechanical properties of nacre-like composites as a function of hot-pressing temperature. A) Representative three-point bending data. B) Flexural strength approaches a limit as sintering temperature increases, while modulus increases continuously. C) Representative single-edge notched bending data illustrate the transition in composite failure behavior from graceful to brittle with increasing hot-press temperature. D) Fracture toughness (K_{IC}) increases and eventually saturates with increasing processing temperature. E) Representative SEM pictures of the crack path illustrate the changes in composite fracture behavior across increasingly sintered scaffolds.

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with platelets distributed stochastically within these layers and as platelets pack, polydispersity in the starting material creates voids and slight deviations from the ideal face-to-face parallel contact, producing regions with slightly lower packing density. As scaffolds densify, this creates local inhomogeneity in the composite and we observe the nucleation of clusters in more densely packed regions, where titania more quickly spreads to continuously connect platelets across fully sintered interfaces. Image analysis shows that the average platelet cluster size increases from about 250 nm (thickness of a single platelet) to nearly 1200 nm with processing temperature (Figure 3C). We also observe that the cluster size polydispersity also increases by a factor of 17 over the same temperature range.

Infiltrating these sintered scaffolds with a polymer phase produces composites with unusually high stiffness, strength, and flaw tolerance (Figure 3). The increase in mineral density, bridge forming titania fraction, and platelet cluster size results in marked changes in the mechanical properties of the material. As the overall mineral density of the composite increases, we observe a surprising simultaneous increase in elastic modulus, strength, and fracture toughness. This trend is seldom observed experimentally in nacre-like composites containing more than 60 vol% of mineral phase.^[14,23,24] However, on the basis of this earlier experimental work, we hypothesize that the density increase alone is not enough to account for the enhanced strength, elastic modulus, and fracture toughness ($K_{\rm IC}$) of the composite as scaffolds are sintered at higher temperatures.

The improvement in mechanical properties with sintering temperature is also accompanied by an increase of the fraction of titania forming mineral bridges (Figures 2 and 3). Rather than continuously increasing with mineral density and platelet cluster size, the fraction of titania bridges reaches a saturation limit. Interestingly, this distinctive saturation behavior in the titania bridge forming fraction coincides with the plateau observed in the composite strength and $K_{\rm IC}$ values at the highest processing temperatures of 900 and 1100 °C (Figure 3B,D), suggesting a correlation between improved mechanical properties and nanoscale mineral connectivity. Since our synthetic platelets are fully inorganic, nacre's toughening mechanisms arising from nanoparticle rotation and plastic deformation within the platelets do not occur in our synthetic composites.

With the above correlation in mind, our analysis focuses on the fracture behavior of composites sintered between 800 and 900 °C where the major gains in nano-interconnectivity occur. At 800 °C, the structure is minimally connected, all titania contacts are small and weak, and the composite fails by delamination across the alumina titania interfaces within the scaffold. Although delamination leads to extensive crack deflection, the mineral connectivity is too weak to cause significant toughening. This makes the composite effectively homogeneous and the strength and K_{IC} are low and tightly distributed. As the average size of the individual bridges becomes larger and covers more area, the force required to break them increases, resulting in a stronger bulk material (Figures 2B and 3B). At a sintering temperature of 850 °C, contacts between platelets are large and strong but the overall density of clusters is still low enough that inelastic deformation within the composite's microstructure is still possible. This results in force-displacement curves for notched samples that indicate substantial inelastic deformation of the composite before failure (Figure 3C).

