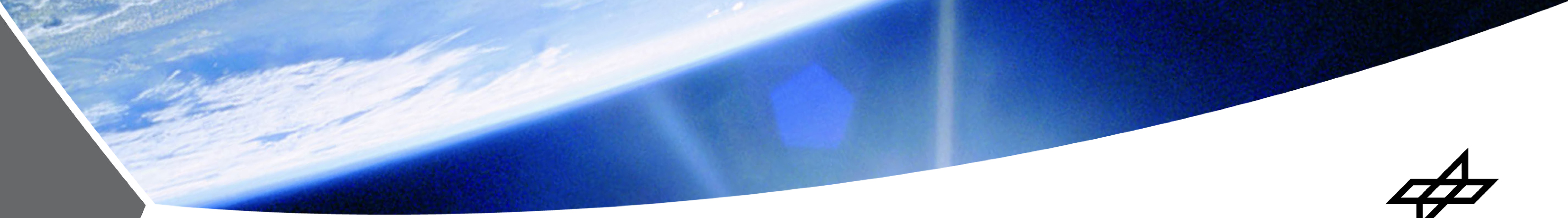


Structural investigations on resorcinol-formaldehyde aerogels and carbon aerogels by means of holotomography

René Tannert[1], Marina Schwan[1], Ameya Rege[2], Julio Cesar da Silva[3], Mario Eggeler[1], Marion Bartsch[1], Barbara Milow[1], Lorenz Ratke[1], Mikhail Itskov [2]

1 *Institute of Materials Research, German Aerospace Center, Cologne, Germany*
2 *Department of Continuum Mechanics, RWTH Aachen University, Aachen, Germany*
3 *Beamline ID16a, European Synchrotron Research Facility (ESRF), Grenoble, France*

MOTIVATION

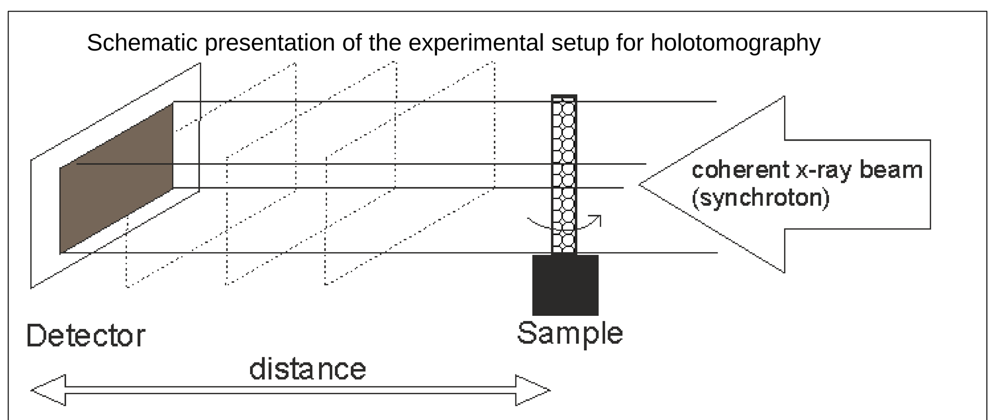
Qualitative assessment of the porous properties of aerogels - Visualization of the 3D-structure:

- REM, TEM etc. are valuable tools for assessment of 2D-structures of high resolution
- No high-resolution 3D-structure of organic aerogels accessible so far due to destruction of the aerogels by absorption of high-energy irradiation
- Holotomography could provide a solution since it does not rely on absorption[1]

Quantitative assessment of porous properties of aerogels – deduction of surface area and pore size distribution:

- Methods based on sorption are limited in scale (e.g. N_2-sorption allows only mesopores to be analyzed)
- Due to aerogel compression mercury porosimetry may lead to erroneous results[2]
- Holotomography can provide highly resolved 3D-reconstructions to be analyzed quantitatively in terms of surface area and pore size using specific software (e.g. Avizo®)
- Well-resolved 3D structure data would be helpful for understanding and tailoring the (nano-)mechanical and thermal properties of aerogels

Schematic presentation of the experimental setup for holotomography



Holotomography involves the treatment of samples with hard x-ray irradiation under variation of the angular position of the sample and its distance from the detector. A subsequent numerical phase retrieval allows the resulting two-dimensional images to be composed to a three-dimensional picture. [1]

