

STIFF MONOLITHIC AEROGEL MATRICES FOR STRUCTURAL FIBRE COMPOSITES

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ABSTRACT

Resorcinol-formaldehyde based aerogel precursors were infused into structural carbon fibre weaves, then gelled and carbonised to generate a continuous monolithic matrix network. This hierarchical carbon preform was subsequently infused with polymeric resins, both multifunctional and structural, to produce dense composites. The resulting hierarchical composites have a nanoscale reinforcement in the matrix at up to an order of magnitude higher loadings than typically available by other techniques. Compression, tension, $\pm 45^\circ$ shear and short beam tests demonstrate the potential of such matrix systems to address matrix dominated failures. However, for the best structural performance it will be necessary to re-optimize the fibre-matrix interface, which is degraded by the current processing regime.

1 INTRODUCTION

The performance and application of polymer-matrix fibre composites is often limited by matrix-dominated failures, both mechanical and functional. There is, therefore, considerable interest in the use of nanocomposite matrices, for example using resins filled with carbon nanotubes or graphene, to introduce both intralaminar and interlaminar reinforcement of the resulting hierarchical composites. The objective is to improve delamination resistance, through-thickness properties, and compression performance, without compromising the in-plane tensile response. The potential to improve thermal and electrical conductivity, as well as solvent resistance and fire retardance, offers additional opportunities. Improvements in fatigue performance or lightning strike resistance would be especially appealing. Although some promising results have been reported, processing constraints typically limit the nanoreinforcements to low loading fractions and discontinuous formats, limiting the level of enhancement achieved [1]. Broadly, two strategies have been followed: the first is to load discrete nanofillers into conventional resins, followed by conventional processing. This approach works well at low loadings, but viscosity increases rapidly at modest loadings (above ~1 vol%), especially for high aspect ratio particles (such as nanotubes, rods, and platelets) preventing simple infusion approaches. In addition, self-filtration effects against the primary fibre constructs create inhomogeneities within the resulting composites. The second approach involves coating or grafting nanomaterials to the surface of the primary fibres before introducing a conventional matrix. This approach works well, particularly for modifying the fibre-matrix interface, and may provide an idealised orientation of the nanomaterial; however, the absolute nanomaterial content remains low, primary fibres may be damaged in the grafting process, and thicker coatings may limit the absolute volume fraction of primary fibres in the final composite.

This paper exploits an alternative strategy to form a rigid bicontinuous reinforcing network throughout the matrix volume. A suitable precursor is first infused into a structural fibre weave or other preform, then converted to form a porous monolithic aerogel/xerogel matrix, with characteristic

lengthscales around a few tens of nanometres. The presence of the reinforcing fibres allows the aerogel/xerogel to form a stable, handleable, structure. Both the rigid network and the porosity are bicontinuous, allowing a second matrix resin phase to be infused. This second phase may be a soft multifunctional phase; for example, one that can support ion conductivity for use in structural supercapacitors and other related applications. Alternatively, it can be a conventional structural epoxy resin, to address the types of matrix dominated failures mentioned above [2].

2 EXAMPLE SYSTEMS

2.1 Carbon aerogel matrices

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 variety are formed by condensation, stabilization and subsequent carbonization of resorcinol-formaldehyde (RF) mixtures, to yield a network structure of amorphous carbon. Usually CAGs are used in powder form, as monolithic precursor gels typically fragment due to internal stresses during processing (see Figure 1). However, it has been shown that embedding non-woven carbon fibre felts within the gels stabilizes them during subsequent processing, allowing large monoliths to be obtained to make effective electrochemical electrodes [3][4]. We have explored this idea further using a variety of woven structural carbon fibre arrangements and found that (semi-)structural laminates can be prepared [2]. The production of such laminates was successfully scaled by adapting conventional composite processing, specifically, using resin infusion under flexible tooling (RIFT) to introduce a RF precursor mixture (AX2000, INDSPEC Chemical Corporation) into the carbon fibre weave. After gelation (at 45 °C and 70 °C), the sample is dried, and carbonized (at ~760°C under inert atmosphere) to form a hierarchical reinforcement preform (Figure 2), with a bicontinuous nanoporous matrix, uniformly surrounding the primary reinforcing carbon fibres. The CAG forms a rigid continuous monolithic matrix in which the carbon fibres are embedded (Figure 3) and contributes around 10 wt% to the sample; the surface area of the CAG component alone is typical of such materials at around 700-800 m²g⁻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.

