ANISOTROPIC NANOSTRUCTURE INSPIRED BY NATURE FOR ENERGY ABOSRBING COMPOSITE INTERFACES

Francois De Luca[1], Alexander Bismarck[1,2] and Milo S. P. Shaffer[3]

[1]Imperial College London, Chemical Engineering department, South Kensington campus SW7 2AZ London, United Kingdom
Email: f.de-luca13@imperial.ac.uk, Web Page: http://www.imperial.ac.uk/polymer-and-composite-engineering/people/
[2]Institute of Materials Chemistry and Research, University of Vienna, A-1090 Vienna, Austria
Email: alexander.bismarck@univie.ac.at, Web Page : http://www.imperial.ac.uk/people/a.bismarck
[3]Imperial College London, Chemistry department, South Kensington campus SW7 2AZ London, United Kingdom
Email: m.shaffer @imperial.ac.uk, Web Page: http://www.imperial.ac.uk/people/m.shaffer

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Abstract

The “brick-and-mortar” structure of natural nacre is well known for its combination of high stiffness, strength and toughness thanks to well organised hard inclusions, experiencing pull-out within a soft organic matrix rather than fracture upon loading. Mimicking the structure of nacre while maintaining the same phase proportions and aspect ratio, but at a smaller length scale, opens up the possibility to create composite materials with high performance and large energy absorption properties through interface deformation. Therefore, Layered Double Hydroxide (LDH) nanoplatelets and poly(sodium 4-styrene sulfonate) (PSS) polylelectrolyte were assembled together with a high degree of alignment using Layer-by-Layer (LbL) assembly, resulting in a dense and well organized nanostructure similar to that of nacre. The mechanical properties of the nacre-nanomimetics were comparable to those of natural nacre while the plastic deformation was found amplified. The amplification of the proportion of plastic deformation can be explained by an increase in the volume of platelet interfaces per unit volume at the nanometer length scale. The known toughening mechanisms of nacre, such as platelet sliding and interlocking as well as crack deflection, were also found to occur in the reduced length scale embodiment.

1. Introduction

The hybrid “brick-and-mortar” structure of nacre is made of 95 % of micrometre-wide brittle inorganic aragonite ($CaCO_3$), yet exhibits exceptional mechanical properties, including high toughness (≈ 1.24 kJ.m^{-2}), strength (≈ 140 MPa) and stiffness (E ≈ 60GPa)[1,2]. When a crack propagates within the structure of nacre, it gets deflected at the platelet interface forcing it to propagate through a tortuous pathway. In addition, a process zone ahead of the crack, in which a large number of platelet sliding occurs, leads to further resistance to crack propagation. These platelets eventually interlock[3,4] through different mechanisms[5] such as platelet roughness, negative poisson’s ratio, waviness, etc. The sliding/interlocking of the platelets provides significant strain hardening and plastic deformation. The plastic index of nacre, based on the ratio of plastic deformation and elastic recovery, was measured to be roughly 0.78[6]. One can predict an amplification of plasticity (energy absorption) by increasing the platelet interface volume by unit volume within this process zone, namely, by a reduction of the inclusion thickness. Therefore, reproducing the “brick-and-mortar” structure of natural nacre, with the

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characteristic high inorganic content and aspect ratios, but with the characteristic lengthscales scaled down by one to two orders of magnitude, sheds light on fundamental scaling behaviour and provides new opportunities for high performance, energy absorbing nanocomposites[7].

LbL assembly of PSS polyelectrolyte and well-defined Mg_2-Al-CO_3 layered double hydroxide (LDH) platelets produced a high inorganic content (~90 wt%) microstructure, similar to natural nacre. Platelet thicknesses in the range 10-20 nm means that a simple polymer organic ‘mortar’ can be around ten times thinner, maintaining the correct geometric ratios. Good alignment of the platelet within a micrometer thick coating was measured. The reduction of scale enables the (self-) assembly of a higher quality nanostructure than conventional mimics, leading to improved mechanical properties, similar to those of natural nacre, and allowing substantial plastic deformation. A plastic index of about 0.95 was measured.