EXPERIMENTAL

Preparation of aerogel samples for holotomography:

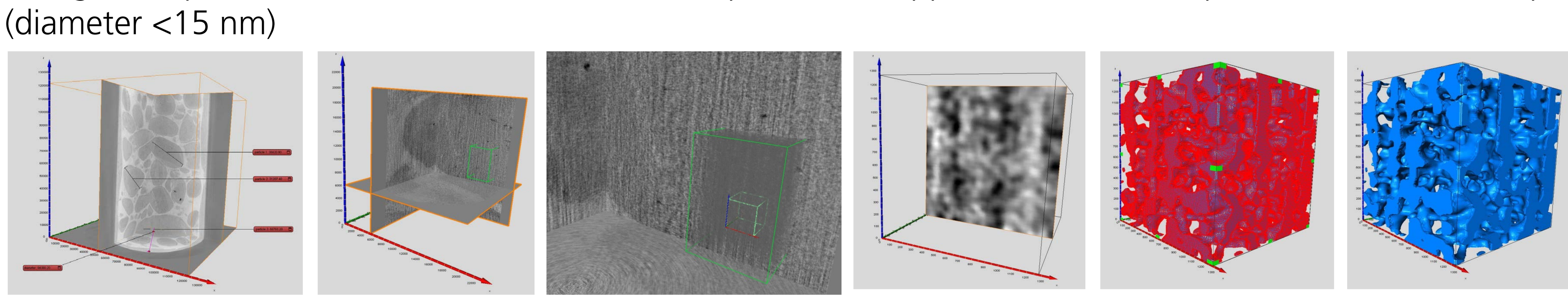
1. Sol-gel synthesis yielded stiff and flexible[3] resorcinol-formaldehyde monoliths.
2. Carbonization yielded monolithic stiff[4] and flexible[5] carbon aerogels.
3. Characterization revealed particle size (scanning electron microscopy), porosity (pycnometry) and surface area (nitrogen sorption isotherms)
4. Suitable milling/ abrasive grinding yielded small particles that retained the properties of the monoliths (as indicated by scanning electron microscopy and nitrogen sorption)
5. The aerogel powder was transferred to thin glass capillaries (100µm diameter), sealed with paraffin wax, and glued onto sample holders for nanotomography.

Tomography and processing of data:

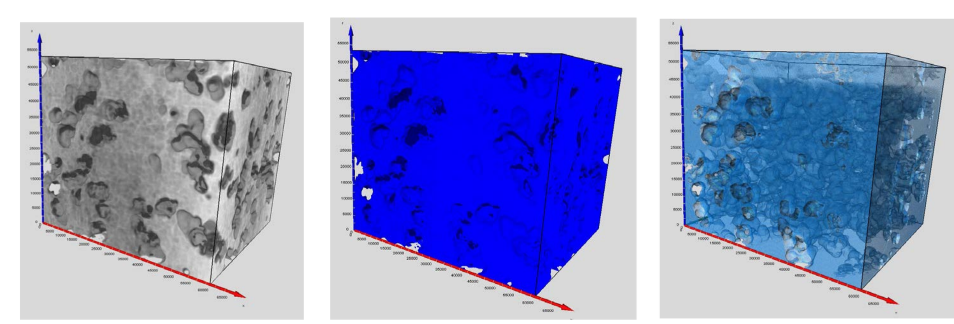
1. Irradiation with hard x-ray at Beamline ID16a with X-ray energy of 17 keV at room temperature. During the tomographic scan the specimens were rotated around the vertical axis. The samples were imaged with 2000 projections at four different distances. Voxel sizes of 10 nm and 60 nm were used.
2. Reconstruction of the projections at ESRF gave raw volumetric data.
3. Processing with "Avizo" allowed visualization and extraction of porous properties.

