

HIERARCHICAL CARBON AEROGEL MODIFIED CARBON FIBER COMPOSITES FOR STRUCTURAL POWER APPLICATIONS

D. B. Anthony¹, S. N. Nguyen², E. Senokos³, A. Bismarck⁴, A. R. J. Kucernak⁵,
E. S. Greenhalgh⁶ and M. S. P. Shaffer⁷

¹ Department of Chemistry, Imperial College London, UK
d.anthony08@imperial.ac.uk, <https://www.dbanthony.com>

² Department of Aeronautics, Imperial College London, UK
s.nguyen06@imperial.ac.uk, <https://cimcomp.ac.uk/people/sang-nguyen>

³ Department of Chemistry, Imperial College London, UK
e.senokos@imperial.ac.uk

⁴ Institute of Materials Chemistry and Research, Faculty of Chemistry, University of Vienna,
Austria
alexander.bismarck@univie.ac.at, <https://mc.univie.ac.at>

⁵ Department of Chemistry, Imperial College London, UK
anthony@imperial.ac.uk, <https://www.imperial.ac.uk/people/anthony>

⁶ Department of Aeronautics, Imperial College London, UK
e.greenhalgh@imperial.ac.uk, <https://www.imperial.ac.uk/people/e.greenhalgh>

⁷ Department of Chemistry, Imperial College London, UK
m.shaffer@imperial.ac.uk, <https://www.imperial.ac.uk/people/m.shaffer>

Keywords: Hierarchical, Aerogel, Energy storage, Structural power composites

ABSTRACT

The desire to reduce overall weight in devices is a key driver for perpetual material development; the ability to combine composites with energy storage functions/capabilities which simultaneously provide structural integrity has the potential to supersede monofunctional components. To achieve this ambition, the multifunctional structure must perform both mechanical and energy storage functions sufficiently, but often there is a trade off in performance which is a significant challenge to overcome. Carbon aerogels have been shown to contribute positively to (electro-chemical double layer) capacitive performance due to an increased surface area in multifunctional carbon fiber based composite electrodes, but have also been shown to reduce mechanical properties; the addition of nano-scale reinforcers, such as carbon nanotubes, graphene or alike, with their superlative electrical and mechanical properties are proposed to address these concerns and create a truly hierarchical structure suitable for structural power applications.

1 INTRODUCTION

The mechanical performance and application of polymer-matrix fiber composites is often limited by matrix-dominated failures. 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 dissipation, fire retardance, as well as solvent resistance and ionic/electrical conductivity, offers additional opportunities especially for multifunctional materials. However, due to processing constraints, the nanoreinforcements are typically present only at low loading fractions and in discontinuous form, limiting the level of enhancement.

Previously, we presented an alternative strategy, to form a rigid bicontinuous reinforcing network throughout the matrix volume [1, 2]. A suitable precursor was first infused into a structural fiber weave or other preform, then converted to form a porous monolithic aerogel/xerogel matrix, with characteristic lengthscales around a few tens of nanometers. The presence of the reinforcing fibers allowed the aerogel/xerogel to form a stable, handleable, (preform) structure. Both the rigid network and the porosity are bicontinuous, which allowed a second matrix resin phase to be infused. This second phase may be a soft multifunctional phase; for example, one that can provide sufficient ionic conductivity for use in structural supercapacitors.

Here, we present the second generation of aerogel modified carbon fiber composites, with carbon nanomaterials incorporated into the aerogel network during synthesis. The addition of carbon nanomaterials (depending on choice) is expected to improve the conductivity of the aerogel structure and provide yet further reinforcement to the network, and subsequently the embedded fibers. The nanomaterials can be suspended in a formaldehyde/aqueous phase directly, simplifying any necessary modifications to the existing aerogel synthesis procedure. The subsequent multifunctional composite materials will be tested to evaluate their mechanical and electrical (electrode) performance. Mechanical measurements will focus on matrix performance (modulus and strength), using $\pm 45^\circ$ tension tests which would indicate intrinsic improvements, with fractography undertaken to establish failure mechanisms and the influence of the carbon nanomaterials in the aerogel. Characterization of electrochemical performance in 2- and 3-electrode system by electrochemical impedance spectroscopy, cyclic voltammetry and charge-discharge test will reveal gained improvement in terms of specific capacitance, energy and power.

2 MATERIALS

Resorcinol (ReagentPlus®, 99%), formaldehyde (ACS reagent, 37 wt.% in H₂O, contains 10-15% methanol as stabilizer to prevent polymerization), HPLC water, potassium hydroxide (ACS reagent, $\geq 85\%$, pellets, EMD Millipore), and graphene nanoplatelets (xGnP® grade C-750, XGScience) were used to synthesize the modified carbon aerogel. All materials were used as-received and sourced from Sigma-Aldrich unless stated.

