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Development of novel composites through fibre and interface/interphase modification

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Abstract. We show how fibre/matrix interface (or interphase) modification can be used to develop a range of novel carbon fibre reinforced polymer (CFRP) composites that open up new applications far beyond those of standard CFRPs. For example, composites that undergo pseudo-ductile failure have been created through laser treatment of carbon fibres. Composites manufactured with thermo-responsive interphases can undergo significant reductions in stiffness at elevated temperatures. Additionally, structural supercapacitors have been developed through a process that involves encapsulating carbon fibres in carbon aerogel.

1. Introduction

Composite materials have a wide range of applications due to their excellent specific strength and stiffness. These composite properties are determined by the fibre type, the fibre volume fraction and fibre alignment. The role of the matrix is to hold the fibres in place, protect them from damage. The matrix determines the composite transverse properties, in relation to the primary fibre axis. Load is transferred from the matrix to the fibres through the fibre/matrix interface. Tailoring the fibre/matrix interface allows control over the final composite properties but clever design of composite interphases also offers new opportunities to introduce additional functionalities, such as active stiffness control or multifunctionality, into composite materials. Three fibre modification concepts are discussed, which include i) the creation of fibres with modulated properties and shapes as a potential route to short fibre composites which form in-situ upon loading, ii) thermo-responsive interphases that allow for active stiffness control in carbon fibre composites and iii) the storage of electrical energy in structural carbon fibre composites.



2. Interfaces for Ductility: Carbon Fibres with Modulated Shape and Properties

It is possible to create a pseudo-ductile response in composites by allowing discontinuous fibre fragments to move within the matrix. Prepregs with discontinuities formed by cut plies have been studied in detail. Fibre fragments are required to be sufficiently small to suppress unstable propagation of shear from the discontinuities before overall tensile failure. It was shown both theoretically and experimentally for cementitious composites that fibres with slip strain hardening fibre/matrix interfaces can undergo multiple fracture events, spreading fibre/matrix debonding and fibre pull-out across large volumes, allowing for significant deformation before a crack localises and the composite fails [1]. More recently, it was shown that machined steel fibres having conical ends [2] with taper angles of 5° dissipated much more energy than straight fibres when being pulled out from a cured epoxy resin. Considering such fibres embedded in composites it should, therefore, be possible to bridge cracks and plough through the matrix, which should contribute to the energy dissipated during the failure process. There is a growing body of evidence from synthetic composite materials [3, 4, 5, 6], which shows that tapered fibre ends do result in an increased work of pull-out, delocalise inelastic deformation and induce strain-hardening. However, it remains challenging to produce outward tapered features and/or an unduloid fibre shape in continuous carbon fibres, which are the preferred reinforcements in high performance composites. From a manufacturing point it is desired to use continuous fibres to produce high fibre volume fraction composites, in which the fibres break *in situ* during loading to form short fibre segments with tapered ends. Such a composite would have a high initial stiffness.

Lasers are being increasingly used to machine high performance unidirectional carbon fibre composites [7, 8] and for cutting composite plies at predefined points to produce highly aligned discontinuous composites mainly aiming to improve manufacturing ductility [9]. Carbon fibres cut via laser ablation have been reported to feature expanded fibre ends near the heat-affected zones of laser-drilled holes [7, 8]. Controlled laser exposure of carbon fibres should present an opportunity to modify the shape of continuous carbon fibres along their lengths.

In order to modify carbon fibres, individual unsized, polyacrylonitrile (PAN) based AS4 fibres (Hexcel Ltd., Cambridge, UK) were fixed on paper frames. These frames allowed for positioning and handling of the fibres for laser treatment and subsequent characterisation. The substrates were positioned underneath the laser beam, such that the laser was run across the fibres perpendicular to the fibre axis. A nanosecond pulsed Nd:YVO₄ laser with a maximum average power of 17.5 W at $\lambda = 1064$ nm operating with an average power of 1.1 - 17.5 W, a repetition rate in the range of 50 - 100 kHz and beam scanning speeds in the range of 50 - 200 mm s⁻¹ was used to treat the fibres. The laser beam was focused to a spot size of ~ 70 μm in diameter. The laser conditions were tuned and resulted in three different fibre shapes (Figure 1), causing: i) local expansion of the fibre at the irradiation site; ii) expansion and ablation of the fibres, and iii) expansion and cutting of the fibres [10] (Fig. 1). Laser parameters 1.1 W of average output power, frequency 100 kHz, and speed 100 mm s⁻¹ resulted in approximately 20% of fibres being cut; at 17.5 W, frequency 50 kHz and speed 50 mm s⁻¹ all fibres were cut. Parameters 1.1 W, frequency 100 kHz and speed 200 mm s⁻¹ consistently resulted in intact fibres. The laser operated at 1.1 W of average power had an energy fluence of 0.3 J cm⁻² (energy per pulse 11 μJ). 1D temperature modelling has been conducted for these conditions with an estimated temperature increase in the area irradiated by a focused beam in excess of 2900 K. The vaporisation temperature of PAN-based carbon fibres is reported to be 3500 K [11]. The same average power but scanning speeds lower than 100 mm s⁻¹ resulted in cutting of the fibres.

