# THE EFFECT OF NACRE-INSPIRED COATING ON THE COMPRESSION BEHAVIOUR OF CARBON FIBRE COMPOSITE

Rupam Gogoi[1], David B. Anthony[2], Stephen J. Eichhorn[3] and Milo S.P. Shaffer[4]

[1] Department of Chemistry, Imperial College London, London, United Kingdom,
rgogoi@imperial.ac.uk, https://www.imperial.ac.uk/people/r.gogoi

[2] Department of Chemistry, Imperial College London, London, United Kingdom,
d.anthony08@imperial.ac.uk, https://www.imperial.ac.uk/people/d.anthony08

[3] Bristol Composites Institute, University of Bristol, Bristol, United Kingdom,
s.j.eichhorn@bristol.ac.uk, https://research-information.bris.ac.uk/en/persons/steve-eichhorn

[4] Department of Materials and Chemistry, Imperial College London, London, United Kingdom,
m.shaffer@imperial.ac.uk, https://www.imperial.ac.uk/people/m.shaffer

**Keywords:** Coating, Layer-by-Layer deposition, Fibre-matrix interphase

## ABSTRACT

The failure mechanism of unidirectional fibre-reinforced polymers in compression is complex and relates to a progression of failure from fibre micro buckling upwards across multiple coupled length scales. The initial fibre instability relates to the shear properties of the matrix and the alignment (or waviness) of the fibre. The initiation may also be affected by local composition/fibre volume fractions, matrix defects (for instance voids), or geometric features of the specimen/component. The use of surface-modified carbon fibres could improve the longitudinal compressive performance of composites by suppressing or delaying the formation of kink bands. A nanostructured hierarchical coating inspired by the brick-and-mortar structure of natural nacre was deposited around each individual fibre in a tow. The nanostructured coating contains layered-double-hydroxide (LDH) platelets which are attached to the carbon fibre surface using a layer-by-layer deposition technique. LDH platelets were selected for their tuneable geometry and high surface charge density. Successful preparation of LDH platelets with an aspect ratio of 8 was confirmed by X-ray diffraction and transmission electron microscopy. The quality of the conformal LDH monolayer coating was assessed by scanning electron microscopy and preliminary results show the formation of a well-ordered LDH multi-layer coating. These coated fibre tows will be converted to unidirectional epoxy-matrix composites and tested in compression in future studies.

## 1 INTRODUCTION

Natural materials are made using relatively weak constituents but display remarkable mechanical properties as a result of evolutionary development and complex hierarchical arrangement of their constituents. Hierarchical composite structures, like those observed in natural nacre, have shown toughening mechanisms that are attributed to their brick-and-mortar structure [1]. This brick-and-mortar structure consists of an inorganic and organic framework in a 95:5 ratio of brittle aragonite ($CaCO_3$) platelets to chitin (a biopolymer), respectively. The architecture and the combination of inorganic platelet and a soft organic constituent produce excellent mechanical properties, including high stiffness (~60 GPa), strength (~140 MPa), and toughness (~1.24 kJ/m$^2$) [1]. When loaded the aragonite platelets slide within the organic framework and eventually interlock via a range of different mechanisms such as; the stretching of the biopolymer, aragonite bridging, or asperities contact, which leads to strain hardening [2], and a progressive failure of the material. In contrast, synthetic materials like structural carbon fibre-reinforced polymers (CFRPs) suffer a sudden catastrophic failure after the formation of a critical cluster of fibre breaks under tension [1]. The fibre-matrix interphase in fibre-reinforced polymers (FRPs) plays a crucial role in load transfer. Introducing additional interfacial

toughening mechanisms can both strengthen the interface and absorb more energy prior to failure, hence delaying the ultimate failure. The most investigated approaches to achieve high strength and toughness in composites involve polymer interlayers and nanoparticle coatings as well as more structure nanostructured interphases [3].

