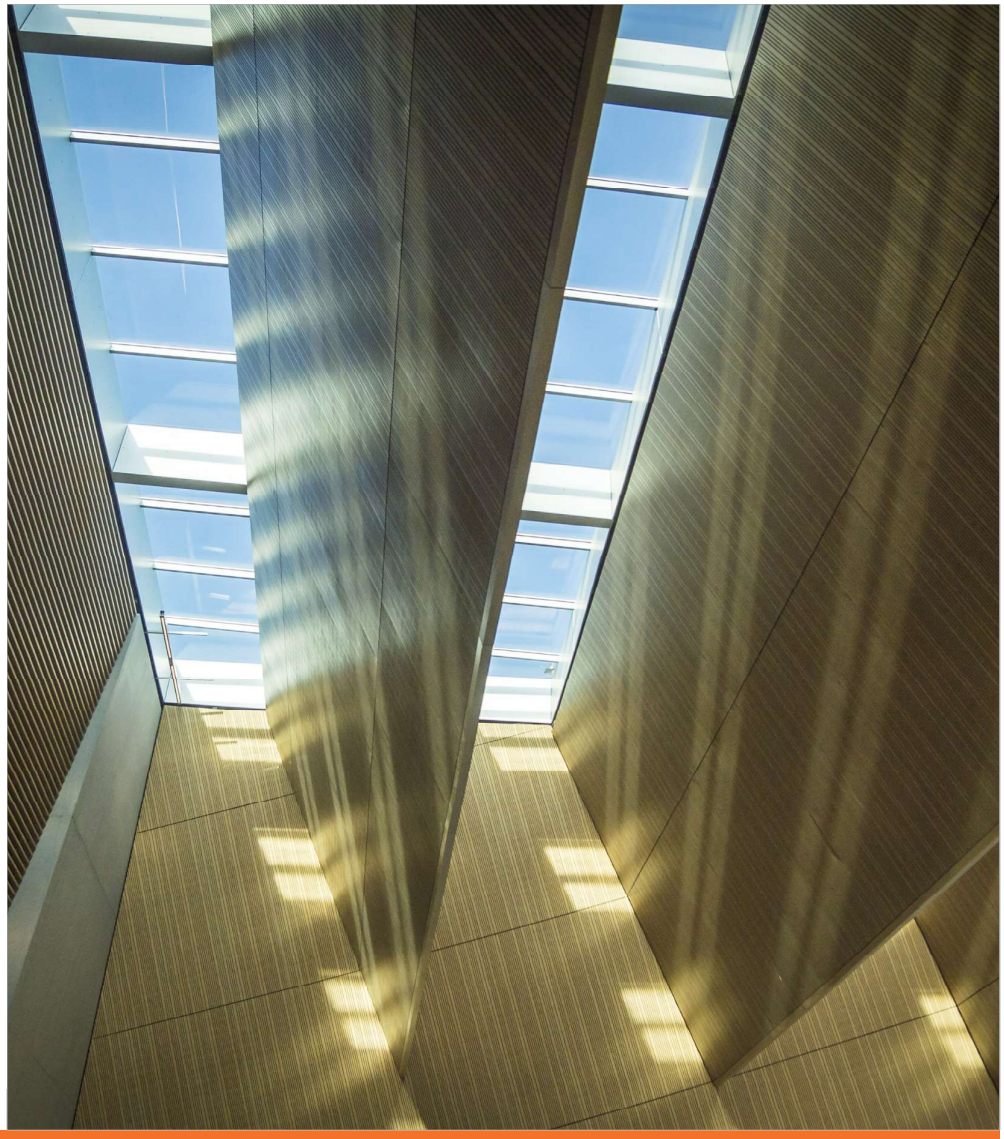
ECCM 20

26-30 JUNE 2022

LAUSANNE SWITZERLAND



Proceedings of the 20th European Conference on Composite Materials

COMPOSITES MEET SUSTAINABILITY

Vol 1 – Materials

Editors : Anastasios P. Vassilopoulos, Véronique Michaud

Organized by :