The laser treated fibres consistently exhibited an affected region along their length. The diameter of laser treated fibres increased from the average diameter of the control fibres 7.0 μm to a maximum of 9.7 μm , corresponding to a diameter increase of 37% (Expanded fibres). The average affected length of these Expanded carbon fibres after a single laser pass was ~ 140 μm , resulting in a taper angle about 1° . Expanded/Ablated fibres exhibited slightly larger affected lengths with narrower midsections, flanked by expanded regions, resulting in taper angles of 1.6° . Cotton-bud end fibres were completely cut and had average affected lengths of ca. 110 μm and taper angles of 1.8° (Fig. 1). The maximum

diameter expansion observed was 53%, after which ablation reduced the expanded fibre diameter, eventually cutting the fibre, resulting in characteristic cotton-bud shaped fibre ends.

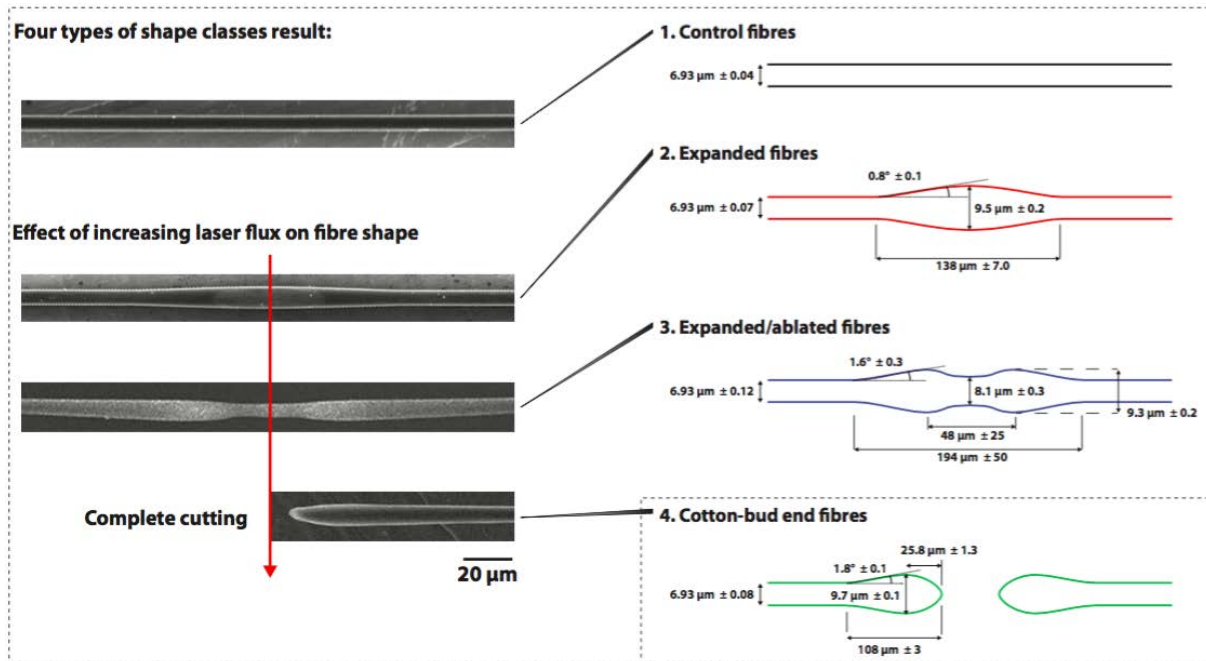


Fig. 1: Characteristic scanning electron micrographs of laser treated carbon fibres; depending on the laser parameters, average power, repetition rate and beam scanning speeds, these typical fibre morphologies were observed: Control, Expanded, Expanded/Ablated and Cotton-bud end fibres. With permission of the American Chemical Society (ACS).