2. Results and discussion

Mg_2-Al-CO_3-LDH nanoplatelets were synthesized via a coprecipitation method followed by hydrothermal treatment[8]. The conditions of the hydrothermal (100°C for 72h) treatment were tuned to achieve hexagonal platelets with a width of about 130 nm, an aspect ratio of 10 and a narrow width distribution. The synthesized LDH platelets formed a stable suspension in water thanks to their cationically charged surface. Top surface and cross-section TEM images of the anisotropic LDH nanoplatelets show a layered structure (Fig. 1-B). An anionic polyelectrolyte, namely PSS, was used to alternately assemble a $(LDH/PSS)_n$ nanostructure via a LbL method based on electrostatic attractions. Indeed, susbsequent dipping of a charged substrate into LDH suspension and PSS solution with intermediate water rinsing steps to wash off the excess of particles, enabled the deposition of oppositely charged monolayers (Fig.1-A).

Homogenous coatings were deposited on glass slides as evidenced by the consistent visible reflection (Fig.1-C). Furthermore, a SEM cross-section image of micrometer thick coating shows consistent thickness of the coating along the slide (Fig.1-D). On the other hand, SEM top-surface images present a dense nanostructure with an evenly deposited final layer of aligned LDH platelets (Fig.1-D). XRD investigation of the $(LDH/PSS)_n$ coatings revealed a platelet misalignment of about ± 8°.

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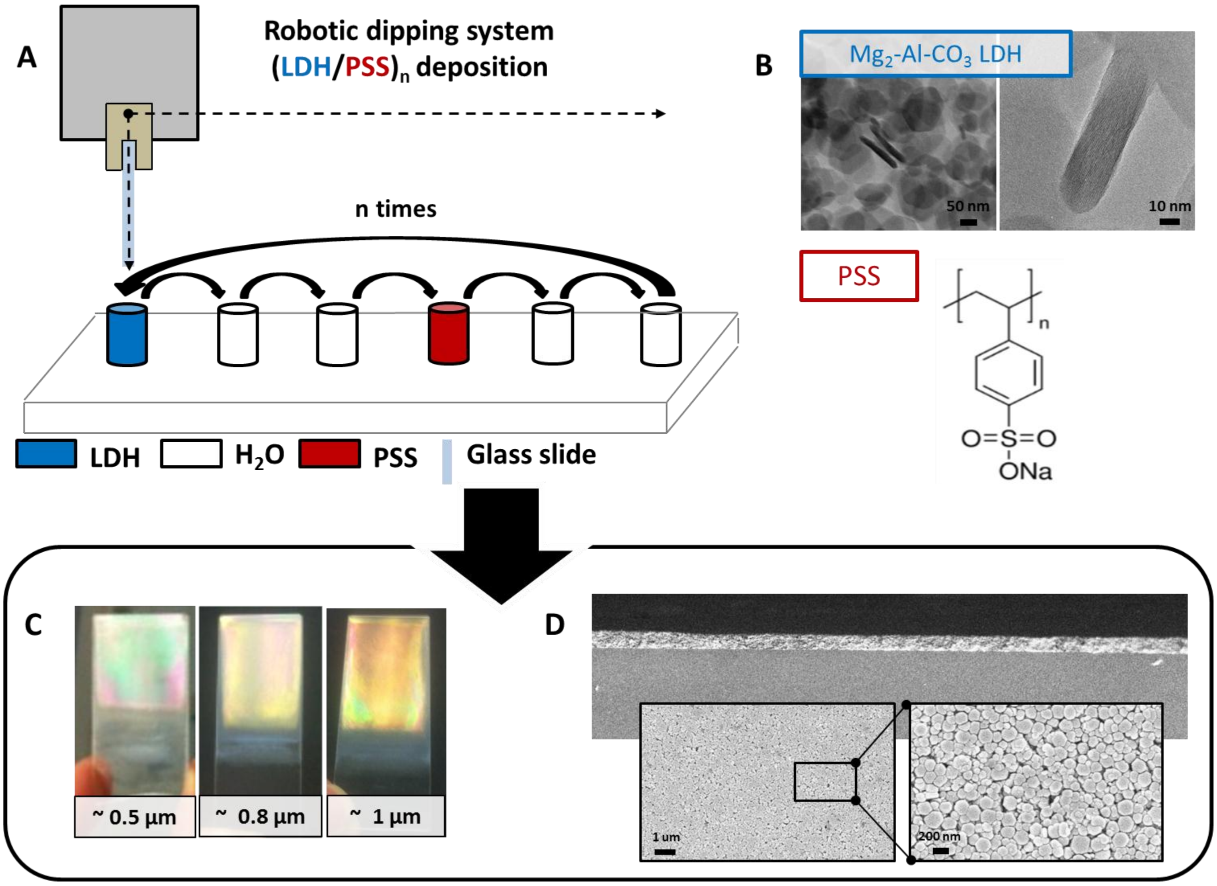