EPFL

Under the patronage of :

CCLAB Composite Construction Laboratory

LPAC Laboratory for Processing of Advanced Composites

ESCM EUROPEAN SOCIETY FOR COMPOSITE MATERIALS

ECCM 20
26-30 JUNE 2022
LAUSANNE SWITZERLAND

EPFL CCLAB Composite Construction Laboratory LPAC Laboratory for Processing of Advanced Composites

Proceedings of the 20th European Conference on Composite Materials

ECCM20

26-30 June 2022,

EPFL Lausanne Switzerland

Edited By :

Prof. Anastasios P. Vassilopoulos, CCLab/EPFL
Prof. Véronique Michaud, LPAC/EPFL

Oragnized by:

Composite Construction Laboratory (CCLab)
Laboratory for Processing of Advanced Composites (LPAC)
Ecole Polytechnique Fédérale de Lausanne (EPFL)

ISBN: 978-2-9701614-0-0
DOI: http://dx.doi.org/10.5075/epfl-298799_978-2-9701614-0-0

Published by :

Composite Construction Laboratory (CCLab)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
BP 2225 (Bâtiment BP), Station 16
1015, Lausanne, Switzerland

https://cclab.epfl.ch

Laboratory for Processing of Advanced Composites (LPAC)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
MXG 139 (Bâtiment MXG), Station 12
1015, Lausanne, Switzerland

https://lpac.epfl.ch

Cover:

Swiss Tech Convention Center
© Edouard Venceslau - CompuWeb SA

Cover Design:

Composite Construction Laboratory (CCLab)
Ecole Polytechnique Fédérale de Lausanne (EPFL)
Lausanne, Switzerland

©2022 ECCM20/The publishers

Disclaimer:

Editorial

This collection gathers all the articles that were submitted and presented at the 20th European Conference on Composite Materials (ECCM20) which took place in Lausanne, Switzerland, June 26-30, 2022.

ECCM20 is the 20th edition of a conference series having its roots back in time, organized each two years by members of the European Society of Composite Materials (ESCM).

The ECCM20 event was organized by the Composite Construction laboratory (CCLab) and the Laboratory for Processing of Advanced Composites (LPAC) of the Ecole Polytechnique Fédérale de Lausanne (EPFL).

The Conference Theme this year was "Composites meet Sustainability". As a result, even if all topics related to composite processing, properties and applications have been covered, sustainability aspects were highlighted with specific lectures, roundtables and sessions on a range of topics, from bio-based composites to energy efficiency in materials production and use phases, as well as end-of-life scenarios and recycling.

More than 1000 participants shared their recent research results and participated to fruitful discussions during the five conference days, while they contributed more than 850 papers which form the six volumes of the conference proceedings. Each volume gathers contributions on specific topics:

Vol 1 – Materials

Vol 2 – Manufacturing

Vol 3 – Characterization

Vol 4 – Modeling and Prediction

Vol 5 – Applications and Structures

Vol 6 – Life Cycle Assessment

We enjoyed the event; we had the chance to meet each other in person again, shake hands, hold friendly talks, and maintain our long-lasting collaborations. We appreciated the high level of the research presented at the conference and the quality of the submissions that are now collected in these six volumes. We hope that everyone interested in the status of the European Composites' research in 2022 will be fascinated by this publication.