The tensile properties of Expanded and Expanded/Ablated carbon fibres were significantly reduced in comparison to control AS4 fibres (Fig. 2). All fibres exhibited a linear elastic behaviour with brittle fracture. As expected the control carbon fibres failed catastrophically, whereas the laser treated fibres broke into two, at their pre-defined weak point (expanded or ablated regions) resulting in outwardly tapered fibre ends (for the expanded carbon fibres). The fibre tensile strength (Fig. 2) was reduced by ~69% for Expanded fibres and 75% for Expanded/Ablated fibres. The tensile modulus of the laser treated fibres (Fig. 2), however, was reduced only by a modest ~17% (averaged over all treated fibres) in comparison to the control fibres. In practice, this reduction in fibre strength is still useful in the right context, for example; fibre manipulation is retained and therefore, it should be possible to use such laser treated fibres to produce unidirectional composites, which should still possess high initial stiffness. A significant reduction in strength is, in fact, a prerequisite to ensure reliable local failure sites to create highly aligned short fibre composites contained cotton bud shaped fibres. Whilst the strength reduction is greater than necessary, in the current guise, a distribution of pre-weakened points can be implemented throughout the composite due to controlled nature of the modification, which can be used to minimise the reduction in overall composite strength.

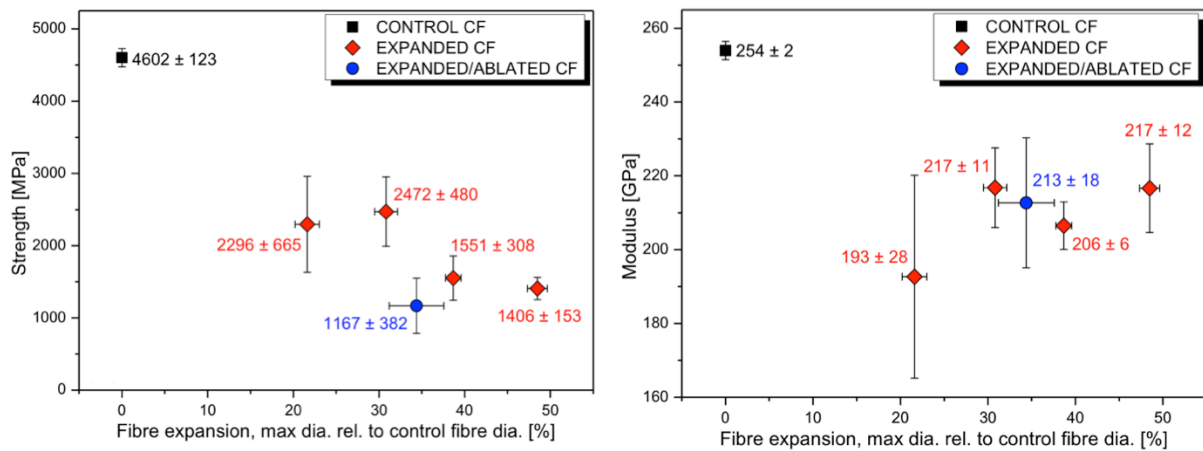


Fig. 2: Tensile strength and modulus of Control and laser treated Expanded and Expanded/Ablated fibres carbon fibres as function of fibre expansion. The fibre tensile strength was normalised to control fibre diameter. With permission of the ACS.

Fibre pull-out tests performed on cotton-bud terminated carbon fibres from a transparent silicone rubber matrix were conducted to visualise the effect of the modified fibre ends on the pull-out behaviour over a long embedded length. Significant ploughing was observed for Cotton-bud end fibres through the matrix in contrast to the control fibres, which were simply pulled from the matrix (Fig. 3). The work of pull-out of the Cotton-bud end fibres increased dramatically. Taper angles of 1-2° are already sufficient to cause cavitation in the matrix along with sliding. The apparent interfacial shear strength determined from the maximum pull-out force normalised by the embedded fibre area increased for cotton-bud fibres by a factor of 5 compared to Control fibres.

