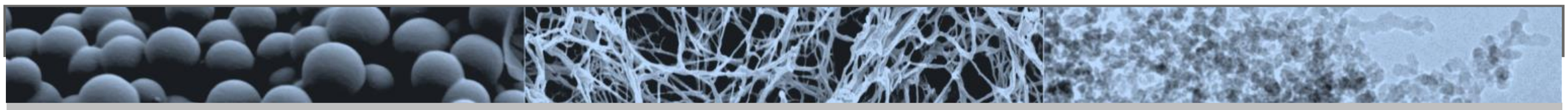
Long-lasting hydrophobization of monolithic phenolic gels via silylation

Fabian Henn, René Tannert, Barbara Milow

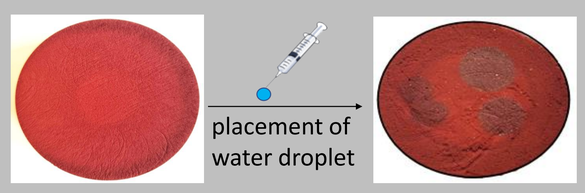
Institute of Materials Research, Department of Aerogels and Aerogel Composites, German Aerospace Center, Linder Hoehe, 51147 Cologne, Germany

fabian.henn@dlr.de



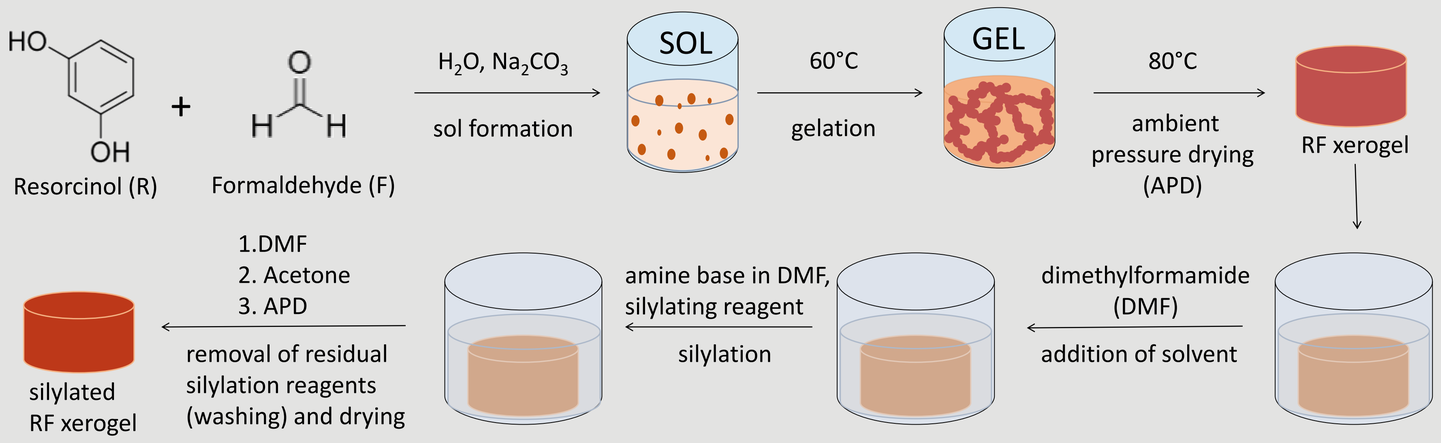
Motivation

- Aerogels and xerogels based on resorcinol-formaldehyde (RF) polymers have promising properties for applications as filters or catalysts[1]
- However, free OH groups of the phenolic gels make them hydrophilic
- Previous publications include post-synthetic silylation of RF gels, but only on powdered materials using small silyl reagents[2-3]
- Our approach is to functionalize monolithic RF xerogels, more specifically to silylate them with sterically demanding silylation reagents to create a long-lasting hydrophobicity



Experimental

Synthesis of silylated RF xerogels

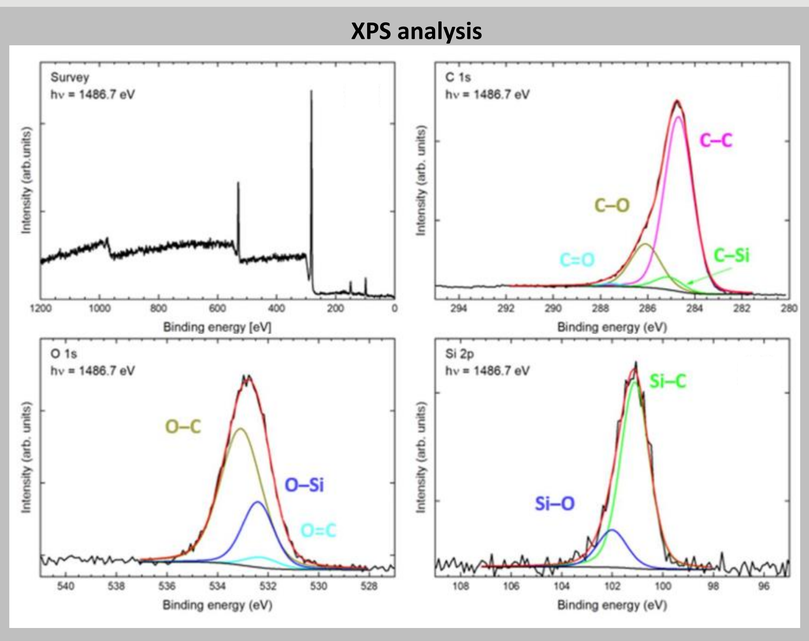


- Silylation using polar aprotic solvents
- Addition of external base
- Use of sterically demanding silylating reagents
- Variation of Si-counterion (electronically activated triflate)