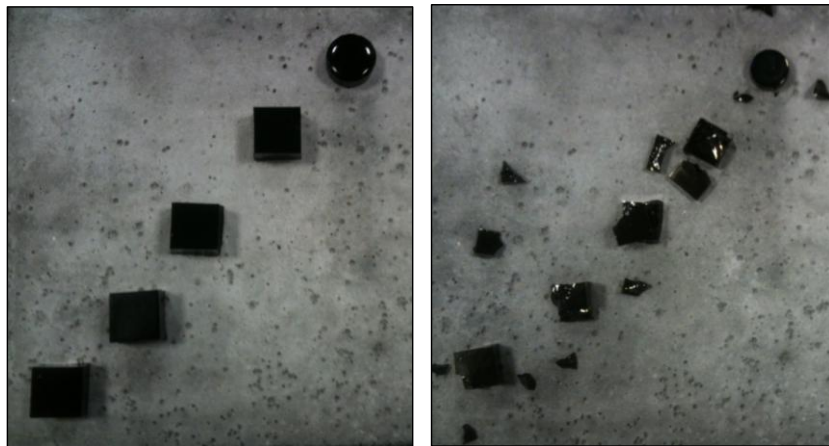


Figure 1: Carbon aerogel-monolith (approx. 1 cm): stabilized precursor (left) and after pyrolysis (right), showing spontaneous fragmentation in the absence of reinforcing fibres.

Initially, the carbon aerogel-carbon fibre (CAG-CF) preform was infused with a non-structural resin, polyethylene glycol diglycidal ether (PEGDGE) which was known to exhibit reasonable ionic conductivity [2] when combined with ionic liquid or other electrolyte salts. The purpose was to provide a multifunctional matrix systems for structural supercapacitors; results were encouraging although further development is requirement to deliver practically useful power densities [5]. On the other hand, the PEGDGE matrix modulus is low (~6 MPa [2]), and hence the resin is unsuitable for

pure (monofunctional) mechanical applications. To investigate whether the CAG network can act as a useful reinforcement, the same types of CAG-CF preforms were infused with a conventional epoxy matrix (Gurit PRIME 20ULV, modulus ~3 GPa [6]) to generate pure structural systems [2].

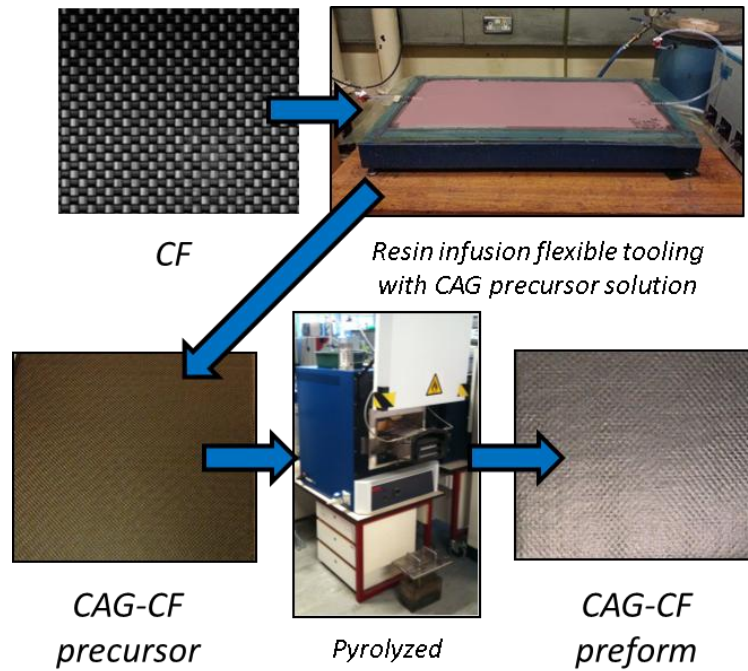


Figure 2: Carbon aerogel-carbon fibre (CAG-CF) preform production.