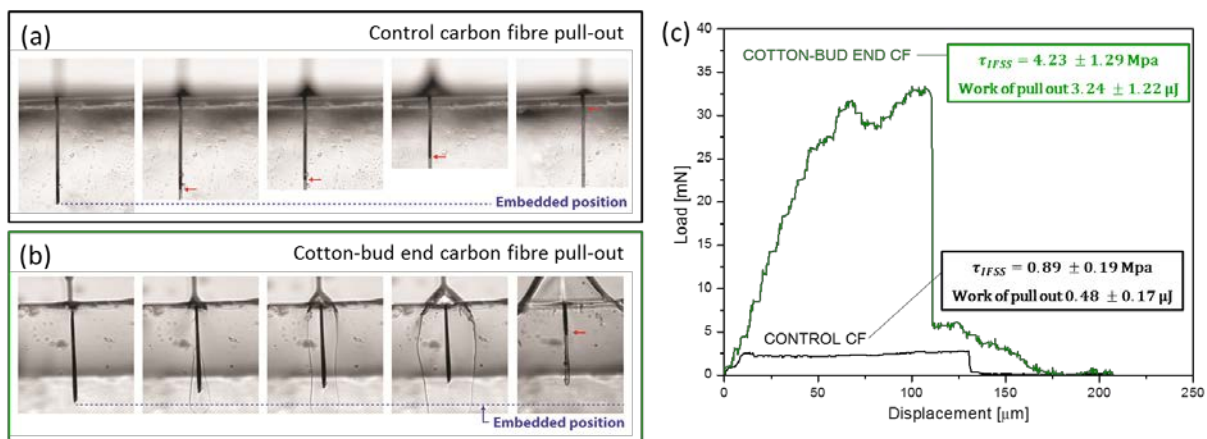


Fig. 3: Optical micrographs taken during the pull-out test of (a) Control (AS4) carbon fibre and a laser treated carbon fibre with a Cotton-bud end carbon fibre. All images have been positioned such that embedded position is maintained (blue dotted line), fibre ends are highlighted with an arrow where appropriate. Characteristic load-displacement curves of the fibre pull-out of the Control and Cotton-bud end carbon fibre with inset proving the average interfacial shear strength (τ_{IFSS}) and work of pull-out. With permission of the ACS.

High power laser treatment on structural carbon fibres was systematically used to create expanded regions at predetermined points; the fibre strength was locally reduced whilst much of their stiffness was preserved. Laser treated fibres consistently fractured in the laser affected regions, producing fibre segments with outwardly tapered ends possessing taper angles of 1 - 2°. The effectiveness of the laser

modification method to modify pull-out characteristics was successfully demonstrated using fibres with 'cotton-bud' ends, which resulted in a significant improvement of the work of pull-out and interfacial shear strength. Modified continuous carbon fibres could be used to form aligned high stiffness unidirectional composites with predefined (and distributed) weak regions. Under load fibre fragmentation will occur resulting in the formation of a well-aligned short fibre composite, in which a high modulus close to that of common unidirectional composites is predicted, but with tapered fragment ends resulting in strain hardening composite interfaces.

3. Composite Interfaces/Interphases for Multifunctionality

Multifunctional materials are specifically developed to improve system performance by integrating subsystem components and functions [12]. Multifunctional composites ought to combine high specific mechanical properties with additional functionalities, such as sensing, actuation, repair or energy storage. Composite interfaces/-phases play a crucial role in order to realise such multifunctional composites, which will be shown using the following two examples.

3.1 Responsive Fibre Coatings: A Route to Composites with Stiffness Control

Recently, the development of composites with controllable stiffness has received considerable interest [13, 14, 15]. Such composites are of particular interest for use in morphing and deployable structures as they offer high stiffness with increased compliance when required [16]. A route to allow fibres within a polymer matrix composite to slide is to switch off the fibre/matrix adhesion. The fibre/matrix adhesion is dramatically above the glass transition temperature (T_g) of the composite matrix. In order to allow carbon fibres to slide within a thermosetting high T_g matrix, all fibres could be coated with a thin low T_g thermoplastic coating.