Two different woven fabrics were embedded with aerogel; a typical aerospace grade (C-WEAVE 200P 3K HS X 125CM, Chomarat Group, plain weave) comprised of Toray T300 fibers FT300B 3000-40B carbon fibers from Torayca, and a low aerial weight spread tow fabric (TeXtreme 43 PW HS40 W0/20:21/20:21-1000, Oxeon AB, plain weave with binder) comprised of PYROFIL™ HS 40 high modulus carbon fibers from Mitsubishi Chemical Carbon Fiber and Composites GmbH.

Table 1: Tensile carbon fiber properties

Fiber	Precursor	Tow size	Filament diameter [μm]	Tensile strength [MPa]	Tensile modulus [GPa]	Strain [%]	Density [g/m^3]	Sizing [%]
FT300B 3000-40B [3, 4]	PAN	3K	7	3530	230	1.68	1.75	1.0
HS 40 [5]	PAN	12K	5	4610	425	1.08	1.85	

Table 2: Woven fabric properties

Fabric	Areal density [g/m^2]	Fiber orientation	Warp [ends/cm]	Weft [picks/cm]	Pattern	Nominal thickness [μm]
C-WEAVE 200P 3K HS [6]	200	0°/90°	4.9	4.9	Plain, 1x1	350
TeXtreme 43 PW HS40	86	0°/90°	0.5	0.5	Plain, 1x1	<100

3 DETERMINATION OF A SUITABLE GRAPHENE NANOPATELET LOADING FRACTION IN A RESORCINOL-FORMALDEHYDE SUSPENSION FOR USE WITH VACUUM INFUSION PROCESSES

Introducing carbon nanomaterials, in this instance graphene nanoplatelets, into the carbon aerogel precursor may restrict its suitability to be incorporated into carbon fibers via vacuum assisted infusion processes. The graphene nanoplatelet suspension should ideally contain a high loading fraction of the nanocarbon, flow freely, have a low viscosity and not contain large particulates - which would lead to self-filtration with the closely packed carbon fibers. Various loadings of graphene nanoplatelets (Figure 1), from 0.2 to 7.5 wt.% in suspension (correlating to 0.5 to 20 wt.% solids content in the final embodiment), were mixed with requisite amounts of resorcinol (R), formaldehyde (F), and water [at R:F molar ratio of 2:1, 40 wt.% RF in suspension, ~15 g each] then bath sonicated for 1 h (USC 300 T, 45 kHz, VWR UK). The viscosity of the carbon aerogel precursor suspension was not significantly altered upon addition of graphene nanoplatelets, with the only exception the 7.5 wt.% loading, in which an apparent increase in viscosity was observed. On increasing graphene nanoplatelet content there was a marked increase in unsuspended material which became more prominent in loadings in excess of 1 wt.%. Suspensions for each loading fraction were drop cast onto microscope slides with cover slips directly after sonication to evaluate particle flocs. Flocculation was observed for 1.2 wt.% and higher loadings (Figure 2). These results indicate that even through a substantial loading of graphene nanoplatelets did not alter the viscosity of the suspension; extensive flocculation and increasing particulate sizes (above 1 wt.%) are likely to be detrimental to the infusion process.



Figure 1. Top: Graphene nanoplatelet powders.
Bottom: Resorcinol/formaldehyde/water with graphene nanoplatelets in suspension at loadings of, from left to right, 0.2, 0.4, 0.8, 1.2, 1.6, 2.0, 4.0, 7.5 wt.% (after bath sonication).

4 GRAPHENE NANOPATELET MODIFIED AEROGEL SYNTHESIS

Typical resorcinol-formaldehyde carbon aerogel synthesis is described in detail elsewhere [1, 7]. Modified carbon aerogel synthesis is briefly given as; requisite amounts of resorcinol (R), formaldehyde (F), water, potassium hydroxide at 1 M (aq) (catalyst, C), and graphene nanoplatelets were weighed to ensure a ratio of R:F molar ratio of 2:1, R:C ratio of 50:1, 40 wt.% RF in suspension, and loading of graphene nanoplatelets to achieve 2 wt.% solids contribution (i.e. 98 wt.% RF polymer) after polymerization. Graphene nanoplatelets were directly mixed into approx. 100 ml of formaldehyde split into three sealed round 100 ml bottom flasks and then bath sonicated (USC 300 T, 45 kHz, VWR UK) for 30 min. Additional water was then added to a maximum volume of 50 ml in each flask and the mixture was further bath sonicated, 30 min (Figure 3, left). Meanwhile, the remaining formaldehyde and resorcinol were mixed by stirring (ca. 200 RPM) at room temperature until fully dissolved (ca. 15 min). After sonication the formaldehyde/water/graphene nanoplatelets suspension was immediately added to the stirring solution of resorcinol and formaldehyde along with any remaining water. The mixture was left stirring for 15 minutes at room temperature, then the catalyst solution was added dropwise (Figure 3, right). After a further 15 minutes the suspension was infused into the carbon fibers using a resin infusion under flexible tooling (RIFT) methodology under the pull of the evacuated bag only (Figure 4, left). Once the uptake of carbon aerogel precursor was finished the bag was sealed and the modified carbon aerogel precursor was left to cure at room temperature, 50 °C, and 90 °C for a duration of 24 h each (Figure 4, right). Once cooled the woven fabric infused with modified aerogel precursor were removed from the bag and then placed in a bath of acetone for solvent exchange at room temperature. The acetone was replenished once a day for 3 days and then the modified carbon aerogel precursor loaded fabrics were then left to dry in a fume hood before being pyrolyzed under nitrogen flow at 800 °C.