Figure 1. LbL assembly of nacre-nanomimetic coating. Schematic of the $(LDH/PSS)_n$ LbL assembly using a robotic dipping system (A). TEM images and chemical representation of LDH nanoplatelets and PSS polyelectrolyte, respectively (B). Images of coated glass slides with varying coating thickness (C) and SEM images of both coating cross-section and as top surface (D).

The mechanical properties of the deposited nacre-nanomimetic coatings onto glass slides were measured by nanoindentation using the Oliver and Pharr method[9]. The maximum load was applied to the coating within 30 seconds and held for another 30 seconds in order to let the material creep. Similarly, the load was fully removed within 30 seconds. An elastic modulus and hardness of 65.79 and 2.34 GPa, respectively, were measured, similar to those of natural nacre.

Table 1. Nacre-nanomimetic structural and mechanical properties

	Platelet misalignment (°)	*Platelet content* (wt. %)	*E (GPa)*	*H (GPa)*	*Plastic index*
$(LDH/PSS)_n$	± 8	88.4	65.79	2.34	0.95

The amount of plastic deformation in the nanostructure was also quantified by using a plastic index via nanoindentation, the ratio of the plastic deformation area of the load-displacement curve over the overall area under the curve, which includes both the plastic deformation and elastic recovery areas. A 4 µm-thick coating deposited on a glass slide was indented with a cube-corner tip at varying

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depth. Therefore, a stabilized degree of plastic index of about 0.95 was measured, higher than that of natural nacre (0.78).