In a previous study [3, 4], a nanostructured brick-and-mortar interphase was developed as a surface modification for CFs, inspired by the natural nacre architecture (Figure 1). Interestingly a pseudo-ductile tensile response with a 30% increase in strain-to-failure was observed for small UD epoxy composites reinforced with the nano-nacre coated CFs, relative to a conventionally sized control. Due to the improved interfacial properties, the tensile strength of the composite also increased by 15% (Figure 2). The hierarchical nacre-like coating was developed using layer-by-layer (LbL) deposition of layered-double-hydroxide (LDH) platelets. In natural nacre, the platelets' size is approximately 5 µm to 8 µm with an organic layer thickness of around 20 nm to 30 nm. However, for LbL deposition around a fibre, the architecture was scaled down to obtain conformal coating. Rational design calculations maintained the inorganic-organic ratio and aspect ratio of the natural nacre architecture. The LbL process is self-limiting and forms a well-ordered structure with a high packing fraction. A multilayer coating of LDH platelets on a glass substrate displayed an elastic modulus on the order of ~65 GPa [4] that was replicated on the coated fibres. Conveniently, the LbL assembly can be performed on full fibre tows (12k), allowing the coating to be formed in parallel on a large effective surface area; this approach usefully accelerates the usually slow LbL process.

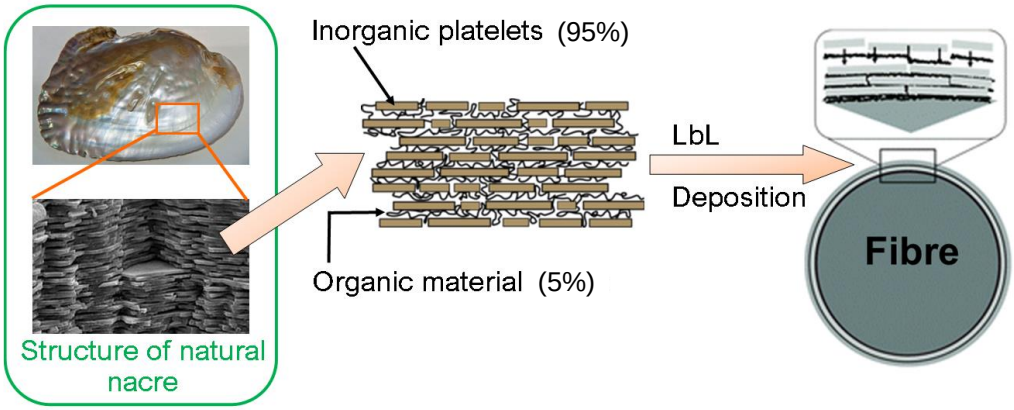


Figure 1: Schematic representations of the nacre-inspired coating. Left: Natural nacre and its internal structure. Centre: Structure of artificial nacre structure [3] (composed of inorganic nanoplatelets which are bound together by polymeric interlayers). Right: Fibre coated with multiple layers of inorganic nanoplatelets using LbL deposition which resembles the internal structure of natural nacre.

CFRPs are efficient under tensile loading, yet there is a concerning design limitation in such material which arises from its poor compressive behaviour [5, 6]. The compressive strength of CFRP is almost half that of tensile strength. High performance CF composites usually fail due to kink band formation under an applied longitudinal compressive load. The formation of such a kink band is primarily governed by the shear of the matrix or fibre-matrix interface at regions of fibre waviness or misalignment. Out of many possible alternatives, improving the polymer matrix/composite's shear modulus whilst maintaining a strong fibre-matrix interphase should in theory contribute to enhancing the bulk compressive performance of composites [5, 6]. However, it is important to maintain interfacial toughness to avoid debonding, splitting, and delamination. Taking motivation from the previous work [4], the current study aims to explore the compressive performance of unidirectional CFRP produced using CFs having a nacre-inspired coating. The nacre-inspired coating seems promising for the compression study as it will toughen the interphase and provide local stiffness

around the fibre. The objective is to potentially suppress, or delay, the kink band formation in the composite under compression and thereby achieve a higher strain-to-failure with improved compressive strength. The preliminary results on the scaled-up production and characterization of LDH platelets along with the LbL deposition of the platelets are reported here.