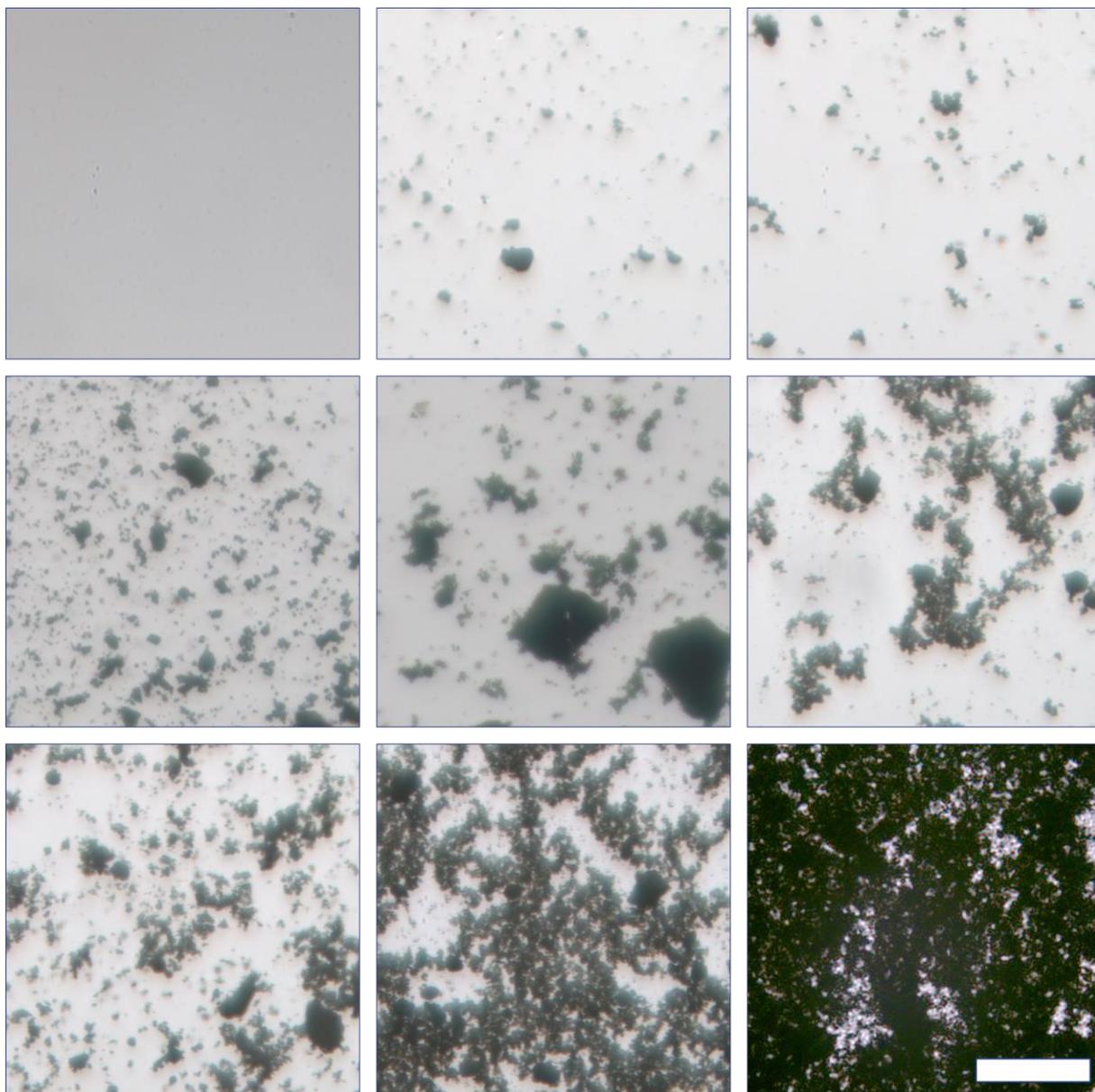


Figure 2. Micrograph 40x magnification for all panes with a common scale bar 50 μm .
Top left: Resorcinol/formaldehyde/water solution (control). Resorcinol/formaldehyde/water
graphene nanoplatelets suspensions with loadings of Top; centre: 0.2 wt.%, right: 0.4 wt.%.
Middle; left: 0.8 wt.%, centre: 1.2 wt.%, right: 1.6 wt.%.
Bottom; left: 2.0 wt.%, centre: 4.0 wt.%, right: 7.5 wt.%.