Sample	Silyl Reagent	Base
TMS-A	Trimethylsilyl chloride (TMS-Cl)	Imidazole
TMS-B	Trimethylsilyl triflate (TMS-OTf)	2,6-lutidine
TBS-A	*tert.*-Butyldimethylsilyl chloride (TBS-Cl)	Imidazole
TIPS-A	Triisopropylsilyl triflate (TIPS-OTf)	Imidazole
TIPS-B	Triisopropylsilyl chloride (TIPS-Cl)	2,6-lutidine
TBDPS-A	*tert.*- Butyldiphenylsilyl chloride (TBDPS-Cl)	Imidazole

Characterization & Results

XPS analysis



Elemental analysis

- Successful incorporation of silicon
- Silicon is present in quantities < 2 % by weight
  - ➢ Not all free hydroxy groups were silylated
  - ➢ Chemical reactivity of the phenolic hydroxyl groups in the gel does not seem to be crucial, but rather their accessbility within the pore network

Sample	Si Content [%] (m/m)
TMS-A	0.61
TMS-B	1.16
TBS-A	1.51
TIPS-A	0.20
TIPS-B	0.27
TBDPS-A	1.23

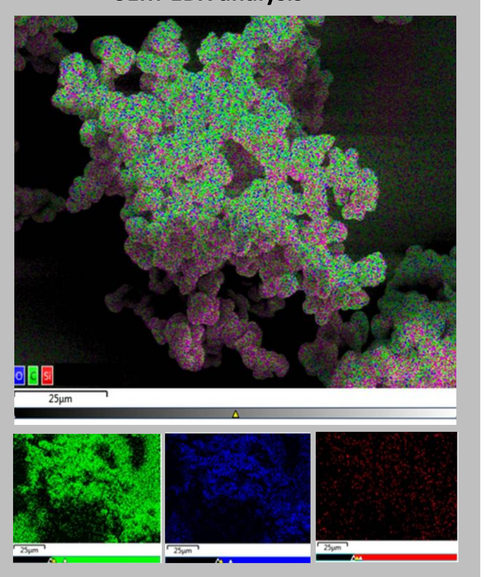
XPS-analysis

- Resulting bond energies clearly indicate the presence of silicon-oxygen bonds
- Ratio of Si-O bonds to Si-C bonds correspond to expected 1:3 ratio for trialkylsilyl ethers
  - ➢ Formation of covalent Si-O bonds

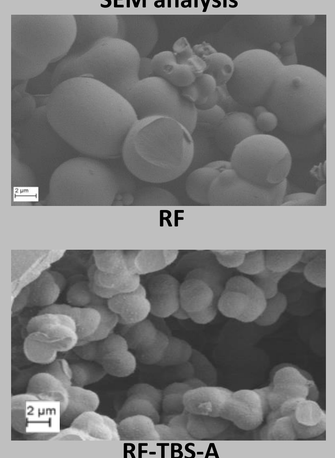
SEM-EDX-Characterization

- SEM-EDX images of an RF xerogel treated with TBS-A
  - ➢ homogeneous distribution of carbon, oxygen and silicon
  - ➢ The lower relative abundance of Si agrees with the hypothesis that not all phenolic hydroxy groups are silylated

SEM-EDX analysis



SEM analysis



Microstructural properties

- Pycnometry revealed slight reduction in porosity for silylated samples
  - ➢ the pore network is not significantly affected by the functionalization process, nor the porous network within the xerogel

Sample	Density [g·cm^{-3}] Envelope	Density [g·cm^{-3}] Skeletal	Porosity [%]	Inner Surface Area [m^2·g^{-1}]
RF	0.3262	1.4453	77.39	0.676 ± 0.003
RF-TMS-B	0.3213	1.3545	76.28	0.411 ± 0.044
RF-TIPS-B	0.3239	1.3685	76.33	0.423 ± 0.008