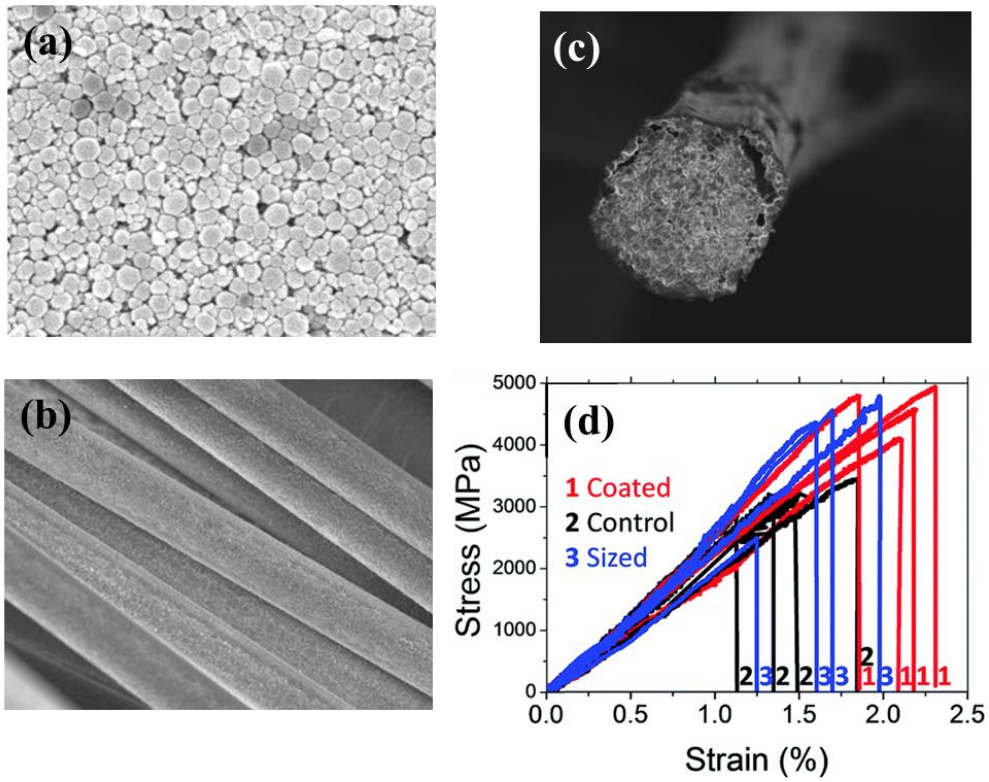


Figure 2: LDH multilayer coating on (a) a glass slide and (b) plasma and $KMnO_4$ oxidized unsized AS4 CFs. (c) bundle composite made from ~300 LDH multilayer coated CFs and (d) stress-strain curve of bundle composites in tension. Note: Coated (1, red) denotes the bundle composites prepared using LDH coated CFs whereas Control (2, black) bundle composite samples were prepared using plasma and $KMnO_4$ oxidized unsized AS4 CFs, and the Sized (3, blue) bundle composite samples were prepared using the commercially available sized AS4 CFs. Adapted from [3].

## 2 MATERIALS AND METHODS

Poly(sodium 4-styrenesulfonate) solution (PSS, $M_w$ 70k, 30 wt.% in $H_2O$), poly(diallyl dimethyl ammonium) solution (PDDA, $M_w$ = 100k–200 k, 20 wt.% in $H_2O$), $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, NaOH, and $Na_2CO_3$ were purchased from Sigma-Aldrich and used as-received. Unsized as-received CF AS4 (HP-5000-CP), 12k tow was procured from Hexcel Corporation.

The LDH nanoplatelets were prepared by coprecipitating metal salts and hydrothermal treatment [4]. The metal salt solution was prepared using 2 mM of $Mg(NO_3)_2{\cdot}6H_2O$ and 1 mM of $Al(NO_3)_3{\cdot}9H_2O$ and the base solution contained 6 mM NaOH and 0.6 mM $Na_2CO_3$. A 10 ml metal salt solution was added to a 40 ml base solution under vigorous stirring. The mixture was subjected to further stirring for 20 min at 750 rpm. The mixture was then centrifuged at 15000 rpm for 15 min to retrieve the LDH slurry. Subsequently, the slurry was washed twice by re-dispersion in deionized water followed by bath sonication (75 W) for 5 min and finally by centrifugation at 15000 rpm for 15 min. After washing, the slurry was dispersed in 25 ml deionized water (0.4 wt.%) via bath sonication and placed in an autoclave for hydrothermal treatment at 100 °C for 72 h. The unsized AS4 CFs were

surface treated prior to the LbL process using plasma oxidation to enhance the surface reactivity for improved adhesion.