Flexible interlayers between reinforcing fibres and matrix were actively researched over 20 years ago as a means to improve the energy absorption characteristics of composites [17]. Such flexible interlayers promote toughness by interfacial debonding, fibre pull-out and post-debonding friction as well as stress redistribution through localised large scale elastic and plastic deformations [18]. However, the presence of a ductile coating promoting toughness can lead to a reduction in strength and modulus of a composite. Various fibre coating methods, such as electropolymerisation, have been used to deposit polymeric coatings around reinforcing fibres. The carbon fibres within the composite can be used as Joule heaters by passing a current through them. This heats the fibres and also the surrounding thermoplastic coating to temperatures above its T_g until the coating softens, which enables the fibres to slide within the high T_g composite matrix (Fig. 4). Manifestation of this effect has shown to reduce greatly the storage modulus (Fig. 5) and flexural stiffness of the composite (by up to 88 %) [19]. This process is reversible as the stiffness returns to its original value once the coating is allowed to cool below its T_g . The choice of fibre coating depends primarily on the thermal properties of the polymer. It should have a T_g or melting temperature (T_m) below that of the thermosetting or thermoplastic composite matrix but well above the maximum service temperature of the final composite part. Successful demonstration of this concept by electrocoating carbon fibres with polyacrylamide (PAAm) using a continuous electrocoating method is reported [19]. The T_g of PAAm can be tailored by adjusting the moisture content of the coating. PAAm, when partially hydrated (20 % moisture content), has a T_g of approximately 84 °C. However, water soluble fibre coatings like PAAm are not suitable for use in high performance applications and for this reason carbon fibres were coated with non-water soluble polymers, such as polymethylmethacrylate (PMMA) and polystyrene [20]. As only a very thin thermoresponsive coating is needed, the coating can be heated quickly by passing a current through the carbon fibres. This means the stiffness can be controlled on demand. It is important that the matrix remains stiff when the carbon fibre coating has softened. This ensures that the composite can withstand loading at elevated temperatures and prevents fibre misalignment. Below the softening temperature of the fibre coating the epoxy composites have a very similar flexural stiffness compared to those containing unsized carbon fibres, which suggests they are suitable for high

performance applications. The major disadvantage of using these composites is that the maximum deflection at elevated temperatures is limited to the maximum strain of the matrix material.

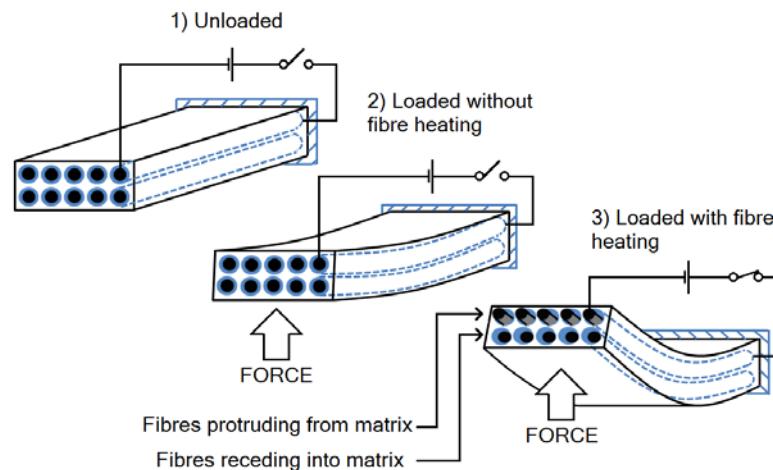


Fig. 4: Concept of the controllable stiffness composite. With permission from the ACS.

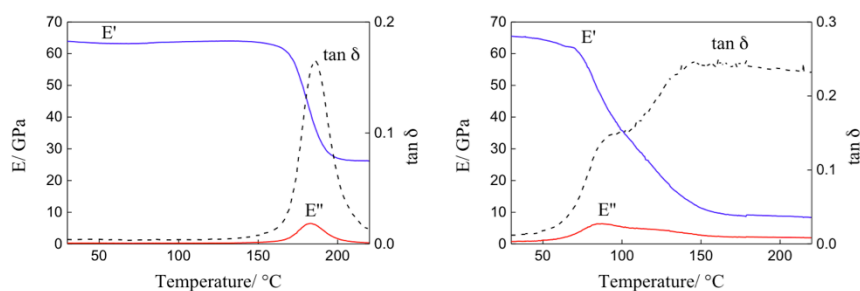


Fig. 5: Storage modulus (E'), loss modulus (E'') and damping ($\tan \delta$) of an epoxy composite containing unsized (left) and hydrated PAAm coated carbon fibres (right) as a function of temperature showing the stiffness loss when (left) the epoxy matrix passes T_g or the PAAm fibre coating (right) passes through T_g allowing the carbon fibres to slide within the coating.