Static contact angles, as determined using tangent or the LB-ADSA (in brackets) method

	time exposed to air / months: 1	2	3	4	5	8	11
sample	contact angle [°]						
RF	n.a.						
RF-TMS-A	n.a.						
RF-TMS-B	139.5±1.8 (147.5±0,7)	137.2±2.9 (143.0±1.1)	136.5±3.7 (137.1±0.7)	135.7±3.4	n. d.	n. d.	n. d.
RF-TBS-A	136.4±3.0 (140.0±2.9)	136.5±1.5 (142.1±1.0)	135.4±2.1 (142.9±2.5)	135.3±2.4	135.0±1.1	134.5±1.5	134.2±1.3
RF-TIPS-A	142.8±1.2	n. d.	142.6±1.7	n. d.	141.1±2.2	137.9±1.9	136.9±1.9
RF-TIPS-B	143.7±2.0 (151.1±1.1)	143.9±0.4 (149.9±0.6)	140.5±1.8 (146.6±1.7)	139.1±1.3	n. d.	n. d.	n.d.
RF-TBDPS-B	138.3±2.2	n. d.	139.3±3.2	n. d.	139.2±2.2	135.1±1.8	133.9±2.5

Dynamic contact angles, as determined using Wilhelmy method

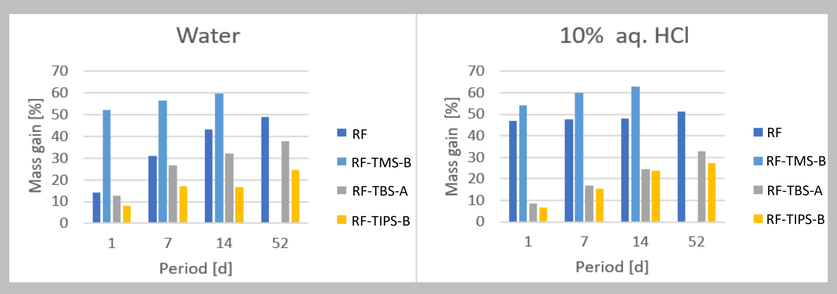
	time exposed to air / months: 1	2	3	4	5	8	11
sample	contact angle [°]						
RF	n.a.						
RF-TMS-A	n.a.						
RF-TMS-B	152.4±1.4	144.9±12.3	143.6±13.0	144.0±1.1	n. d.	n. d.	n. d.
RF-TBS-A	123.8±15.9	121.6±2.4	123.4±12.8	124.3±2.0	136.1±1.7	132.3±2.9	125.3±16.5
RF-TIPS-A	151.9±8.3	n. d.	150.1±7.4	n. d.	146.2±4.8	132.2±2.4	129.8±2.3
RF-TIPS-B	139.1±8.0	137.9±4.0	138.0±1.9	137.4±1.4	n. d.	n. d.	n. d.
RF-TBDPS-B	101.8±11.3	n. d.	112.5±17.1	n. d.	120.0±6.4	112.8±10.7	119.2±5.9

n.a. = not applicable (droplet was absorbed by monolith); n.d. = not determined

Static and dynamic contact angles

- Static contact angles between sample surface and water droplet (tangent method): 133.9 - 143.9°
- Automatized positioning of the tangent using low-bond axisymmetric drop shape analysis (LB-ADSA) consistently results in higher values (137.1 - 151.1°)
- Contact angles determined by Wilhelmy method in range of 101.8 - 152.4°

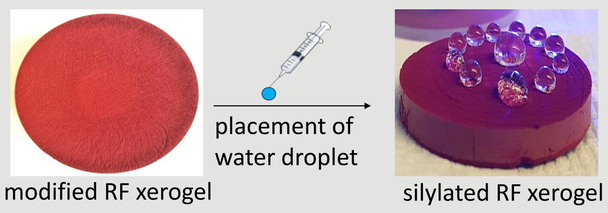
Determination of wetting behavior



- The monoliths in water and 10% aq. HCl were more inert between the silylated variants compared to the RF reference, except for RF-TMS-B
- The effect was still pronounced after 7 weeks

Conclusion

- ➢ A procedure for the silylation of monolithic resorcinol-formaldehyde xerogels has been established
- ➢ Sterically and electronically varied silyl reagents including electronically activated triflates could be applied in solution phase using auxiliary amines as external base
- ➢ Xerogels displayed marked hydrophobicity with contact angles consistently exceeding 130°
- ➢ The hydrophobic properties remained when the monoliths are exposed to humid air for several months
- ➢ RF gels with sterically demanding silyl groups sustained water and even dilute hydrochloric acid for weeks[4]



Acknowledgement

We gratefully acknowledge funding by the German Aerospace Center for the projects NGC FS II and FFAE.

References

[1] M. A. Aegerter, N. Leventis, M. M. Koebel, *Aerogels Handbook*, Springer New York, **2011**.
[2] S. Schwarz, *Organic gels, US6288132B1*, E. I. du Pont de Nemours and Company, U.S.A., **2001**.
[3] I. D. Alonso-Buenaposada, M. A. Montes-Morán, J. A. Menéndez, A. Arenillas, *Reactive and Functional Polymers*, **2017**, *120*, 92-97.
[4] F. Henn, R. Tannert, *Gels*, **2022**, *8*, 304.

24. Symposium Verbundwerkstoffe und Werkstoffverbunde
Verbund 2024

FFAE Fokusanwendungen Fahrzeugstruktur Antriebsstrang Energiemanagement

NGC Next Generation Car

Supported by:
Federal Ministry for Economic Affairs and Climate Action
on the basis of a decision by the German Bundestag
DLR