Although the composite strength and K_{IC} continue to increase between 800 and 900 °C (Figure 3A,B), the spread in these values becomes much larger, reflecting the increasing inhomogeneity of the composite as platelet clusters form (Figure 2C). By 900 °C, the composite failure mode transitions from "graceful" deformation to more ceramic-like "pop-in behavior," in which bursts and unstable crack propagation are evident (Figure 3C). We hypothesize that this may arise from cracks that form in less dense regions but become trapped by denser clusters, forcing the material to store more elastic energy before failure. By 1100 °C, the cluster density has increased to the point that paths through lower density regions have become scarce and/or discontinuous and contacts are sufficiently strong to drastically minimize platelet pull-out mechanism (Figure 3E). The less anisotropic shape of the platelet clusters eventually reduces the number of deflection events. decreasing the tortuosity of the crack path. Composites sintered at this high temperature display brittle fracture behavior, reduced strength, and flaw sensitivity that is typical of bulk ceramics.

By increasing mineral connectivity while maintaining fracture under pull-out mode, it is possible to produce composites with stiffness and strength that compete with those of engineering materials, as illustrated in **Figure 4**. Within the processing conditions explored in this work, we achieve a combination of specific strength and specific modulus higher than any other bulk nacre-like polymer–ceramic composite reported in the literature (Figure 4A) and now occupy a thus far empty region of the specific strength–modulus Ashby diagram, making a new set of properties accessible using state-of-the-art nacre-like composites. Our composites not only outperform previously reported nacre-inspired materials in terms of normalized specific properties compared above (Figure 4A,B) but absolute fracture toughness and elastic modulus (Figure 3B,D) as well.

Detailed analysis of this comparison of nacre-like polymer and mineral composites in the literature reveals further insights into the role of nano-interconnectivity on the mechanical properties of such composites. For example, scaffolds sintered at 700 °C lack mineral contacts, thus these composites are directly comparable with previously reported composites of similar density which also lack mineral nanoasperities and bridges. Since our specimens processed at 700 °C show similar specific strength and modulus to the epoxy/alumina-based composites produced by Libanori et al.,^[13,23,27] we infer that the inherent properties of titania-coated alumina platelets are not significantly different from the alumina platelets used in other studies. The work of Gurbuz et al.^[14] using similar alumina platelets shows that simply increasing the volume fraction of platelets in epoxy up to 68 vol% without sintered mineral contacts does not improve the specific strength or elastic modulus of the material. In contrast, this work shows that increased mineral density, accompanied by increased interplatelet connectivity, ultimately leads to a simultaneous improvement of the composite stiffness and strength.

Compared to engineering structural materials, our nacre-like materials display a specific strength that is on par with that of

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Figure 4. Survey of nacre-like ceramic/polymer matrix bulk composites.^[14,15,18,21,23,25,26] A,B) Specific elastic modulus and specific strength compared to (A) other nacre-like composites and (B) traditional engineering materials. C,D) Elastic modulus and fracture toughness compared to (C) other nacre-like composites and (D) structural engineering materials.

continuous glass fiber composites, but with a much higher specific modulus comparable with that of continuous carbon fiber composites (Figure 4B). In terms of K_{IC} , the nacre-like composites show values well above what one would expect from a rule of mixture estimate based on the toughness of epoxy and alumina alone (Figure 4D), which illustrates how design principles found in nacre are captured in these composites. While additional work is needed to increase the material's toughness further, the K_{IC} values achieved here approach the level expected from continuous fiber reinforced composites (Figure 4D).

Here, we demonstrate that by introducing nano-interconnectivity, the intrinsic strength, stiffness, and toughness of a discontinuously reinforced composite can be improved so much that they approach values associated with continuous fiber reinforced composites. Furthermore, as discontinuous composites, they have the potential to be molded into near net shapes and more complex macroscale architectures designed to maximize structural stiffness, strength, and toughness, giving them higher added value.^[28] This approach is a hallmark of natural materials, in which hierarchical designs are used to produce multiscale structures to fulfill specific, localized structural needs.