The Conference Chairs

Anastasios P. Vassilopoulos, Véronique Michaud

ECCM 20
26-30 JUNE 2022
LAUSANNE SWITZERLAND

Hosting Organizations

Composite Construction Laboratory (CCLab)
Laboratory for Processing of Advanced Composites (LPAC)
Ecole Polytechnique Fédérale de Lausanne (EPFL)

Venue

Swiss Tech Convention Center (https://www.stcc.ch)

Conference Chairs

Chair : Prof. Anastasios P. Vassilopoulos, EPFL, Switzerland
Co-Chair: Prof Véronique Michaud, EPFL, Switzerland

International Scientific Committee

Prof. Malin Åkermo SE
Dr. Emmanuel Baranger FR
Prof. Christophe Binetruy FR
Prof. Pedro Camanho PT
Prof. Konstantinos Dassios GR
Prof. Brian Falzon UK
Prof. Kristofer Gamstedt SE
Prof. Sotiris Grammatikos NO
Prof. Christian Hochard FR
Prof. Marcin Kozlowski PL
Prof. Stepan Lomov BE
Dr. David May DE
Prof. Stephen Ogin UK
Prof. Gerald Pinter AT
Prof. Silvestre Pinho UK
Prof. Yentl Swolfs BE
Dr. Julie Teuwen NL
Dr. Panayota Tsotra CH
Prof. Wim van Paepegem BE
Prof. Dimitrios Zarouchas NL
Dr. Andrey Aniskevich LV
Prof. Christian Berggreen DK
Dr. Nicolas Boyard FR
Prof. Valter Carvelli IT
Prof. Klaus Drechsler DE
Prof. Bodo Fiedler DE
Dr. Nathalie Godin FR
Prof. Roland Hinterholzl AT
Prof. Ian Kinloch UK
Dr. Thomas Kruse DE
Prof. Theodoros Loutas GR
Prof. Veronique Michaud CH
Prof. Alessandro Pegoretti IT
Prof. Joao Ramoa Correia PT
Prof. Jose Sena-Cruz PT
Prof. Antonio T. Marques PT
Prof. Thanasis Triantafillou GR
Prof. Albert Turon ES
Prof. Anastasios P. Vassilopoulos CH
Prof. Martin Fagerström SE
Dr. Alexandros Antoniou DE
Prof. Lars Berglund SE
Prof. Michal Budzik DK
Prof. Lucas Da Silva PT
Dr. Andreas Endruweit UK
Prof. Mariaenrica Frigione IT
Dr. Larissa Gorbatikh BE
Dr. Martin Hirsekorn FR
Prof. Vassilis Kostopoulos GR
Prof. Jacques Lamon FR
Prof. Staffan Lundstrom SE
Prof. Peter Mitschang DE
Dr. Soraia Pimenta UK
Prof. Paul Robinson UK
Dr. Olesja Starkova LT
Prof. Sofia Teixeira de Freitas NL
Dr. Stavros Tsantzalis GR
Prof. Danny van Hemelrijck BE
Prof. Michele Zappalorto IT
Dr. Miroslav Cerny CZ

Local Organizing Committee

Prof. Anastasios P. Vassilopoulos, EPFL
Prof. Véronique Michaud, EPFL
Angélique Crettenand and Mirjam Kiener, Lausanne Tourisme
And all those who helped, colleagues who reviewed abstracts and chaired sessions, and CCLab and LPAC students and collaborators who worked hard to make this conference a success.

ECCM 20
26-30 JUNE 2022
LAUSANNE SWITZERLAND

Sponsors

SHIMADZU
Excellence in Science

Bristol Composites Institute

JEC GROUP

suprem

Surface Measurement Systems
World Leader in Sorption Science

INSTRON

9T LABS

Anton Paar

DIA-STRON
DELIVERING MEASUREMENT SOLUTIONS

AELER

HRC

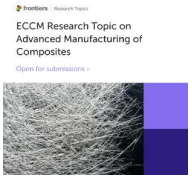
ICCM 23
BELFAST 2023
30 JULY - 4 AUGUST

TEIJIN

Functional Composite Materials

materials
an Open Access Journal by MDPI

ELSEVIER



Supporting partners

JEC

CertBond
COST Action CA18120

EsSENce

Switzerland Tourism.

