NANOSTRUCTURED “BRICK-AND-MORTAR” INTERPHASE INSPIRED BY NACRE TO IMPROVE CARBON FIBRE COMPOSITE PERFORMANCE

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Keywords: “Brick-and-Mortar” nanostructure, composite interphase, interfacial properties, mechanical properties, energy absorption

ABSTRACT

Carbon fibre-reinforced composites are well-known for their high mechanical performance and low weight, but suffer from sudden failure caused by the correlation of fibre breaks leading to local stress concentration. Mechanisms for energy dissipation at the fibre/matrix interface while maintaining good load transfer represents a route to improve the tensile properties of the composites. Here, we developed a conformal “brick-and-mortar” nanostructure inspired by the architecture of nacre around the surface of carbon fibres, which provides mechanisms for energy absorption and plasticity at fibre breaks. A Layer-by-Layer assembly method enabled the deposition of the nanostructured coating onto multiple fibres simultaneously, allowing for the manufacture of unidirectional bundle composites. Absolute improvements in tensile strength and strain-to-failure of the composites containing the nanostructured interphase were measured.

1 INTRODUCTION

During progressive loading of unidirectional fibre-reinforced polymer composites in tension, the fibres fragment throughout the whole material at locations determined by their stochastic strength distribution. At a fibre break, the load that was previously carried by the fibre is transferred to the neighbouring fibres through the matrix, which locally increases the stress concentration in these neighbouring fibres. The load is therefore redistributed in the material as long as the stress concentration does not locally reach a critical point. Further increase in the tensile load leads to more fibre breaks in the composite, eventually causing a cluster of fibre breaks to form [1-3], which is associated with a critical stress concentration that cannot be carried by the remaining fibres. The critical stress concentration leads to a sudden and catastrophic failure of the composite, limiting its mechanical performance.

Engineering the interphase of composites has been widely investigated over the past few decades [4-6]. The interphase of composite material has been receiving much attention as the onset of mechanical damage often occurs in this region. Theoretically, simultaneous improvement in composite
energy absorption and strength could be achieved by combining toughening and adhesion enhancement at the fibre/matrix interface [7], but still remains a challenge. Usually, while a strong interphase leads to high composite strength and stiffness with brittle failure and low energy absorption, a weak interphase enables multiple delamination and high energy absorption at the cost of a reduction in the mechanical properties of the composite [5]. There is therefore a need to tailor the interphase and balance these two motivations. In order to increase both strength and toughness of composites, computational work support the development of layered anisotropic interphase, promoting the use of a highly anisotropic [8]. Graphene oxide nanosheets have gained a lot of interest over the past few years for their high mechanical performance and anisotropy, providing effective crack deflection and stress redistribution at the interface of composite materials [9]. However, the window of dimensions and geometry of suitable nanostructured interphase is narrow for typical reinforcing-fibres. The use of such nanosheets cannot lead to conformal layered nanostructure around the fibres. Ideally, a conformal layered interphase would allow for crack deflection along multiple platelet interfaces, stable fibre debonding through platelet sliding/interlocking of the platelet (limited anisotropy to trigger pull-out) and excellent stress transfer. The latter mechanisms can significantly increase the amount of energy dissipated while maintaining effective interface, potentially hindering the correlation of fibre breaks and, therefore, the formation of critical clusters.

The classic “brick-and-mortar” structure of natural nacre and its toughening mechanisms of natural nacre, such as crack deflection at the platelet interface [10] and platelet sliding/interlocking via pull-out [11], providing energy absorption and strain hardening in shear, respectively, have been reproduced at the nanometre length scale and transferred to the fibre/matrix interfaces of carbon fibre composites. The concept relies on the ability of the interphase to absorb the energy arising from a fibre break through crack deflection at the platelet interface and along the length of the fibre, followed by stable fibre debonding/slippage via strain hardening in shear. The combination of the latter mechanisms can potentially avoid the correlation of fragmented fibre breaks in a composite and delay the formation of critical clusters as well as provide plastic deformation in the composite. Typical nacre platelets, both in natural and artificial nacre, are in the order of few micrometres long [12], which cannot form a coherent layered coating around fibres with diameters of the same length scale. The working assumption, based on existing models, is that nacre-like properties can be replicated independently of absolute scale, as long as the aspect ratio of the reinforcing platelets is maintained (at about 10) and the relative thickness of the soft organic layers remains about 5 to 10% of the thickness of the platelet [13-14]. Therefore, assuming a polymer layer of around 1-2 nm, ideal platelet dimensions should be approximately 10 to 20 nm thick and about 100-200 nm wide. Rigid hexagonal double layered hydroxide (LDH) platelets and soft PSS polyelectrolyte was selected to reproduce the classic “brick-and-mortar” structure of nacre at the circumference of carbon fibres. The toughening mechanisms of the coating once deposited on fibres were investigated in single fibre composite models, such as energy absorption after fibre breakage and stable fibre slippage. Finally, small bundle composites were manufactured with an optimal interphase thickness and tested in tension to investigate the potential improvement in the tensile response of the composites.