3.2 High Surface Aero Composite Interfaces for Structural Energy Storage Devices

The combination of structural properties with electrochemical energy storage in a single material, to provide multifunctional structural energy storage devices [21], offer the prospect to decrease the weight and volume of systems, which otherwise do require independent energy storage devices [22], such as batteries or supercapacitors, such electric/hybrid vehicles. The easiest route to a multifunctional structure is to embed energy storage devices into conventional fibre-reinforced composites. Alternatively, truly multifunctional materials could be developed that simultaneously have both structural and electrochemical energy storage capabilities [23, 24]. Show here is the possibility to create multifunctional structural supercapacitor composites. Figure 6 shows a design for a structural supercapacitor consisting of two modified structural carbon fibre fabric electrodes, separated by a structural glass fibre fabric infused with a multifunctional polymeric electrolyte. The critical components for such a device are the electrolyte, which has to provide sufficient mechanical support while being an ionic conductor, and the multifunctional electrode having both a high energy storage capability and good mechanical properties. In order to achieve this goal structural carbon fibres were encapsulated into a carbon aerogel (CAG). Carbon aerogels (CAGs) are widely used for their high surface area and electrical conductivity, particularly in the context of electrochemical electrodes and

devices. The most common carbon aerogels are formed by condensation, stabilisation and subsequent carbonisation of resorcinol-formaldehyde (RF) mixtures, to yield a network structure of amorphous carbon.

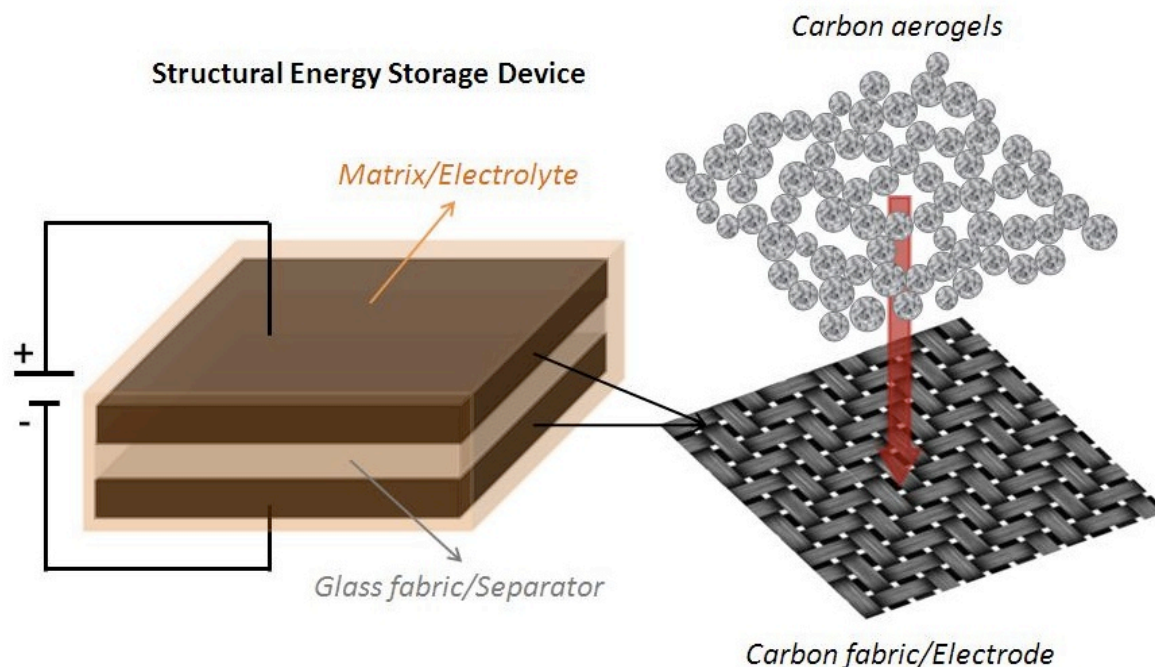


Fig. 6. Schematic of a structural supercapacitor concept based on CAG-modified structural carbon fibre fabrics as electrodes, structural glass fabrics as separator impregnated with a polymer-based electrolyte. With permission of the ACS.