SWISS

SBB CFF FFS

sampe
Switzerland

COMPOSITES UNITED | SWITZERLAND

canton de vaud

Lausanne

Contents

DESIGNING BICONTINUOUS SILICA-EPOXY NANOCOMPOSITES

Charles M.D. Shaw[a], David B. Anthony[b], Joseph Garguili[c], Ian Hamerton[c], Milo S.P. Shaffer[b]

a: Department of Materials, Imperial College London, UK – c.shaw20@imperial.ac.uk
b: Department of Chemistry, Imperial College London, UK
c: Bristol Composites Institute, Department of Aerospace Engineering, University of Bristol, UK

Abstract: *A nanocomposite reinforced with a 3D, connected, stiff framework should offer better performance than a simple dispersion of nanoparticles. Monolithic porous silica can be used as this framework by providing a fully connected but open porous supporting skeleton for reinforcing organic polymers. Infusion of epoxy resin into silica aerogel pores may produce a bicontinuous material that more efficiently exploits the intrinsic properties of each solid phase: bicontinuous aerogel and polymer matrix component. Matrix infusion into an aerogel monolith in principle allows greater silica content than shear mixing (of particles) which is limited by aggregation and high shear viscosities. Silica content is maximised by producing aerogels of unusually high envelope density (0.2 g.cm^{-3} – 0.8 g.cm^{-3}).*

Keywords: Silica; Aerogel; Bicontinuous; Hybrid; Nanoreinforcement

1. Introduction

Epoxies are widely used in structural composites due to their high toughness, ease of processing, and good interfacial compatibility with reinforcing materials. However, they lack stiffness when compared to inorganic materials and some high-end thermoplastics. Silica particles dispersed within epoxy resin can improve elastic modulus without loss of toughness [1]. However, this approach increases resin viscosity which hinders processing [2], and lacks any long-range connectivity between the particles. By pre-forming a porous silica monolith, and backfilling with epoxy, a structure consisting of a fully bicontinuous, silica-epoxy network may be achieved. In this architecture, the reinforcement is evenly distributed. forming an interlocked inorganic-organic hybrid with characteristic lengthscales of less than 10 nm. The bicontinuous structure facilitates improved load transfer for greater stiffness and introduces additional failure modes for greater energy absorption [3].

Silica aerogel was chosen as the porous silica phase for this material for its simple, low-temperature synthesis and controllable mesoporosity. Pure silica aerogel is intrinsically brittle due to the weakness of interparticle neck regions in its “pearl necklace” morphology. Improved mechanical performance has been reported when the fragile network is crosslinked with organic polymers to give an X-aerogel [4]. Aerogel-based hybrids are typically made with low loadings of secondary materials to preserve the characteristic low density and thermally insulating properties of the aerogel. In this work, we aim to use the aerogel as a 3D reinforcing element in which the pores are completely backfilled with a commercially available epoxy resin, encasing the silica network as a stiff skeletal reinforcement to the epoxy. A comparison of the microstructures of the various silica-epoxy nanocomposites so far described is shown in Figure 1.