2 RESULTS AND DISCUSSION

A “brick-and-mortar” coating inspired by the structure of natural nacre was developed at the nanometre length scale while maintaining the classic geometry, aspect ratio and phase proportion, reproducing the mechanical properties and toughening mechanisms. A Layer-by-Layer assembly method, based on electrostatic attractions of oppositely charged particles/molecules, was previously developed to assemble PSS molecules and LDH inorganic platelets in a well-ordered planar nanocomposite [15]. The nanostructure was then conformally transferred onto the surface of modified carbon fibres pre-coated with a precursor PDDA layer to enhance coating adhesion. A high surface density of the carbon fibres was needed to initiate the LbL deposition and ensure good adhesion of the coating. Carbon fibre surface oxidation is well-known to increase acidity and, therefore, provide high $\zeta$-potential at high pH. The presence of oxygen-containing groups on the surface of the fibres can lead to negative charge through deprotonation. Hence, the fibres were oxidised to increase the ratio of
oxygen on their surface (Fig.1.A). A maximum platelet width determined by a tangential deviation to the fibre curvature smaller than the roughness of the precursor PDDA layer (≈1 μm) led to a very narrow window of suitable dimensions (Fig.1.B). Therefore, the dimensions of the platelets were carefully selected to allow for conformal deposition onto 7 μm wide carbon fibres (AS4, Hexcel), namely, 130 nm wide and 13 nm thick (aspect ratio of 10). Being self-limited, the LbL process allowed for the deposition of the coating onto multiple fibres simultaneously. The repetition of (PSS/LDH) deposition cycles was done on carbon fibre bundles containing few hundreds of fibres. A pH of 10 was used throughout the all process, including polyelectrolyte solutions, LDH suspension and water rinsing solutions (Fig.1.C).

Figure 1. “Brick-and-mortar” nanostructured coating deposition on carbon fibre bundles. Schematic of the surface of as-received, oxidised and coated carbon fibres (A). Window of suitable platelet dimensions for the deposition of conformal “brick-and-mortar” coating (9:1 inorganic:organic and aspect ratio s = 10) onto the surface of typical reinforcing fibres with varying diameters (B). Schematic of the Layer-by-Layer deposition of PDDA/(PSS/LDH)_n coating onto a bundle of oxidised carbon fibres (C).