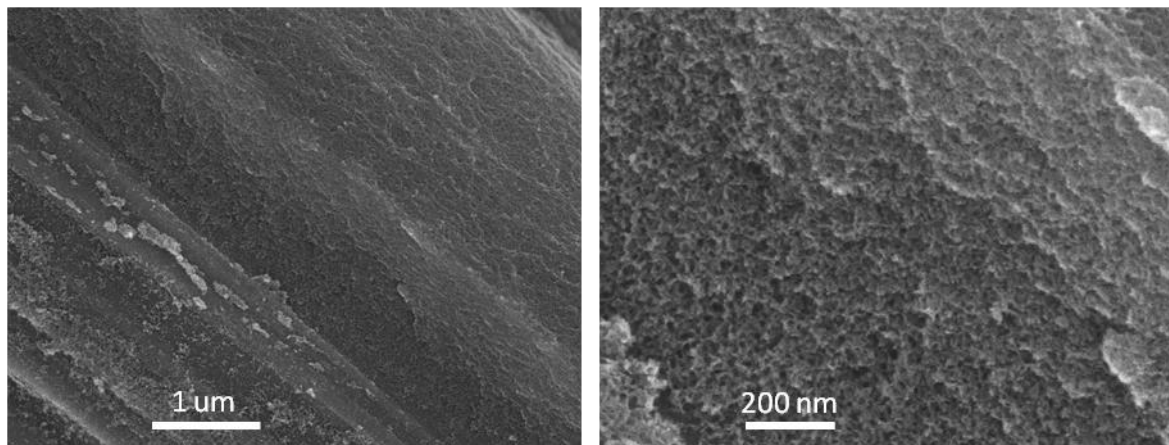


Figure 3: Scanning electron micrographs of CAG-CF, infused with 40 wt% RF solution, showing T300 carbon fibres (3k, 5-satin-harness weave, 283 gm⁻², Cytec Engineered Materials) embedded in CAG (left) and detail of the CAG nanostructure (right).

The mechanical performance was first examined using $\pm 45^\circ$ shear tests (ASTM Standard D3518 [7]) in order to explore the response of the matrix (Table 1). The shear strength and the shear modulus of both multifunctional and structural epoxy matrices increased. Unsurprisingly, the soft PEGDGE system is most dramatically improved; however, it is striking that even the structural epoxy is apparently enhanced, particularly its shear modulus. To explore whether these improved matrix characteristics translate into improved overall composite properties, specifically improved resistance to microbuckling, a fresh set of samples were prepared, and tested in compression (Table 2). Again, the soft PEDGE matrix shows significant improvements in strength and stiffness. The structural matrix also shows a significant improvement in modulus; however, there is a significant decrease in compression strength. In tension (ASTM Standard D3039 [8], Table 3), a similar trend is observed.

The original of this decline in strength for the structural PRIME resin, is indicated by the interlaminar shear strengths (ILSS), obtained by short beam shear measurements (ASTM Standard D2344 [9]), and the associated fractography. The value of the ILSS drops from around 60 MPa to 43 MPa on introducing the CAG into the CF weave. In SEM micrographs, cusps and matrix ductility were observed in the baseline PRIME system, but there were a larger proportion of smooth fibre imprints in the CAG-containing samples (Figure 4). In addition, in the CAG samples, the cusps were more block-like and had fewer tufted feet features than in the control, which is consistent with a poorer fibre/matrix interface [10]. 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.

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 1: In-plane shear response tensile test on $\pm 45^\circ$ monolithic laminates [2] with woven carbon fibre fabrics (HTA, 3k, plain weave, 200 gm⁻², TISSA Glasweberei AG), ASTM D3518.

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

Table 2: Longitudinal compression test on monolithic laminates in a $0^\circ/90^\circ$ lay-up with woven carbon fibre fabrics (HTA, 3k, plain weave, 200 gm⁻², TISSA Glasweberei AG), ASTM D3410.