The LbL deposition is based on electrostatic interactions, and it is possible to obtain a well-ordered structure due to its self-limiting nature. Figure 3 depicts the LbL process on CFs using PDDA and PSS as a buffer layer and intermediate layer, respectively. The concentrations of the PDDA solution and PSS solution were maintained at 0.1 wt.%, the LDH solution was kept constant at 0.3 wt.%. As the process is sensitive to pH changes, all the solutions, including the washing steps ($H_2O$), were maintained around pH ~9 using 0.1 M NaOH. A bundle of unsized AS4 CFs containing about 200 to 300 fibre count was used for the LbL deposition. For a multilayer coating of PSS/LDH the LbL deposition was repeated as denoted by *N* in Figure 3.

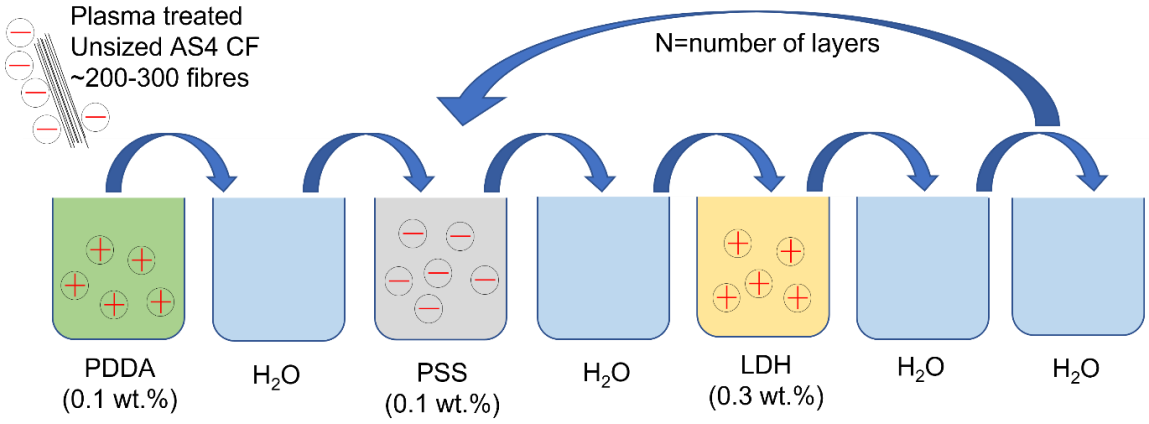


Figure 3: Schematic of the LbL dipping process for the deposition of LDH particles. Aqueous solutions of PDDA, PSS and water maintained at a pH ~10. PDDA acts as the buffer layer whereas PSS acts as the organic interlayer, N denotes the number of layers of PSS/LDH.

The zeta potential and particle size of the LDH solution were determined using a particle analyser, Zetasizer Ultra (Malvern Panalytical), while the morphology of the platelets was analysed using a transmission electron microscopy (TEM), JEM 2100Plus (JEOL Ltd.). To confirm the structure and thickness of the LDH platelets X-ray diffraction (XRD) analysis was employed using a Bruker D2 Phaser. Scanning electron microscopy (SEM) analysis of the LDH-coated CF, Gemini 1 Zeiss Sigma 300 confirmed macroscopic features and uniformity on samples.