  doi:10.5075/epfl-298799_978-2-9701614-0-0

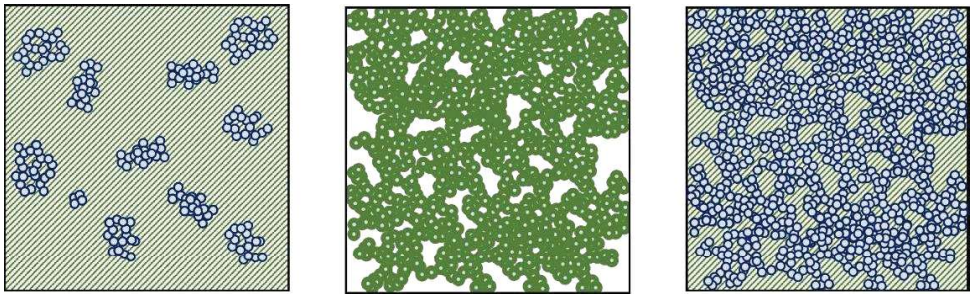


Figure 1. Cartoons depicting the microstructures of epoxy-silica nanocomposites. Left: Epoxy resin (green) reinforced with powdered silica aerogel (blue). Centre: Epoxy-crosslinked silica X-aerogel (light blue aerogel with dark green epoxy crosslinking. Right: Bicontinuous silica-epoxy hybrid monolith (blue aerogel and green epoxy).

Silica aerogel has previously been used produce a composite polymer electrolyte by backfilling with poly(ethylene oxide) (PEO) under reduced pressures [5]. In this material, the stiff silica backbone reinforces the mechanically weak PEO enabling suppression of lithium dendrite formation. We propose that a similar vacuum technique can be applied to fill mesoporous silica monoliths with epoxy resin, combining tough epoxy with stiff silica to produce a bicontinuous composite with greater stiffness than unreinforced epoxy without loss of toughness. Silica content is maximised by producing aerogels of unusually high envelope density (0.2 $g.cm^{-3}$ - 0.8 $g.cm^{-3}$). Aerogel density is restricted by the limited miscibility of siloxane precursors with water; high densities are achieved by maximising miscibility to give high siloxane concentrations. In this work, gels are dried from supercritical CO_2 to limit the influence of pore shrinkage on the final monolith density and, hence, envelope density is controlled directly from the precursor siloxane concentration. We describe the process to make such materials on a scale suitable for mechanical testing, and these tests will be conducted at a later stage.

2. Experimental

2.1 Materials

For the synthesis of silica aerogel monoliths tetramethylorthosilicate (98%, TMOS) and chlorotrimethylsilane (≥ 98%, TMCS) were purchased from Sigma Aldrich, and acetone (technical grade), ethanol (absolute), water (HPLC grade), and *n*-hexane (dehydrated) were purchased from VWR. An epoxy resin with its associated hardener (Gurit Prime 27 epoxy resin and Prime Extra Slow hardener, Marineware Ltd.) were infused into the silica aerogel monoliths to produce silica-epoxy bicontinuous composites. The epoxy and hardener were mixed according to manufacturer's instructions and degassed before use. All chemicals were used as received.

2.2 Silica Aerogel Synthesis and Characterisation

Silica aerogel monoliths were produced by combining water and TMOS in a molar ratio of 24:1. This mixture was stirred for 1 h at 25 °C to give a single transparent sol phase which was then poured into a mould. Cylindrical aerogel samples were cast in moulds made by machining 20 mm thick high-density polyethylene (HDPE) sheet (PE 300, Direct Plastics) on an AXYZ CNC router. Gelled samples were aged for 4 days at 25 °C to ensure complete reaction before exchanging from residual solvent to ethanol. Hydrophobisation of the silica surface was performed by immersion in a TMCS:*n*-hexane:ethanol mixture (1:1:8 ratio by volume). Samples were then

  doi:10.5075/epfl-298799_978-2-9701614-0-0

exchanged back to ethanol before a final exchange to acetone over 3 days. Finally, samples were dried from supercritical CO_2 using a Leica EM CPD300 critical point dryer. Envelope densities were determined by Archimedes' balance method in de-ionised water. Skeletal density was determined by helium pycnometry (Micrometrics AccuPyc II 1340). Specific surface area, pore volume, and pore radius distributions were determined from gas sorption isotherms (N_2) using a Quantachrome NOVAtouch gas sorption analyser.