The oxidation surface treatment of carbon fibres did not roughen the surface of the fibres (Fig.2.A-B) but significantly increased their charge density (Fig.2.C). At pH 10, a ζ-potential of -58 mV was measured for oxidised fibres as compared to -19 mV for as-received carbon fibres. The highly negative ζ-potential was deemed suitable for LbL deposition (> |50 mV|). The deposition of PDDA/(PSS/LDH)_n coatings on carbon fibre bundles showed a linear increase in coating thickness as a function of the number of deposited (PSS/LDH) bilayers, n, indicating a coherent deposition of LDH and PSS monolayers after each LbL cycle. A coating thickness from roughly 0.2 to 0.8 μm was measured by cross-section SEM images, corresponding to 12 and 50 (PSS/LDH) bilayers deposition on PDDA, respectively (Fig.2.D-K). The deposition of thicker coatings such as PDDA/(PSS/LDH)_{75} led to heterogeneous deposition; the coating thickness was found to be erratic along the length of the fibres, as a result of significant fibre surface roughness.
The length along which the fibres can stably slide prior to full interface debonding, through deformation in shear of the interphase, is of great interest. Stable fibre slippage through occurring through strain hardening of the interphase can provide a route to increase plasticity in fibre-reinforced composite materials. A debonding length ratio (DLR), establish as the ratio between the debonding length and the embedded length, taking into account the elastic and plastic deformation of the interface, can provide qualitative investigation of the interphase ability to trigger stable fibre slippage. Yet again, the incorporation of the PDDA/(PSS/LDH)$_n$ coating at the fibre/matrix interface was found to produce longer fibre slippage prior to interfacial failure (Fig.3.C). A maximum DLR of about $0.17 \pm 0.01$ obtained for PDDA/(PSS/LDH)$_{25}$ coated fibres was measured, as compared to $0.09 \pm 0.01$ for bare control fibres. A maximum in both IFSS and DLR was achieved when coating the fibres with a 0.4 μm thick coating [PDDA/(PSS/LDH)$_{25}$]. Further increase in the coating thickness led to a reduction in both IFSS and DLR. The latter trend can be explained by the radial compliance of the coating, leading to reduced fibre clamping force at high coating thickness. The ability of the nanostructured interphase to dissipate the energy released by a fibre break, through crack deflection, was investigated by in-situ single fibre fragmentation tests. Optical microscopy, using cross-polarised light in transmission, was used to investigate the formation, accumulation and dissipation of stress in the vicinity of a fibre break through the observation of birefringence patterns at the fibre/epoxy interface (Fig.3.D-E). Two different stress fields were observed during fragmentation of single carbon fibres; bare oxidised carbon fibres exhibit an intense and large stress field building up near a fibre break (Fig.3.D.i), while PDDA/(PSS/LDH)$_{25}$ coated oxidised carbon fibres present a less intense stress field, which seems to spread along the length of the fibre (Fig.3.E.i). Continuous imaging (Fig. 3.D-E.i-iii) of the stress field, whilst increasing macroscopic strain at the interface, provided evidence of the propagation of the stress during progressive fibre sliding/debonding of the interface, accompanied with a noticeable reduction of the stress field intensity. On the other hand, the stress field intensity observed for fragmented bare fibre does not seem to change. Hence, following the breakage of the fibre, part of the energy release is absorbed within the nanostructured “brick-and-mortar”, followed by further stress relief via progressive fibre debonding and slippage.
Figure 3. Single fibre composite model testing. Load-displacement pull-out curves of bare and PDDA/(PSS/LDH)$_n$ coated oxidised carbon fibres in epoxy (A). Interfacial shear strength (IFSS) and debonding length ratio (DLR) obtained from pull-out tests of the different single fibre systems (B and C, respectively). Optical images of in-situ fragmentation tests of bare (D) and PDDA/(PSS/LDH)$_{25}$ coated (E) oxidised carbon fibres using cross-polarised light in transmission at a given strain (i) and at +1.2 % (ii) and +2.4 % strain (iii) – vertical arrows pinpoint fibre fragments and horizontal arrows and dashed line highlight progressive sliding of the fibre.

Small oxidised carbon fibre bundle composites were manufactured, with and without the optimal PDDA/(PSS/LDH)$_{25}$ nanostructured interphase and tested in tension. 100 to 300 carbon fibres were held vertically and impregnated with an ultra-low viscosity epoxy resin that cures at 50°C to avoid dehydration of the coating, in order to produce unidirectional cylindrical bundle composites (Fig. 4.A). The epoxy was directly poor over the bundles with excess to ensure full impregnation. The excess of the resin was self-drained by gravity. The good wettability of the resin with the –LDH terminated coating as well as the very low viscosity epoxy resin allowed for the manufacture of uniform bundles with a fibre volume fraction in the range of 50 to 60 %. Both the strain-to-failure and strength of the coated bundle composites were improved as compared to bundles without the interphase, up to 2.12 % and 4.61 GPa, respectively (Fig.4.B), as a result of a higher degree of fibre fragmentation in the composites (pseudo-isolated fibre breaks). The current properties of the coating are limiting further improvement in the hierarchical composites. The degree of fibre fragmentation in the composite still remains too low to promote plastic deformation via the activation of fibre slippage sites.

Figure 4. Bundle composite tensile testing. Cross-section SEM images of bundle composites containing the nanostructured interphase (A). Tensile strain-stress curves of bundle composites with and without PDDA/(PSS/LDH)$_{25}$ interphase (B).
3 CONCLUSION

A novel nanostructured “brick-and-mortar” composite interphase, inspired by natural nacre, was developed and adapted to the surface of carbon fibres. The classic deformation and toughening mechanisms of nacre, that were previously reproduced in planar nanomimic, were successfully implemented at the fibre/matrix composite interface. While good adhesion of the coating allowed for an efficient load transfer at the interface, the strain hardening properties of the coating in shear was found to also promote stable slippage of the fibre within the matrix, as observed in single fibre composite models. In addition, the anisotropy of the nanostructure, and more especially, its ability to deflect a crack at the platelet interface enabled for stress dissipation at fibre break.

Small cylindrical fibre-reinforced bundle composites were manufactured using an ultra-low viscosity epoxy resin with a fibre volume fraction of about 50 to 60%. The incorporation of an optimal nanostructure interphase with a thickness of about 0.4 μm in the composite led to improvement in the tensile properties of the composites.

ACKNOWLEDGEMENTS

This work was funded under the UK Engineering and Physical Sciences Research Council (EPSRC) Programme Grant EP/I02946X/1 on High Performance Ductile Composite Technology in collaboration with the University of Bristol. Supporting data are available, subject to a non-disclosure agreement. Please contact the corresponding author in the first instance.

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