

# BIOINSPIRED COMPOSITES BY VACUUM ASSISTED MAGNETIC ALIGNMENT

Madeleine Grossman<sup>1</sup>, Florian Erni<sup>1</sup>, Florian Bouville<sup>1</sup>, Rafael Libanori<sup>1</sup>, André R. Studart<sup>1</sup>

<sup>1</sup>Complex Materials Laboratory, Department of Materials, ETH Zürich, 8093 Zürich, Switzerland  
Email: madeleine.grossman@mat.ethz.ch, Web Page: <http://www.complex.mat.ethz.ch>

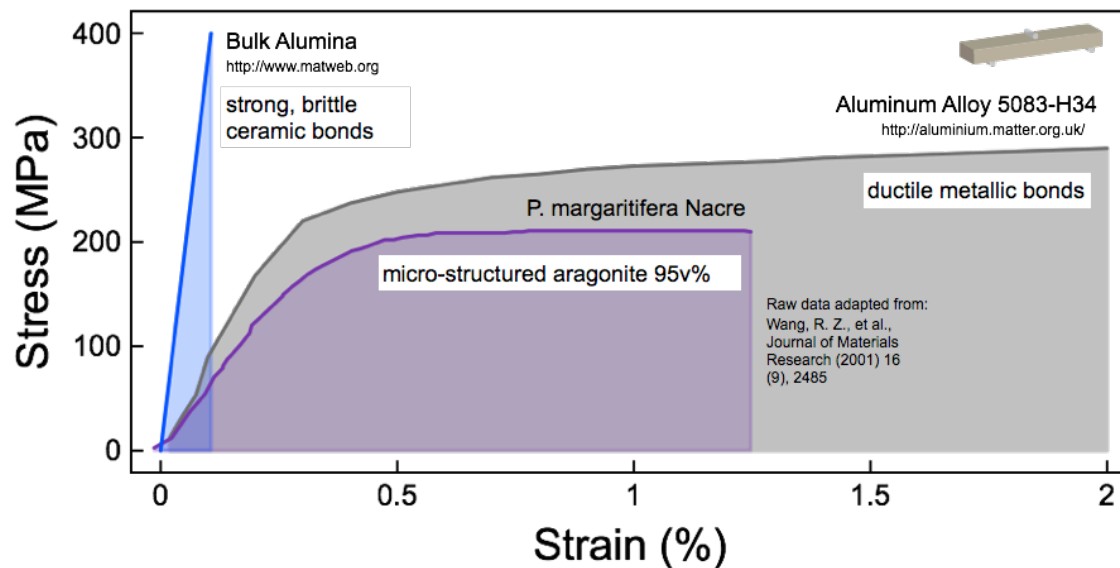
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## Abstract

The rational design of high strength composites with high fracture toughness is a major challenge in materials science because dissipation of fracture energy requires inelastic deformation, and the molecular origins of strength and ductility conflict. However, nature demonstrates that it is possible to create composite materials that are both strong and tough by subdividing strong materials into hierarchical mesostructures, which become pseudo ductile only after the composite sustains damage. Nacre, aka mother of pearl, materializes this latent functionality as a brick and mortar structure or mineral platelets in a biopolymer matrix. When damaged, fractures along weak interfaces between platelets allow the mineral phase to rearrange, forming an energy dissipating process zone. This work aims to translate this structure into a synthetic bulk polymer matrix composite. Using our new technique of Vacuum Assisted Magnetic Alignment (VAMA), it is now possible to quickly and easily produce bulk nacre-like ceramic-reinforced polymer matrix composites several cubic centimeters in volume. We present one approach for optimizing the strength of the platelet-platelet interfaces and show optimized interfaces improve the strength and prevent brittle fracture behavior in this composite.

## 1. Introduction

Polymer matrix composites are important commercial materials for the design and production of lightweight structures, ranging from sporting equipment, to cars, airplanes, and architectural elements. Their specific strength and modulus position them as attractive replacements for much heavier metal alloys; however, they are prone to brittle, catastrophic failure when overloaded, making them unsuitable for safety critical applications. Current high strength composites follow the traditional fiber reinforcement model: a strong polymer matrix, reinforced by even stiffer and stronger long fiber reinforcements, results in a material with maximal strength and stiffness. However, when the long fibers do rupture, it usually initiates catastrophic failure. Fracture tough materials dissipate energy through inelastic deformation, but strength and stiffness are fundamentally in conflict with ductility[1]. Thus, designing a damage-tolerant composite material, with a specific strength and modulus high enough to meet engineering demands, is a challenge requiring a new structural paradigm. One biological composite, Nacre, has long been identified as a promising model[2]. Composed of 95v% aragonite, Nacre has a stiffness and strength in the range of a composite material, but, due to its evolutionarily optimized microstructure, its stress strain curve looks remarkably similar to a metal alloy: it has a defined yield point and followed by a significant window of load-bearing inelastic deformation.



**Figure 1.** Bulk ceramics have low flaw tolerance, limiting their strength and making them prone to brittle failure. Metals yield under stress, becoming ductile rather than brittle. Surprisingly, nacre, a heavily mineralized biological composite, has evolved a functional structure that fails more like a ductile metal alloy than a ceramic.