Reinforcement	Matrix	Tensile Strength* (MPa)	Tensile Modulus* (GPa)
As-received	PRIME- 20ULV epoxy	717.2 ± 3.8	55.2 ± 0.6
CAG-modified		398.7 ± 6.9 (44% decrease)	63.6 ± 0.5 (15% increase)

* normalised to 55 vol%

Table 3: Tensile test on monolithic laminates in a 0°/90° lay-up with woven carbon fibre fabrics (HTA, 3k, plain weave, 200 gm⁻², TISSA Glasweberei AG), ASTM D3039.

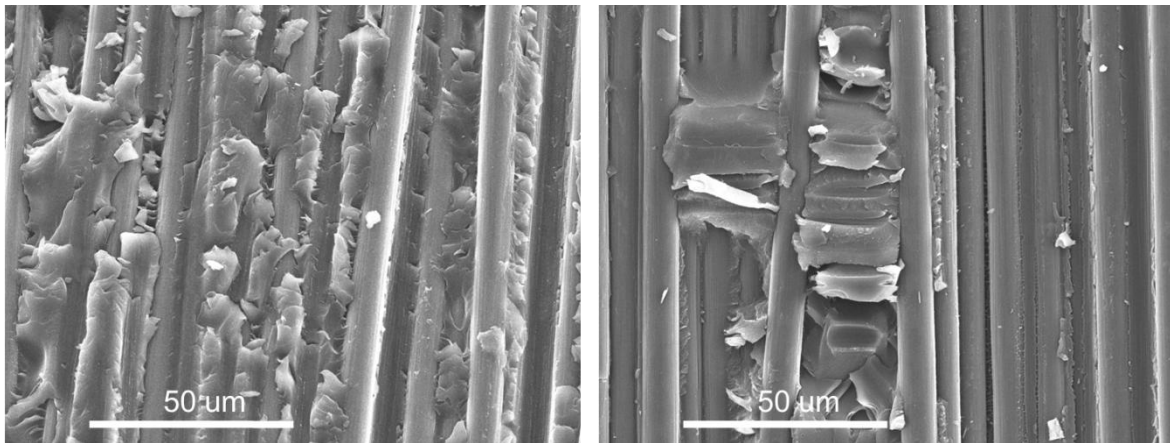


Figure 4: Scanning electron micrographs images of ILSS fracture surfaces for HTA plain weave specimens, showing features associated with poorer fibre matrix interfaces for CAG-CF samples (right) than the original CF control (left).

3 CONCLUDING REMARKS

The preparation of continuous nanostructured aerogels or xerogels as matrices for structural reinforcing fibres provides an exciting new strategy for enhancing both mechanical and physical performance, using a relatively high loading of nanostructured material. The bicontinuous nature of the structure maximizes the constraint offered by the stiff phase (for example, as compared to the use of dispersed nanoparticles), whilst maintaining the continuous network of tougher polymeric resin. Such systems can be prepared at reasonable scale, using adaptations of standard composite processing techniques (RIFT); requiring only a second iteration to introduce the additional matrix phase. We have successfully demonstrated that curved CAG-CF composites can be produced, in the context of creating a structural power body component for a model car [5]. Unsurprisingly, the relative improvements in mechanical performance are greater for the softer baseline matrices, which have immediate relevance to multifunctional composites [2]. However, there are suggestions that absolute mechanical performance of structural systems may also be improved. It is clear from shear tests that the intrinsic performance of the matrix system is improved. Tension and compression tests confirm an enhanced modulus. The remaining challenge relates to the reduced strength which can be attributed to degradation of the fibre/matrix interface. Optimisation of this interface, for example using gas phase modification chemistries, may resolve the current issues, and allow an improved overall performance. In any case, improvements in electrical conductivity, thermal diffusivity, solvent resistance, and other matrix dominated properties can also be anticipated. The general strategy can be extended to

other aerogel/fibre systems, as we have already explored for combinations of glass fibres with silica aerogels, with promising results; in this case the high temperature treatment and associated desizing is avoided, and a strong fibre-matrix interface can be anticipated.

ACKNOWLEDGEMENTS

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