

Synthesis and Properties of Resorcinol-Formaldehyde Aerogels

Marina Schwan, Barbara Milow, Lorenz Ratke

Institut für Materialphysik im Weltraum, DLR Köln, 51147 Köln, Germany

Introduction

Aerogels are highly porous solid materials with a fascinating combination of properties. In dependence of their nano-structured texture aerogels have a porosity of up to 99.9%. Bulk densities between 0.03 and 0.5 g cm⁻³, thermal conductivities of 0.012 W K⁻¹ m⁻¹ and a low sound velocity lead to applications in the field of thermal and acoustic insulating light weight materials.

Pekala et al. [1] firstly reported of organic aerogels based on resorcinol (R) and formaldehyde (F) in 1989. RF-aerogels are synthesized by a polycondensation reaction via the sol-gel process. The wet gels have to be dried without shrinkage by supercritical drying method. Only if the amount of catalyst is very low it is possible to save the 3D-network structure during ambient pressure drying with a density around 0.3 g cm⁻² [2].

Up to now all RF-aerogels are rigid with strengths of about 100kPa and Young moduli of 1-2 MPa which break easily.

We observe that special conditions of aerogel preparation yield surprisingly flexible aerogels. They can be bent easily (see figure 1), similar to the well-known flexible silica aerogels.



Figure 1: Monolith of a flexible RF-aerogel.

They have a low density, a very low elastic modulus of around 70 kPa and are elastically deformable by more than 40% in an almost reversible manner.

Experimentals

Synthesis of flexible aerogels

RF aerogels are synthesized using resorcinol (98% Aldrich) and formaldehyde (37% in water, stabilized with 10% methanol, Merck), sodium carbonate anhydrous (Aldrich), nitric acid (2N standardized solution, Alfa Aesar) and deionized water.

The molar ratio of R/F is fixed at 0.5 and the R/C at 50 while the R/W is systematically varied from 0.005 to 0.013. At room temperature resorcinol is solved in deionized water, and then formaldehyde is added. After several minutes of stirring sodium carbonate is added as a catalyst and the value of pH is adjusted with nitric acid between 5.4 and 5.6. The solution is filled into vessels, sealed and stored in an oven at 80°C for one week. Afterwards the samples are washed with acetone at room temperature for three days and then dried at 80°C under ambient conditions within 24 hours.

Characterisation

Uniaxial compression tests are carried out using a Chatillon TCD 200-SS Ametek machine. The density is calculated measuring the volume of the samples and their weight. The microstructure is determined using a scanning electron micrographs (Merlin, Zeiss).

Results and Discussion

Influence of R/W molar ratio

RF-aerogels synthesized with a molar ration R/W in the range of 0.006 to 0.010 show flexible behavior. They can be bent and deformed easily and reverted back to their initial shape. RF-aerogels with 0.005 < R/W < 0.006 are hard and brittle. If R/W is lower than 0.005 gelation is not occurred. And if R/W is above 0.010 the synthesized aerogels are corky.

Figure 2 shows the ternary diagram of the system water, resorcinol and formaldehyde.

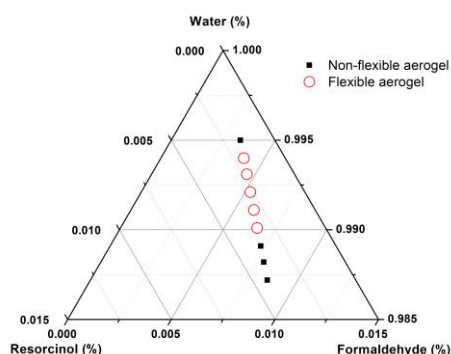


Figure 2: Ternary diagram of water, resorcinol and formaldehyde (red dots: range of R/W leading to flexible R/F-aerogels).

Effect of pH on the bulk density

As reported by Pekala and Schäfer [3, 4] highly cross-linked and branched structures are formed at higher values of pH. The synthesis conditions are primarily responsible for the 3D-network structure of the RF-aerogels. It is observed that in the range of pH 5.05-5.30 the number of resorcinolate ions decrease, weak the cross-linked structure and shrinkage of this gels is bigger. The flexible RF-aerogels presented within this paper are ambient dried even R/C is 0.5 and can only be produced in the pH range between 5.05 and 5.65. For these samples no shrinkage is observed. The density is much lower than for conventional RF-aerogels, it is around 0.075 g cm^{-3} . This is really unusually, because normally shrinkage is not negligible under these conditions. We observe that for samples synthesized with pH values above 5.65 shrinkage is, as expected, huge and the density is around 0.4 g cm^{-3} . In figure 3 the small process window is shown.

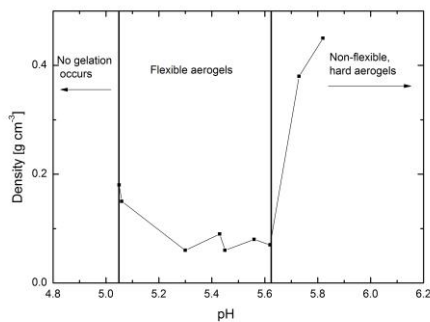


Figure 3: Effect of pH on the bulk density, $R/W=0.008$.