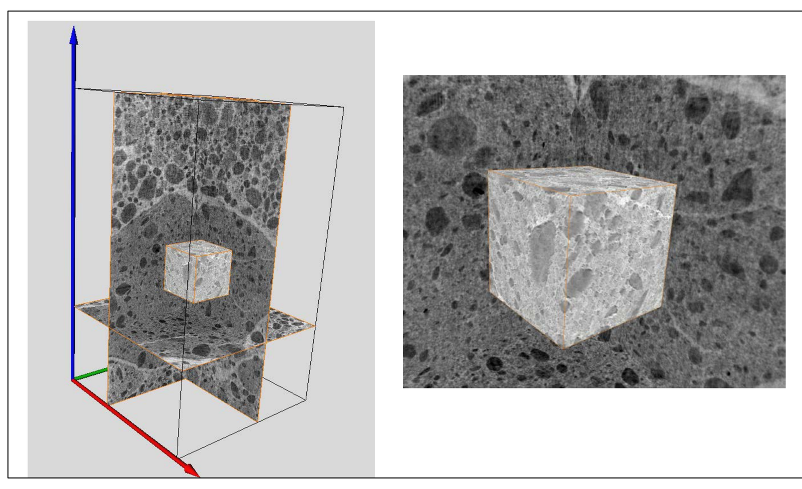
RESULTS & DISCUSSION

Flexible carbon aerogels could be visualized for the 10 nm voxel size experiments. The computed porosity accounts for approximately half of the porosity and the surface area as determined by pycnometry and nitrogen sorption (BET isotherms). Unaccounted pores are supposed to be micropores and small mesopores (diameter <15 nm)



Stiff carbon aerogels could be visualized for experiments with 60 nm voxel size. Little pore space and hardly any surface area were identified indicating that only micropores and mesopores yet almost no macropores are present in that material.