Mineralization allows animals to form a stiff and strong protective shells at low metabolic cost [3], but minerals are inherently brittle, so evolutionary pressures have resulted in structural solutions to control and limit crack propagation. Nacre subdivides its mineral phase into nano-crystalline micro-platelets, close-packed, brick-and-mortar style, in a biopolymer matrix. This creates paths for controlled failure at platelet-platelet interfaces, to guide propagating cracks. As cracks begin to open, neighboring platelets, shift around the crack tip into a fracture energy dissipating process zone [4]. The toughening capacity of this process zone depends on the species, since platelet size, packing configuration and interfacial morphology all vary [5]. Some species have slightly wavy interlocking platelets, some have central mineral cores between platelets, and some have many small mineral bridges and mineral nano-asperities decorating the platelet surfaces [6, 7]. Whatever the combination of mineral bridges, frictional contacts and matrix interactions at work, it is clear that evolution continues to optimize these interfaces for both strength and cohesion, because these two properties are key to the functionality of this structure. For the bulk material to be stiff and strong, platelet-platelet interfaces must resist inelastic deformation, while still providing a favorable crack path around the mineral platelets; but at the same time no increase in toughness will be observed if platelets cannot transfer enough stress between them to rearrange into a process zone as cracks form. As we produce our own nacre-like composites, developing strategies to create optimized platelet-platelet interfaces is our primary concern.

## 2. Materials and Methods

The process of optimizing nacre-like mineral morphology in a polymer matrix composite has several requirements. As in any optimization process, is key; we are looking to produce a nacre-like mineral scaffold with variable interfacial strength and morphology using as few process variables as possible; scaffolds must be large enough to reliably evaluate by standard mechanical testing; and the optimization-feedback cycle must be fast enough to progress in a reasonable timeframe. Building on a previously established technique, we use external rotating magnetic fields to align magnetized mineral

micro-platelets [8]. In our approach, large volumes of magnetized titania coated alumina microplatelets are packed from aqueous suspension by vacuum filtration in the presence of an external magnetic field. Typical samples (20g mineral in 100mL aqueous suspension, filter size 48 mm in diameter,) take just 25 minutes to go from fluid suspension to cohesive green body ready to be fired. When sintered under pressure, we obtain denser scaffolds with microstructure that resembles biological nacre. During sintering, the titania coating dewets the alumina surface forming predictable surface morphology that trends with temperature.

### 3. Results and Discussion

We evaluated variation of the sintering temperature as a handle for modulating the size and number of mineral contacts, observing a useful processing window. In samples sintered below this range, negligible sintering occurs; above this temperature range fully sintered titania interfaces form at all contact areas between platelets. The mechanical properties of the final composite clearly trend with the extent of interfacial sintering. Similarly to conventional polymer matrix composites, while modulus appears to scale linearly with the density of the mineral reinforcements, the composite strength is governed by more complex mechanisms. As these scaffolds become increasingly sintered, we observe a corresponding increase in composite strength and resistance to crack initiation,  $K_{IC}$ , which plateaus as fully sintered interfaces begin forming. However, composites with fully sintered interfaces are brittle and show no evidence of latent functional microstructure.

### 4. Conclusions

This process is a fast and streamlined approach to make bulk ceramic-reinforced polymer matrix composites with nacre-like latent microstructural functionality. Scaffolds with sub-optimal contact strength between platelets produce composites that yield and deform under small loads. Too-strong interfaces between platelets result in purely elastic composites, which fail catastrophically when they reach their ultimate strength. However, by tuning the mineral morphology of the platelet-platelet interfaces, we are able to optimize the contact strength between platelets, creating a composite with improved strength and while still avoiding brittle fracture behavior.

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### References

1. Ritchie, R.O., *The conflicts between strength and toughness*. Nature Materials, 2011. **10**(11): p. 817-822.
2. Jackson, A.P., J.F.V. Vincent, and R.M. Turner, *The Mechanical Design of Nacre*. Proceedings of the Royal Society Series B-Biological Sciences, 1988. **234**(1277): p. 415-+.
3. Palmer, A.R., *Calcification in Marine Mollusks - How Costly Is It*. Proceedings of the National Academy of Sciences of the United States of America, 1992. **89**(4): p. 1379-1382.

4. Wang, R.Z., et al., *Deformation mechanisms in nacre*. Journal of Materials Research, 2001. **16**(9): p. 2485-2493.
5. Dastjerdi, A.K., R. Rabiei, and F. Barthelat, *The weak interfaces within tough natural composites: Experiments on three types of nacre*. Journal of the Mechanical Behavior of Biomedical Materials, 2013. **19**: p. 50-60.
6. Lin, A. and M.A. Meyers, *Growth and structure in abalone shell*. Materials Science and Engineering a-Structural Materials Properties Microstructure and Processing, 2005. **390**(1-2): p. 27-41.
7. Lopez, M.I., P.E.M. Martinez, and M.A. Meyers, *Organic interlamellar layers, mesolayers and mineral nanobridges: Contribution to strength in abalone (Haliotis rufescence) nacre*. Acta Biomaterialia, 2014. **10**(5): p. 2056-2064.
8. Erb, R.M., et al., *Composites Reinforced in Three Dimensions by Using Low Magnetic Fields*. Science, 2012. **335**(6065): p. 199-204.