Exploring this idea further using a variety of woven structural carbon fibres, semistructural supercapacitor laminates can be prepared [23]. Scaled production of such laminates is achieved by adapting conventional composite processing techniques. The multifunctional electrode material developed was prepared by resin infusion under flexible tooling (RIFT) of a plain weave carbon fibre fabric (3k, 5-satin-harness weave, 283 gm^{-2} , Cytec Engineered Materials) with resorcinol-formaldehyde (AX2000, INDSPEC Chemical Corporation) diluted with formaldehyde solution and using sodium hydroxide as catalyst. The specimens prepared were both cured at room temperature, 50°C and 90°C with a period of 24 h at each temperature. The dried specimens were then carbonised at 800°C for 30 min in a furnace under flowing nitrogen (Fig. 7). The carbon fibre supported CAG forms a hierarchical reinforcement preform (Fig. 8) consisting of a bicontinuous nanoporous matrix, uniformly surrounding reinforcing carbon fibres. The CAG contributes around 10 wt% to the sample; the surface area of the CAG component alone is typical of such materials at around $700\text{--}800 \text{ m}^2\text{g}^{-1}$, with pore sizes of a few tens of nanometres. This preform is then infused via a second RIFT cycle with the desired polymeric matrix resin system to form a dense composite. To create a structural supercapacitor the carbon aerogel-carbon fibre (CAG-CF) preform was infused with a non-structural resin, polyethylene glycol diglycidal ether (PEGDGE), which has a low modulus of about 6 MPa but was shown to have reasonable ionic conductivity [23] when combined with a suitable electrolyte. To examine whether a CAG network can be a useful reinforcement, the same types of CAG-CF preforms were infused with a conventional epoxy matrix (Gurit PRIME 20ULV, modulus of about 3 GPa) to generate pure structural systems.

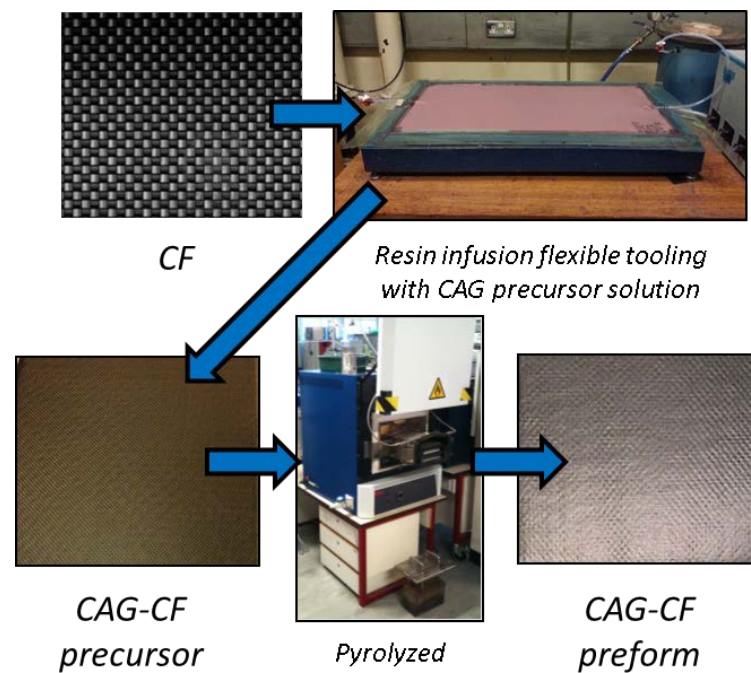


Fig. 7: Schematic flow diagram illustrating the synthesis of carbon aerogel-carbon fibre preforms.