2.4 Epoxy Infusion in Silica Aerogel Monoliths to Produce Composites

Silica aerogel cylinders (diameter ≈ 5.5 mm, length ≈ 15 mm) were backfilled with epoxy by immersion in epoxy resin/hardener mixture under reduced pressure. The chosen commercially available resin system has low viscosity (170 cP to 180 cP at 25 °C) and long vacuum flow time (7 h 40 min at 25 °C). Owing to their fragility, aerogel monoliths were supported in heat-shrink tubing during infusion. Once immersed, the entire system was evacuated to 1 mbar in a vacuum oven for 6 h at 25 °C.

2.5 Composite Characterisation

The degree of infusion of epoxy into the porous silica structure was quantified as a backfill volume percentage (β) using Equation (1),

$$\beta = \frac{\Delta\rho_b}{\varphi.\rho_e} \quad (1)$$

where $\Delta\rho_b$ is the difference in envelope density between the unmodified silica aerogel monolith and the epoxy-infused silica aerogel monolith, φ is the porosity of the silica aerogel monolith, and ρ_e is the cured epoxy density determined by Archimedes' balance method. The change in morphology following epoxy backfilling is observed by scanning electron microscopy using a LEO Gemini 1525 FEG SEM set at 5 kV with In lens detector.

3. Results and Discussion

The silica aerogel synthesis employed here was designed for scalability and processability. TMOS was chosen for its ability to react with water and self-mix from an initially biphasic liquid by evolving methanol without the need for additional solvents or catalysts. This miscibility is higher than that for alternative orthosilicates facilitating the formation of aerogels with higher bulk density giving a higher loading of silica reinforcement in the silica-epoxy composite. Samples were dried from supercritical CO_2 to eliminate capillary pressures resulting from solvent evaporation. This process minimises pore collapse which would otherwise result in increased envelope density and smaller pore radii which may inhibit infusion of epoxy. Samples were hydrophobised by reacting TMCS with surface silanol (OH) groups. This treatment was performed for the following reasons:

- Hydrophilic (non TMCS-treated) samples formed in this work were found to fracture in the presence of ambient moisture.
- Hydrogen bonded water molecules would be difficult to remove ahead of epoxy infusion. This residual water could affect the epoxy cure and produce voids in the composite structure.
- Furthermore, functionalisation with trimethylsilyl groups prevents silanol groups from reacting chemically with epoxy resin or hardener. This reaction may alter the

  doi:10.5075/epfl-298799_978-2-9701614-0-0

stoichiometry of the epoxy resin/hardener mixture. Silica-epoxy bi-continuous materials with a designed covalent interface will nevertheless be explored in future work.

Density and pore structure characteristics for the silica aerogel are summarised in Table 1. The BJH pore size distribution indicates that most of the porosity comprises mesopores with radii between 2 nm and 3.2 nm (Figure 2). The large specific surface area of silica aerogel (951 $m^2.g^{-1}$) results in an equally large silica-epoxy interface. This may increase the toughness of the material through crack pinning and deflection. Dry silica aerogel monoliths were translucent and bluish in colour due to Rayleigh scattering in the porous structure (Figure 3). Following epoxy infusion, the composite was uniform in appearance with greater transparency than uninfused aerogel (Figure 3) due to reduced scattering and closer matching of refractive indices [5]. Once cured, excess epoxy was removed, and the dimensions of the cylinder were measured to ensure that only the epoxy-silica composite remained. The mean backfill vol.%, β = 99.3% was calculated for six samples using Eq. (1) as summarised in Table 2. This value indicates that infusion of liquid epoxy into the porous epoxy structure was almost complete. Scanning electron microscopy images show the filling of pores by epoxy (Figure 4).

Table 1: Silica aerogel monolith properties where ρ_b is envelope density, ρ_s is skeletal density, SSA is specific surface area, r_{pore} is mean pore radius and V_{pore} is pore volume.