## 3 RESULTS AND DISCUSSIONS

The synthesised 2D platelet-like LDH structure is evident through TEM analysis, Figure 4 (a) and (b). LDH were stable (after days of preparation) in aqueous pH 9.6 suspensions with a zeta potential of +30 mV with an average particle size of ~122 nm, distributions shown in Figure 5. XRD analysis confirmed the formation of phase pure $Mg_2$-Al-$CO_3$ LDH platelets. A diffraction peak at $2\theta = 11.48°$ is characteristic of the (003) crystallographic plane parallel to the surface of the anisotropic LDH platelets [4]. The thickness of the platelets was evaluated using the Scherrer equation (1) [7],

$$t = (k.\lambda)/(\beta.cos\theta), \quad (1)$$

where $t$ is the mean thickness of LDH platelets, $k$ is a dimensionless shape factor (0.89), $\lambda$ is the X-ray beam wavelength (1.5418 Å), $\beta$ is the full width at half maximum (FWHM) of the diffraction peak, and $\theta$ is the Bragg angle. Using equation (1) the average platelet thickness obtained was ~15 nm. Thus, the aspect ratio of the prepared LDH platelets is ~8, Figure 6.

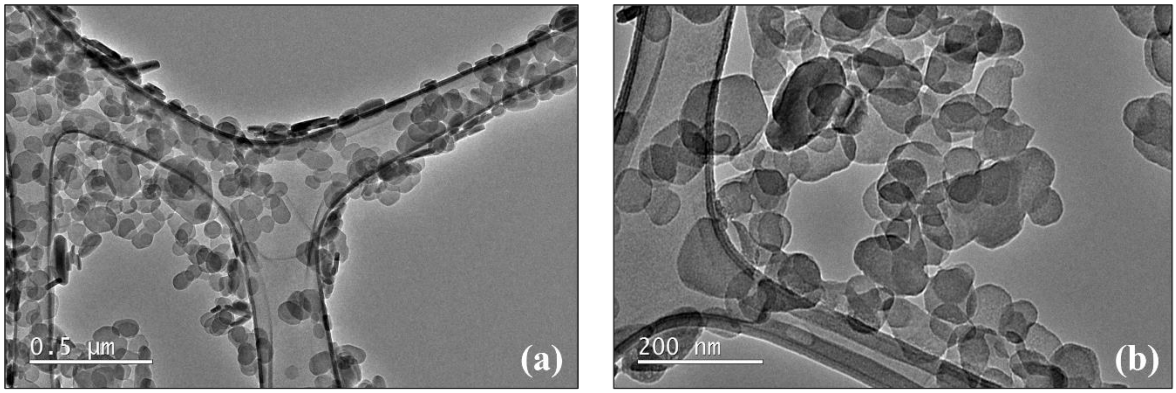


Figure 4: TEM images of LDH at low and high magnification (a) and (b), respectively.

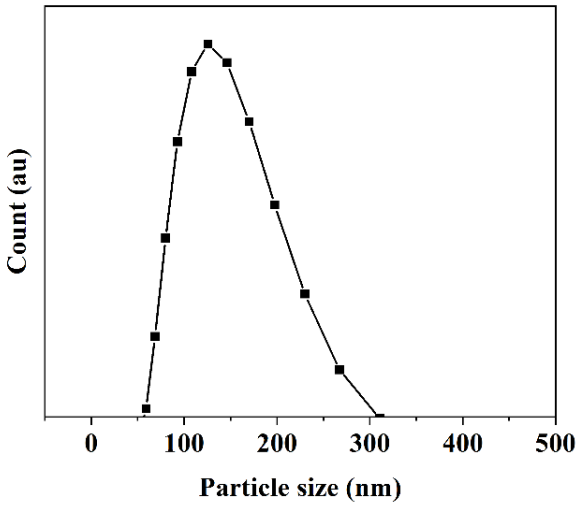


Figure 5: The particle size distribution of LDH platelets.