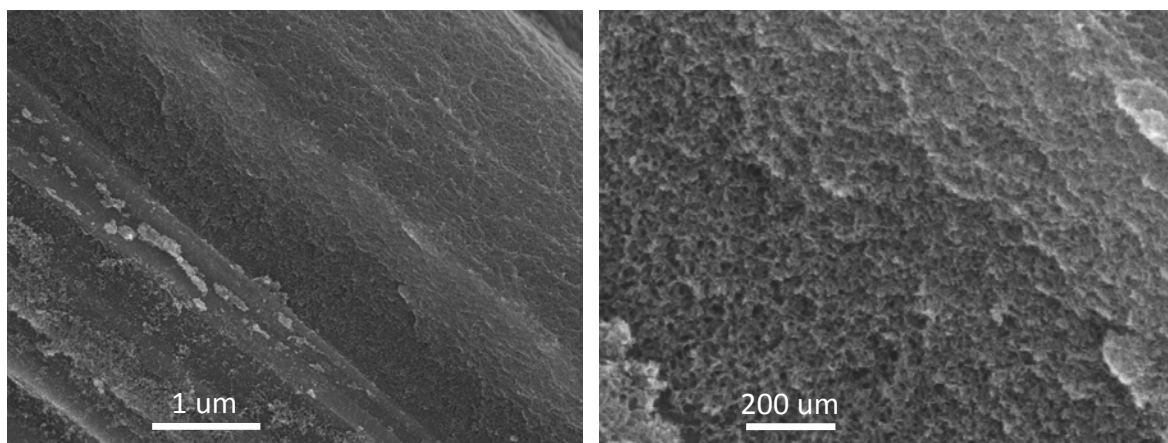


Fig. 8: Scanning electron micrographs of CAG-CF, infused with 40 wt% RF solution, showing carbon fibres embedded in CAG (left) and detail of the CAG nanostructure (right).

The mechanical performance of the hierarchical CF-CAG composites was first examined using $\pm 45^\circ$ shear tests (ASTM Standard D3518) in order to investigate the response of the CAG reinforced matrix (Table 1). The shear strength and the shear modulus of both multifunctional and structural epoxy matrices increased. Predictably, the properties of the non-structural PEGDGE matrix system are most dramatically improved but surprisingly even the properties of the structural epoxy are apparently improved. To explore whether these improved matrix characteristics translate into better composite properties composites were tested in compression (Table 2). Again, the compression strength and stiffness of the soft CF-CAG PEDGE composite increased significantly. Also, the modulus of CF-CAG composites with the structural epoxy matrix increased but a significant decrease in compression strength was observed in this case. This observed decrease in strength the CF-CAG composites with the structural matrix was due to the reduced adhesion between the CAG modified carbon fibres and the matrix as indicated by interlaminar shear strengths (ILSS), obtained by short beam shear tests (ASTM Standard D2344); the ILSS decreased from 60 MPa to 43 MPa. The heat treatment involved in carbonizing the CAG precursor, can be expected to remove both sizing and surface oxidation from the CFs. The resulting lack of chemical interaction with the subsequently infused resin may be the source of the degraded fibre/matrix interface, and hence mechanical properties.

Table 1: In-plane shear response tensile test of $\pm 45^\circ$ laminates on monolithic laminates [23] with woven carbon fibre fabrics, ASTM D3518.

Reinforcement	Matrix	Shear Strength (MPa)	Shear Modulus (MPa)	Volume fraction of fibre reinforcement (vol%)
As-received	DGEBA-based epoxy	25.9 ± 2.2	4380 ± 60	45.0
CAG-modified		26.2 ± 0.5	5050 ± 210	40.7
As-received	PEGDGE-based epoxy	5.83 ± 0.14	201 ± 10	47.2
CAG-modified		8.88 ± 0.12	911 ± 60	42.0

Table 2: Longitudinal compression on monolithic laminates in a $0^\circ/90^\circ$ lay-up with woven carbon fibre fabrics [25], ASTM D3410.

Reinforcement	Matrix	Compressive Strength (MPa)	Compressive Modulus (GPa)	Volume fraction of fibre reinforcement (vol%)
As-received	PEDGE-based epoxy	50.4 ± 3.8	16.6 ± 1.5	57.1
CAG-modified		174.8 ± 9.2 (3.47-fold)	60.5 ± 3.6 (3.65-fold)	55.7
As-received	PRIME-20ULV epoxy	535.7 ± 52.2	65.4 ± 5.1	56.3
CAG-modified		345.2 ± 29.2 (35.6% decrease)	80.6 ± 4.5 (23.2% increase)	56.5

4. Conclusions

We introduced a novel fibre modification concept to produce carbon fibres with tapered shapes in-situ in a composite during loading and two fibre modification methods which highlight the importance of composite interfaces for the development of truly multifunctional composites. We showed that coating carbon fibres with thin thermoplastic polymers and using such fibres as reinforcement for structural thermosetting resins allows for active stiffness control; the thermoplastic coating can be softened when heating it to temperatures above its glass transition temperature, which has to be below that of the composite matrix allowing the fibres to slide through the matrix when the composite is loaded in bending resulting in large deformations. Furthermore, modifying carbon fibres with a carbon aerogel not only allows for the development of functional structural supercapacitors but also improves the mechanical properties of structural polymer electrolytes.

Acknowledgements

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