ρ_b ($g.cm^{-3}$)	ρ_s ($g.cm^{-3}$)	SSA ($m^2.g^{-1}$)	r_{pore} (nm)	V_{pore} ($cm^3.g^{-1}$)
0.226 ± 0.009	1.50 ± 0.02	951 ± 25	2.60 ± 0.17	3.81 ± 0.25

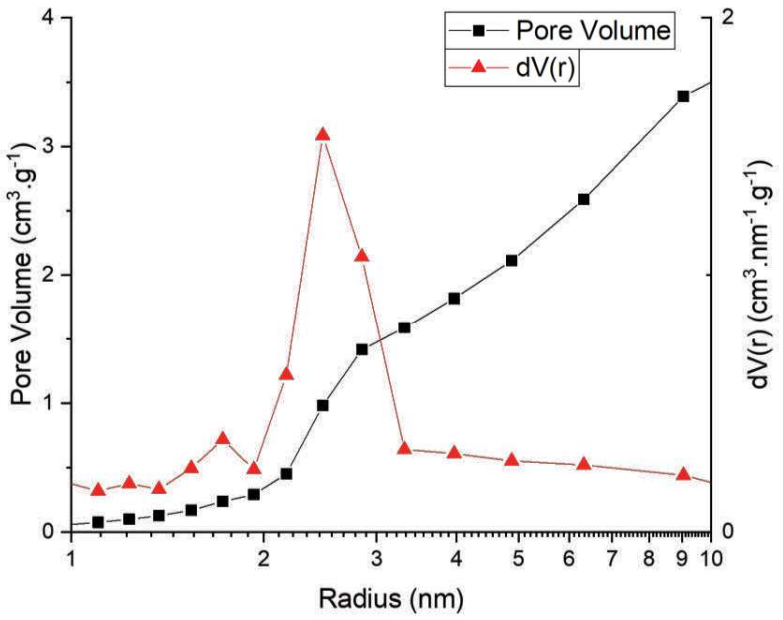


Figure 2: BJH plot calculated from silica aerogel gas sorption isotherm with the differential with respect to the pore radius included.

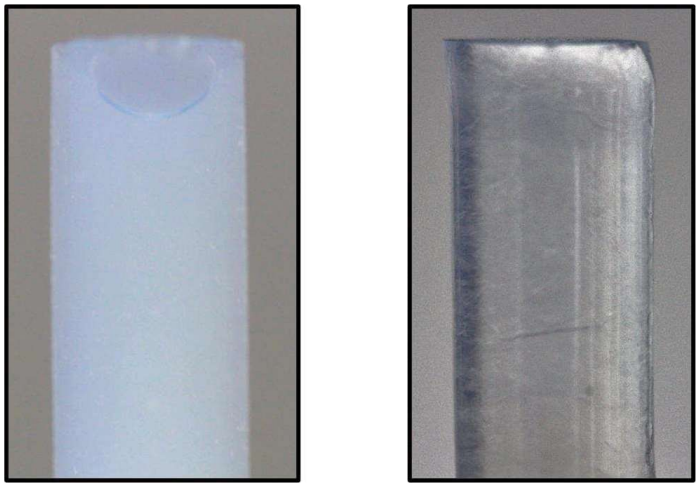


Figure 3: Photograph of silica aerogel monolith (left) and epoxy-infused silica aerogel monolith (right).

Table 2: Summary of composition of bicontinuous silica-epoxy material. Uncertainty is given as one standard deviation.

ρ_f ($g.cm^{-3}$)	Backfill vol.%	Void vol.%	Silica wt.%	Epoxy wt.%
1.189 ± 0.016	99.3 ± 1.9	0.6 ± 1.6	18.5 ± 0.7	81.5 ± 0.7