Figure 3. Left: Photograph of suspension of formaldehyde, water and graphene platelets sonicating. Right: Photograph of modified carbon aerogel precursor suspension stirring before infusion.

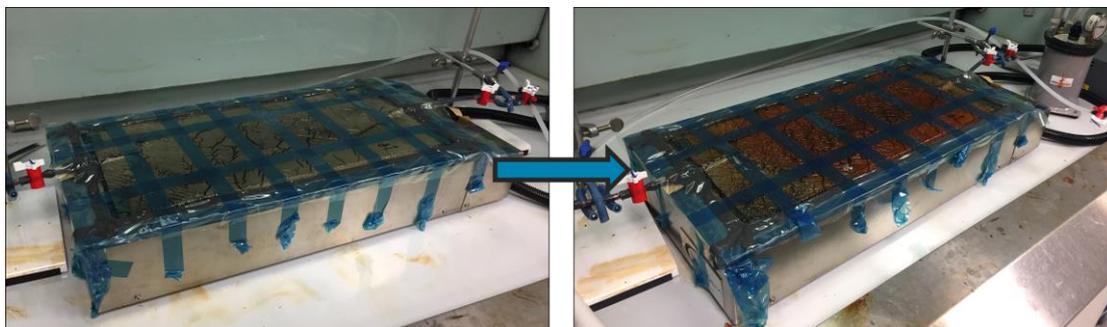


Figure 4. Left: Photograph of RIFT bag containing carbon fiber fabric immediately after infusion of modified carbon aerogel precursor. Right: Photograph of RIFT bag after the curing cycle (3 days later).

5 CONCLUSIONS

An investigation into the suitable loading fractions of graphene nanoplatelets into a carbon aerogel precursor was successful. Graphene nanoplatelet modified carbon aerogel infused carbon fiber samples (at 2 wt.% solids loading) was produced through a vacuum infusion process. The resultant material will be mechanical and electrochemically tested to evaluate its effectiveness as a multifunctional structural electrode material. The investigation will also be expanded to include other suitable nanomaterials in the future. These studies highlight a family of bicontinuous nanostructured matrix systems for hierarchical composites and structural power applications, the development of which has great potential for both purely structural and multifunctional performance enhancements via scalable manufacturing processes.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the funding provided by the EPSRC Future Composites Research Manufacturing Hub (EP/P006701/1), the EPSRC Beyond Structural project (EP/P007465/1), the European Office of Aerospace Research and Development (IOE Grant FA9550-17-1-0251) and EU Clean Sky 2 (SORCERER Project #738085).

REFERENCES

- [1] H. Qian, A.R. Kucernak, E.S. Greenhalgh, A. Bismarck and M.S.P. Shaffer. Multifunctional structural supercapacitor composites based on carbon aerogel modified high performance carbon fiber fabric. *ACS Applied Materials & Interfaces*, **5**(13), 2013, pp. 6113-6122. <http://doi.org/10.1021/am400947j>.
- [2] H. Qian, S.N. Nguyen, D.B. Anthony, A. Singh, S. Xu, E.S. Greenhalgh, A. Bismarck and M.S.P. Shaffer. Stiff monolithic aerogel matrices for structural fiber composites. *Proceedings of 20th International Conference on Composite Materials*, **5212-4**, 2015, pp. 6. <http://www.iccm-central.org/Proceedings/ICCM20proceedings/papers/paper-5212-4.pdf>.
- [3] Toray Carbon Fibers Europe. FT300B-3000-40B Data Sheet. 2012.
- [4] Toray Carbon Fibers Europe. T300 Data Sheet. 2018.
- [5] Mitsubishi Chemical Carbon Fiber and Composites. Pyrofil HS 40 12K Data Sheet. 2018.
- [6] Chomarat Textiles Industries. C-Weave 200P 3K HS Data Sheet. 2010.
- [7] A.M. Elkhatat and S.A. Al-Muhtaseb. Advances in Tailoring Resorcinol-Formaldehyde Organic and Carbon Gels. *Advanced Materials*, **23**(26), 2011, pp. 2887-2903. <http://doi.org/10.1002/adma.201100283>.