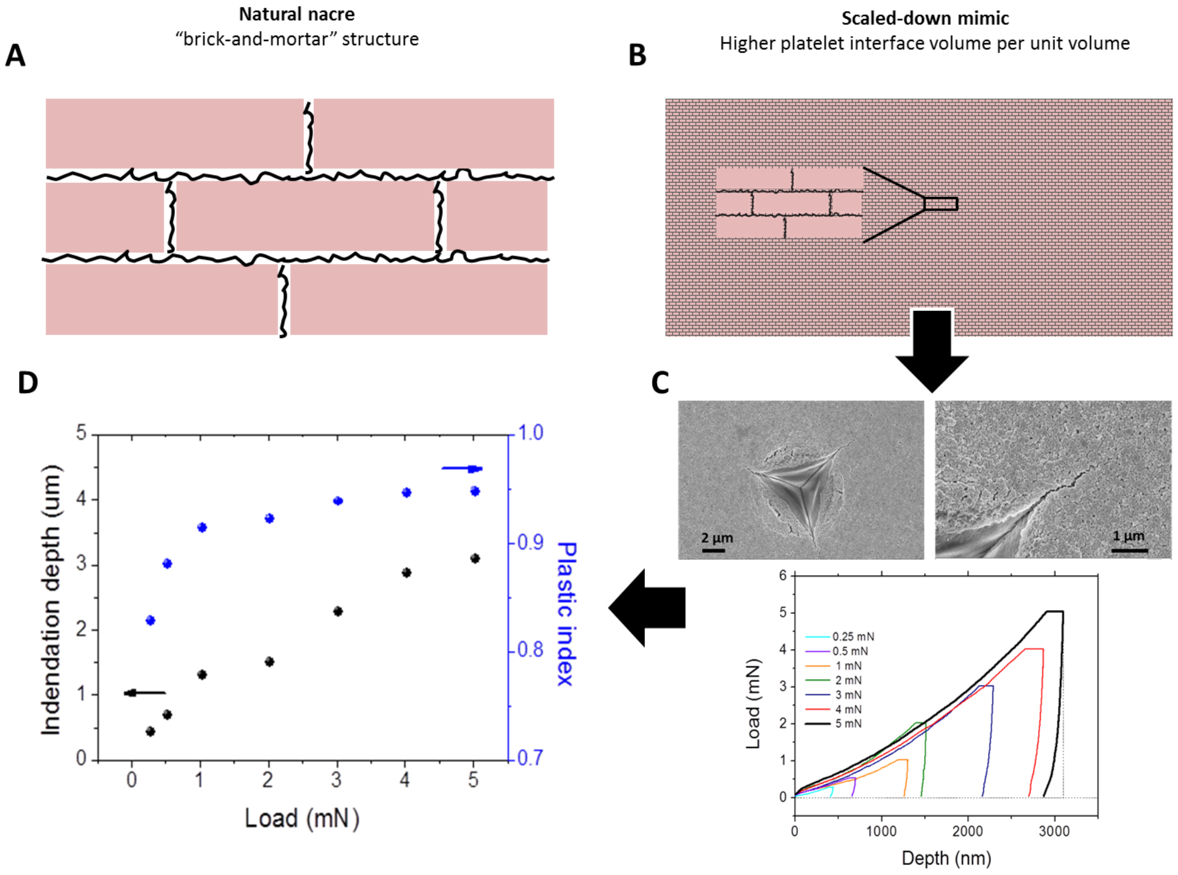

Figure 2. Amplification of interface energy absorption at the nanometre length scale. Schematic of the structure of natural nacre and nanomimetic (A and B. respectively). SEM images of indents carried out in a 4 µm-thick nacre-nanomimetic coating and nanoindentation load-depth curves (C). Plastic index values of nacre-nanomimetic nanostructure measured from nanoindenation (D).

At relatively high load, the formation of pile-ups in the vicinity of the indent occurs. These pile-ups are formed as a result of progressively arrested waves of materials in shear, signature of an in-plane platelet sliding followed by progressive friction and eventual interlocking, leading to strain hardening. The strain hardening behavior of the material in shear can actually be evidenced by the curvature of the load-displacement curve, especially at high loads. Furthermore, the crack deflection phenomenon occurring at the platelet interface in natural nacre was also found to take place in the mimics. Indeed, SEM images of the edge of the indents reveal the presence of cracks triggered by the indentation load with multiple deflections at the LDH nanoplatelet interface.

3. Conclusions

Nacre-nanomimetic coatings were assembled via LbL assembly onto glass fibres using LDH nanoplatelets as inorganic reinforcements and PSS polyelectrolyte as an organic soft matrix. The mimics made at the nanometer length scale showed good platelet alignment and packing into PSS with a platelet content as high as 88.4 wt.% when suitable platelets were used (130 nm wide with an aspect ratio of 10). The phase proportions and geometry of the "brick-and-mortar" structure of natural nacre were maintained at the nanometer length scale. The classic deformation mechanisms occurring in

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natural nacre were also observed in the nanomimetics, such as platelet sliding and interlocking as well as crack deflection. The mechanical properties of the coatings were investigated by nanoindenation, a hardness and elastic modulus similar to those of natural nacre were measured. On the other hand, a larger proportion of plastic deformation was measured in the mimics as compared to natural nacre as a result of a higher volume of interface per unit volume in the nanostructure, leading to more platelet sliding/interlocking sites and, therefore, more energy dissipated throughout the materials. The well-arranged bio-inspired hybrid nanocomposites open-up the possibility to manufacture lightweight materials with excellent mechanical performance, such as the combination of high toughness, strength and stiffness along with unprecedented robustness.

Acknowledgments

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