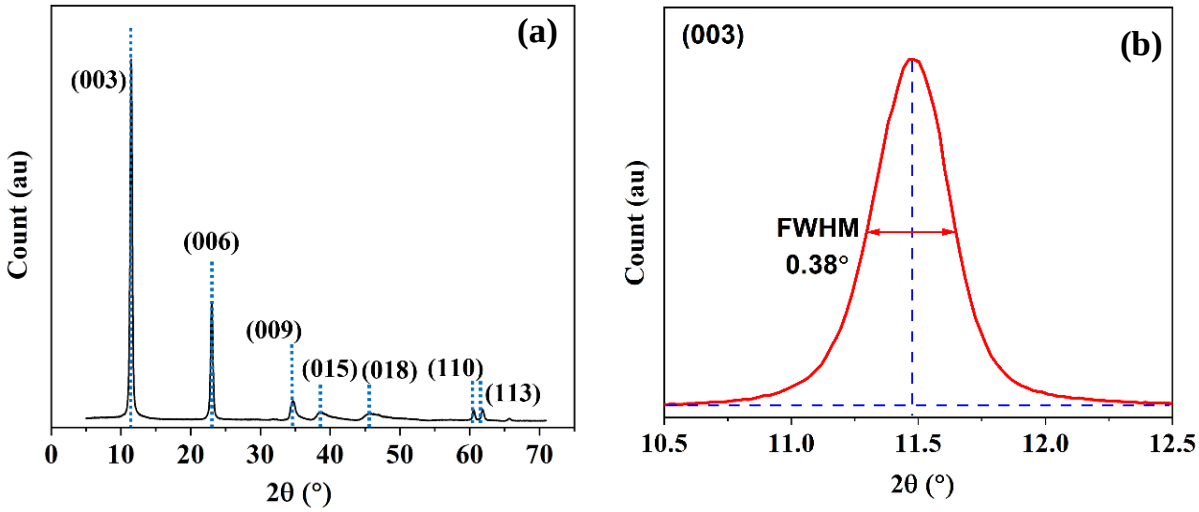


Figure 6: XRD diffractogram (a) and (003) XRD diffraction peak of LDH platelets.

A homogeneous coating of LDH is observed through SEM analysis, Figure 7 (a). It is important to have an even coating when applying multiple layers of successive PSS/LDH layers to ensure that the nacre-like architecture in the coating is preserved. Previous studies have shown that nacre-like coatings of up to N<25 are uniform in thickness from the fibre surface are possible [4].

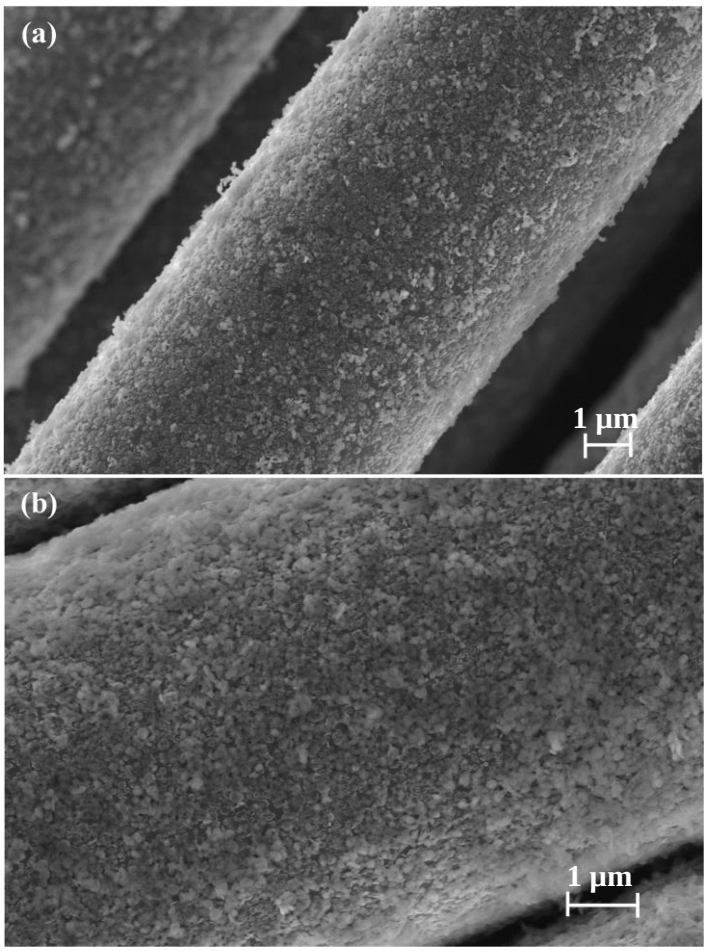


Figure 7: SEM images of unsized CF coated with a monolayer (a) and a bilayer (b) of LDH platelets.