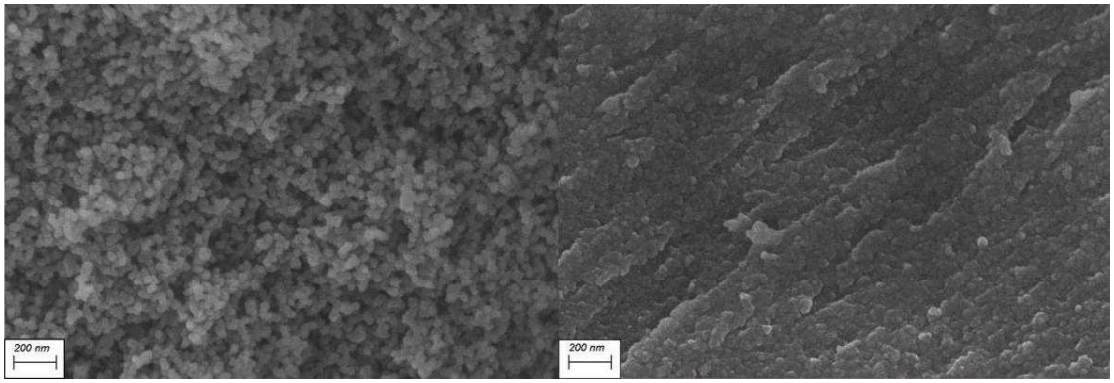


Figure 4: Scanning electron micrographs for silica aerogel before (left) and after (right) infusion with epoxy resin.

4. Conclusions

A silica-epoxy inorganic-organic bicontinuous hybrid composite material has been produced by backfilling mesoporous monolithic silica aerogel with liquid epoxy resin. Backfill vol.% was calculated from pre- and post-infusion envelope densities and indicated that 99.3 pore vol.% was filled resulting in a void content of 0.6 vol.%. This low void content shows that silica pores with radii of 2.0 nm - 3.2 nm uptake liquid epoxy resin. The resulting composite has a continuous 3D silica reinforcement which will provide the epoxy resin with improved stiffness by facilitating long range load transfer. Pre-forming the silica network as a monolithic structure also enables

high weight loadings of reinforcement without incurring the high viscosities seen in dispersed particulate systems. A simple two component silica aerogel synthesis has been employed which could enable modification of precursor composition to produce higher silica aerogel envelope densities leading to a higher silica content in the bicontinuous composite. Future work will test monolithic samples in compression to determine the optimum silica content for improved mechanical performance. Higher silica volume fractions could also be achieved through application of a lower porosity aerogel with a larger mean pore radius. Such a material may be achieved through selection of appropriate alternative monomers and catalysts or application of templating techniques. This material is currently limited to small scale test samples due to the geometric limitations imposed by critical point drying. Large scale structural elements will require the use of mesoporous silica materials which are stable to ambient pressure drying.

Acknowledgements

The authors kindly acknowledge the funding for this research provided by 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 collaboration with University of Bristol.

5. References

1. Salimian S, Zadhoush A. Water-glass based silica aerogel: unique nanostructured filler for epoxy nanocomposites. Journal of Porous Materials. 2019; 26(6):1755-65.
2. Rahatekar SS, Koziol KKK, Butler SA, Elliott JA, Shaffer MSP, Mackley MR, *et al.* Optical microstructure and viscosity enhancement for an epoxy resin matrix containing multiwall carbon nanotubes. Journal of Rheology. 2006; 50(5):599-610.
3. Quaresimin M, Schulte K, Zappalorto M, Chandrasekaran S. Toughening mechanisms in polymer nanocomposites: From experiments to modelling. Composite Science and Technology. 2016; 123:187-204.
4. Meador MAB, Fabrizio EF, Ilhan F, Dass A, Zhang G, Vassilaras P, *et al.* Cross-linking Amine-Modified Silica Aerogels with Epoxies: Mechanically Strong Lightweight Porous Materials. Chemistry of Materials. 2005; 17(5):1085-98.
5. Lin D, Yuen PY, Liu Y, Liu W, Liu N, Dauskardt RH, *et al.* A Silica-Aerogel-Reinforced Composite Polymer Electrolyte with High Ionic Conductivity and High Modulus. Advanced Materials. 2018; 30(32):1802661.