Mechanical behavior

Compression tests show a Young's modulus around 70 to 350 kPa for the flexible compared to 1 to 2 MPa for conventional RF-aerogels. Figure 4 and 5 show the stress-compression curves.

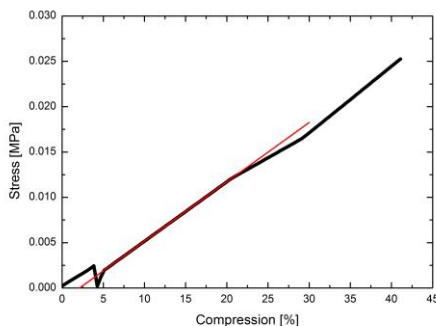


Figure 4: Stress-compression curve of a flexible RF-aerogel, $R/W=0.008$.

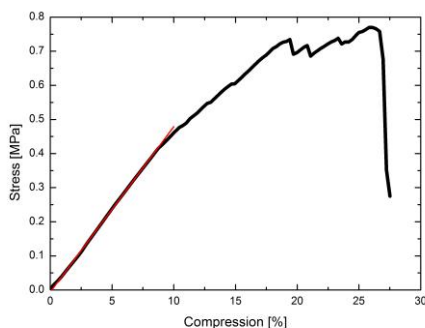


Figure 5: Stress-compression curve of a corky RF-aerogel, $R/W=0.012$.

Microstructure of RF-aerogels

The microstructure of flexible RF-aerogels is more coarsen than the structure of conventional RF-aerogels. In figure 6 and 7 the SEM pictures of flexible and conventional RF-aerogels are shown. The particle size of flexible RF-aerogels is in the range of 1 to $1.2 \mu\text{m}$ while the pore size is between 10 and $20 \mu\text{m}$, the structure looks like it is covered. Conventional RF-aerogels particle size is much smaller, 40 to 80 nm , the structure is more dense and interconnected.

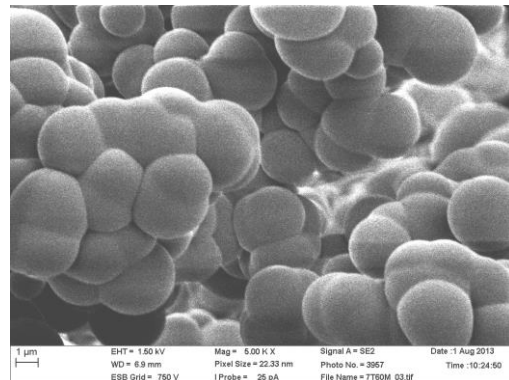


Figure 6: SEM picture of flexible RF-aerogel, $R/W=0.008$.

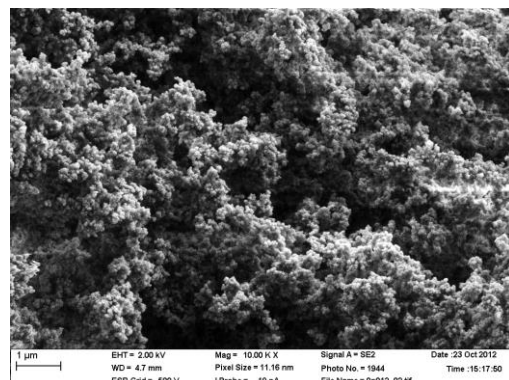


Figure 7: SEM picture of conventional RF-aerogel, $R/W=0.012$.

Leventis et al. [5] predict an increase of bending resistance by a reinforced surface (s. figure 8).

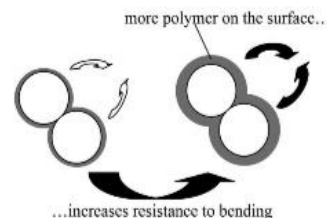


Figure 8: Conformal polymer coating strength the polymer structure.

The structure of the flexible RF-aerogels show that the 3D-network is stronged by covered coarsen structure and is able to withstand shrinkage induced by capillary forces during drying.

Conclusion

Flexible RF-aerogels can be synthesized within a small process window via the well-known Sol-Gel-Process using a well defined molar ratio of R/W at a certain pH value. Large sized particles and huge pores lead to a low density. The reversible bendability is a new property in the class of organic aerogels.

References

- [1] R.W. Pekala, J. Mater. Sci., 1989, **24**, 3221-3227
- [2] U. Fischer, R. Saliger, V. Bock, R. Petricevic, J.J. Fricke, Porous Mater., 1997, 4, 281-285
- [3] D.W. Schaefer, R.W. Pekala, J. Non-Cryst. Solids, 1995, **186**, 159-167.
- [4] R.W. Pekala, D.W. Schaefer, Macromolecules, 1993, **26**, 5487-5493.
- [5] Leventis, N.; Lu, H. Polymer-Crosslinked Aerogels. In Aerogels Handbook; Aegerter, M.A., Leventis, N., Koebel M.M., Eds.; Springer: New York, Dordrecht, Heidelberg, London, 2011, pp 251-285.

Contact

Dr. rer. nat. Barbara Milow
Institut für Materialphysik im Weltraum
Deutsches Zentrum für Luft und Raumfahrt e.V.
51170 Köln, Germany
E-mail:Barbara.Milow@dlr.de
www.dlr.de

You exceed the permitted number of pages!