We have produced exceptionally strong, stiff, and tough nacre-like composites by implementing submicron interplatelet mineral bridges in a brick-and-mortar structure with length scales comparable to those found in biological nacre. Using alumina platelets precoated with a second low-sintering titania phase in our streamlined magnetic alignment process enables the in situ formation of mineral bridges during sintering of nacre-like scaffolds while preserving the brick-andmortar microstructure. We observe a surprising simultaneous increase in elastic modulus, strength, and fracture toughness for increasing mineral contents in the polymer-infiltrated scaffolds, which has never been achieved for mineral volume fractions higher than 60 vol%. Our materials are significantly stiffer, stronger, and tougher than previously reported nacrelike composites of similar density and chemical composition, and display a level of stiffness and strength usually associated with continuous fiber composites, yet they are processed as discontinuous composites, opening new possibilities to produce www.advmat.de

parts with more complex designs to address more demanding engineering requirements.

Experimental Section

Composite Fabrication: Titania coated alumina microplatelets (Xirallic crystal silver T-50, Merck GMBH, Germany) were rendered magnetically responsive by electrostatic surface adsorption of superparamagnetic iron oxide nanoparticles (SPIONs), as detailed by Erb et al.^[13] Dry magnetized platelets (20 g, 5 vol%) were suspended by vigorous stirring in a 100 mL solution of 1% polyvinyl alcohol ($M_W = 13-23$ kDa, Sigma-Aldrich, Germany,), 1% polyvinylpyrrolidone ($M_{\rm W}$ = 360 kDa, Sigma-Aldrich, Germany), 0.25% Poly acrylic acid (PAA) sodium salt $(M_{\rm W} = 8 \text{ kDa}, \text{ Polysciences}, \text{USA})$, and one drop of Antifoam 204 (Sigma-Aldrich, Germany). This mixture was then transferred to a laboratory custom-made vacuum filtration setup, encircled by four solenoids generating an in-plane rotating magnetic field. A color change, indicating that platelets had aligned and become more reflective, was observed within 30 s. The aligned platelets were subsequently consolidated into a disc-shaped compact (46 mm diameter) by pulling vacuum (100 mbar) for 25 min. Green bodies were prefired in air (500 °C, 3 h) to remove the organics and transferred to a ceramic hot-press (FCT Systeme GmbH, Germany). Samples were sintered in a 50 mm argon purged graphite die (20 kN external pressure, 20 °C min⁻¹ ramp, 10 min dwell, natural cooling) varying only the target temperature. Isostatic pressure (KIP 100E, P.O. Weber, Germany) was used to infiltrate each sintered ceramic scaffold with a commercial epoxy (Sikadur-300, Sika, Switzerland), which was then oven cured (120 °C, 2 h).

Characterization: Flexural tests were performed on a universal testing machine (Autograph AGS-X, Shimadzu, Japan) on samples cut and polished to 25 mm \times 2 mm \times 1.5 as specified by ASTM designation C1161 – 13. Single-edge notched bending tests were performed on samples cut and polished to 15 mm \times 3 mm \times 3 mm with a 1.5 mm razor sharpened notch, perpendicular to the plane of platelet alignment, as specified by ASTM designation D5045 – 99. Quantification of titania feature size and platelet cluster size was performed by image analysis (see details in the Supporting Information) of scanning electron micrograph cross-sections. Cross-sections were flat polished with a broad ion beam mill (IM4000, Hitachi, Japan) and imaged using a (LEO 1530) scanning electron microscope (SEM) in backscatter mode to differentiate between phases by relative density. Images were processed using the Fiji software packages.^[29–32]

Supporting Information

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

Acknowledgements

The authors thank the Swiss Competence Center for Energy Research (Capacity Area A3: Minimization of Energy Demand) for financial support. This work was also carried out within the framework of the National Center of Competence in Research for Bio-Inspired Materials financed by the Swiss National Science Foundation. Technical support from the Center for Optical and Electron microscopy of ETH Zürich (ScopeM) is also acknowledged.

Received: September 19, 2016

- Revised: November 9, 2016
- Published online: December 22, 2016



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