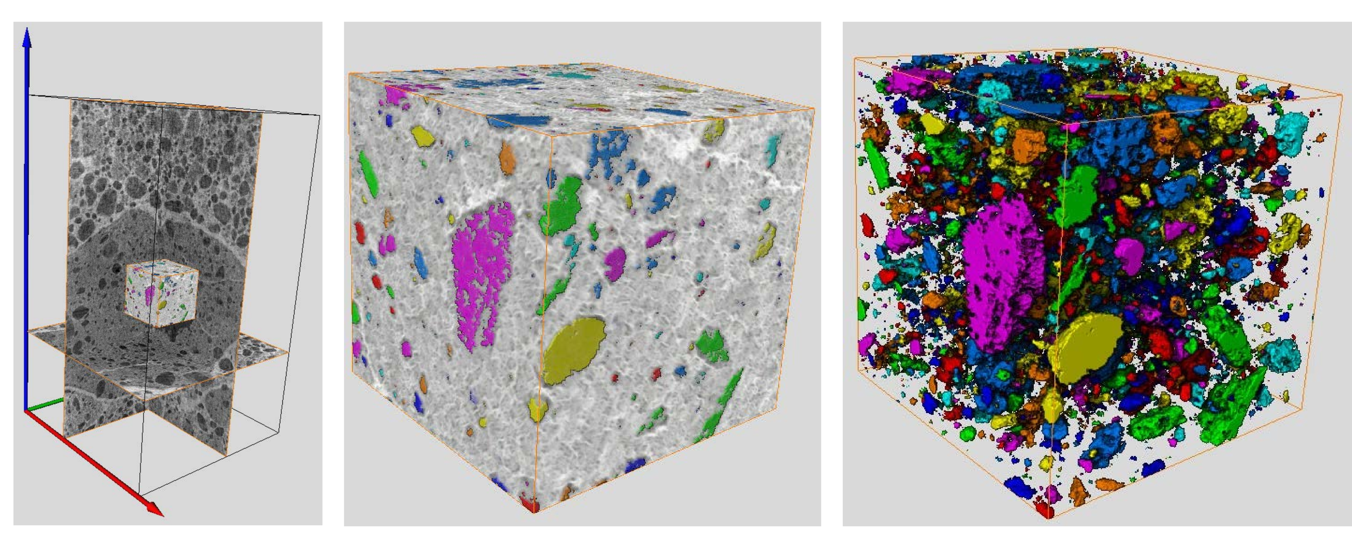


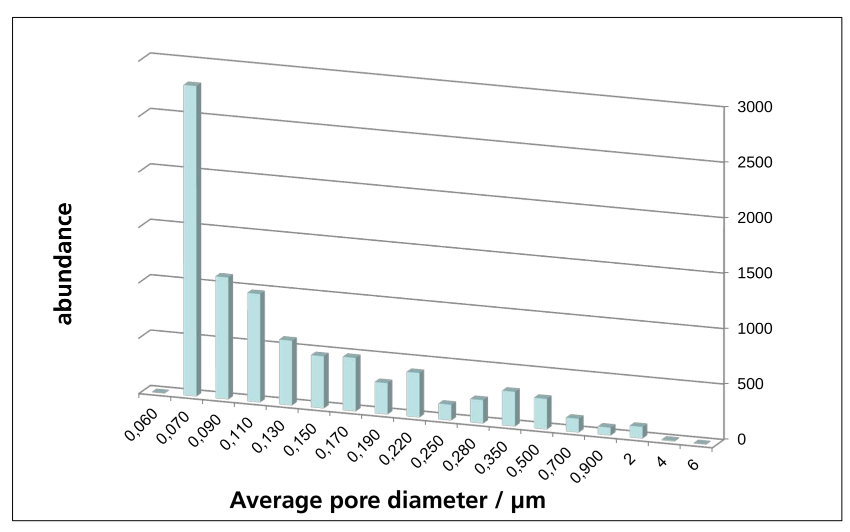
For **flexible RF aerogels**, experiments with 60 nm voxel size were computed to account for a large fraction of the total pore volume (72 % porosity), but only approx. 20 % of the surface area. So, although mesopores seem to account for only a quarter of the total pore volume, the surface area is still dominated by mesopores (80 % mesopores and small macropores).

Porous properties of aerogels subjected to holotomography

Aerogel	Mean aggregate size	Envelope density	BET surface area (N_2 sorption)	Porosity (Pycnometry)	Computed surface area (Avizo software)	Computed porosity (Avizo software)
Flexible Carbon	120 nm +/- 30 nm	0,05 g / cm^3	574 m^2 / g	97 %	267 m^2 / g	55 %
Stiff Carbon	not determined	0,2893 g / cm^3	557 m^2 / g	86%	1,19 m^2 / g	30 %
Flexible Resorcinol-Formaldehyde	110 nm +/- 23 nm	0,06 g / cm^3	52 m^2 / g	96 %	10,0 m^2 / g	72 %

Additionally, flexible RF aerogels could be evaluated in terms of **pore size distribution**. Our processing resulted in 8317 macropores with average diameter > 60nm within a box of 15 µm edge length. This size distribution of these macropores was then calculated indicating a multimodal distribution of pores in the sub-micrometer level. Since many pores appear at the size of one voxel (here: 60 nm), a higher resolved structure would be needed in order to discriminate the size of the smallest macropores further.





Conclusion:

Holotomography could successfully be applied to resorcinol-formaldehyde and carbon aerogels yielding 3D-structural data in the higher nanometer range. Therefore, macropores could be visualized , and the porosity and surface area were computed. In the case of flexible resorcinol-formaldehyde, the (macro)pore size distribution could be calculated and pointed towards a multimodal size distribution at the macropore level.

The pore size distribution of carbon aerogels is subject to current investigations. Further studies will be devoted to extracting further data from experiments with 10 nm voxel size.

References

[1] P. Cloetens, W. Ludwig, J. Baruchel, D. Van Dyck, J. Van Landuyt, J. P. Guigay, M. Schlenker, *Appl. Phys. Lett.* **1999**, *75*, 2912-2914.
[2] G. W. Scherer, D. M. Smith, D. Stein, *J. Non-Cryst. Solids* **1995**, *186*, 309-315.
[3] M. Schwan, R. Tannert, L. Ratke, J. Supercrit. Fluids **2016**, *107*, 201-208.
[4] A. M. ElKhatat, S. A. Al-Muhtaseb, *Adv. Mater. (Weinheim, Germany)* **2011**, *23*, 2887-2903.
[5] M. Schwan, L. Ratke, *C* **2016**, *2*, 22.

Acknowledgements

The authors gratefully acknowledge funding of the project by the German Aerospace Center (DLR-Programmdirektion Verkehr: Program "Next Generation Car") and the European Synchroton Research Facility (grant ID SC-4154).

Contact details

Dr. René Tannert, German Aerospace Center,
Institute of Materials Research, Linder Höhe, D-51147 Köln
Telephone: +49 2203 601-4292; Email: rene.tannert@dlr.de