## 4 CONCLUSIONS AND FUTURE WORK

Stable layered double hydroxide (LDH) platelets in an aqueous suspension were successfully produced and characterised in this study. The size of the LDH platelets were suitable for a conformal coating on the CFs with an aspect ratio close to 8. The morphological analysis revealed a close-packed uniform mono- and bi-layer nacre-like coating of LDH particles on the CF's surface, which can be used to form well-ordered multilayer nacre-like architectures. The next step in this study is to prepare multilayer LDH coating on CFs by repeating this LbL deposition for N>10 on suitably long sections of fibres. Subsequently, these modified fibres can be consolidated into a unidirectional tow composite and tested in compression. New test methods are being developed within the Next Generation Fibre-Reinforced Composites project [8] to evaluate composites at the tow level, which will be suitable for samples that consist of nanostructured interphase-modified fibres shown here.

## ACKNOWLEDGEMENTS

The authors kindly acknowledge the funding for this research provided by the UK Engineering and Physical Sciences Research Council (EPSRC) programme Grant EP/T011653/1, Next Generation

Fibre-Reinforced Composites: a Full-Scale Redesign for Compression in a collaboration between the University of Bristol and Imperial College London.

## REFERENCES

[1] F. De Luca, R. Menzel, J.J. Blaker, J. Birkbeck, A. Bismarck and M.S.P. Shaffer, Nacre-nanomimetics: Strong, Stiff, and Plastic, *ACS Applied Materials & Interfaces*, **7**(48), 2015, pp. 26783–26791 (doi: 10.1021/acsami.5b08838).

[2] H.D. Espinosa, J.E. Rim, F. Barthelat and M.J. Buehler, Merger of structure and material in nacre and bone–Perspectives on de novo biomimetic materials, *Progress in Materials Science*, **54**(8), 2009, pp. 1059-1100 (doi: 10.1016/j.pmatsci.2009.05.001).

[3] F. De Luca, *Fibre-reinforced composites with nacre-inspired interphase: a route towards high performance toughened hierarchical composites*, PhD Thesis, Imperial College London, 2017, pp. 41-50 (doi: 10.25560/49423).

[4] F. De Luca, A.J. Clancy, N.R. Carrero, D.B. Anthony, H.G. De Luca, M.S.P. Shaffer and A. Bismarck, Increasing carbon fiber composite strength with a nanostructured "brick-and-mortar" interphase, *Materials Horizons*, **5**(4), 2018, pp. 668–674 (doi: 10.1039/c7mh00917h).

[5] A. Makeev, S. Ghaffari and G. Seon, Improving compressive strength of high modulus carbon-fiber reinforced polymeric composites through fiber hybridization, *International Journal of Engineering Science*, **142**, 2019, pp. 145–157 (doi: 10.1016/j.ijengsci.2019.06.004).

[6] S. Ghaffari, A. Makeev, G. Seon, D.P. Cole, D.J. Magagnosc and S. Bhowmick, Understanding compressive strength improvement of high modulus carbon-fiber reinforced polymeric composites through fiber-matrix interface characterization, *Materials & Design*, **193**, 2020, pp. 108798 (doi: 10.1016/j.matdes.2020.108798).

[7] V. Drits, J. Środoń, and D.D. Eberl, XRD measurement of mean crystallite thickness of illite and illite/smectite: Reappraisal of the Kubler index and the Scherrer equation, *Clays Clay Miner*, **45**, 1997, pp. 461–475 (doi: 10.1346/ccmn.1997.0450315/metrics).

[8] G. Quino, P. Robinson and R.S. Trask, Design of a bending experiment for mechanical characterisation of pultruded rods under compression, *Proceedings of the 20th European Conference on Composite Materials (Eds. A.P. Vassilopoulos, V. Michaud) Lausanne, Switzerland, June 26-30, 2022*, Vol 3-Characterization, pp. 167–172 (doi: 10.5075/epfl-298799_978-2-9701614-0-0).