

## **Reduction of shrinkage and brittleness for resorcinol-formaldehyde aerogels by means of a pH-controlled sol-gel process**

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### Abstract

Aerogels have attracted remarkable attention as porous low-density superinsulating material. However, they are typically brittle and tend to shrink during preparation or work-up preventing their use as a composite material. In that context, we have developed a sol-gel-process towards resorcinol-formaldehyde aerogels that includes a precise pH-adjustment at an early stage of the polymerization. As a result, less brittle analogues of Pekala aerogels were obtained that resemble Pekala gels in many aspects (skeletal density, porosity, thermal properties). However, significant differences were found in terms of inner surface area and compressive modulus, which are smaller for lower pH-values. Since pH-adjustment leads to minimal gel shrinkage, this sol-gel-process may be useful for the development of aerogel composites.

Keywords: Aerogels · Sol-Gel Process · Shrinkage · Density · Compressive modulus· Thermal conductivity

### **Introduction**

Due to their remarkable thermal insulation properties in conjunction with a very low bulk density and high porosity aerogels are materials with a wide range of interesting applications [1-5]. They have already proven applicability in aerospace research [6] and are under investigation as insulation material of the future in the building sector [7, 8]. Especially, the incorporation of aerogels in novel composites is in the focus of current research and development of functional materials [5, 9].

In 1989, Pekala and coworkers demonstrated that organic aerogels can be prepared by a base-catalyzed polycondensation of resorcinol and formaldehyde (RF aerogels) using a sol-gel process followed by drying of the solvent using supercritical carbon dioxide [10, 11]. Such aerogels were later shown to display an extremely low thermal conductivity [12].

Just as their inorganic counterparts, however, RF and related organic aerogels are typically brittle in nature which renders them difficult to handle and process [13].

In addition, aerogels prepared by the base-catalyzed route tend to shrink significantly even though supercritical drying is involved in the work-up procedure [14]. Shrinkage, however, is one of the key problems to be addressed when an aerogel is to be embedded into a composite [9].

Pekala and others have conducted first studies regarding the structure-property relationship of RF aerogels. A dependence of thermal conductivity on aerogel bulk density was described by the groups of Pekala, Fricke and coworkers with minimal thermal insulation of  $0.012 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  identified at a density of approximately  $0.16 \text{ g}\cdot\text{cm}^{-3}$  [12, 15].

After Pekala's pioneering studies on base-catalyzed RF polymerizations, Lin and Ritter studied the influence of variations of pH on some properties of the resulting carbon

xerogels. They found that a moderate acidification of the sol using nitric acid resulted in xerogels with an increased surface area, content of mesopores, and average pore volume [16]. Further studies have been published that describe the addition of acids such as perchloric acid (in acetone) [17], HNO<sub>3</sub> [18] or acetic acid [19, 20] for the synthesis of RF aerogels. At Lawrence Livermore National Institute, a process using a combination of trimethylamine and hydrochloric acid in organic solvents was developed [21]. More recently, the Leventis group studied the use of hydrochloric acid without prior addition of base and came up with a synthetic process for RF aerogels that lasts only minutes at 80 °C in acetonitrile [22]. However, these procedures relying on the addition of acids alone typically yield aerogels with different morphology when compared to base-catalysis (lower BET surface area, bigger particles and pores) [23, 24].

Using an approach similar to that of Lin and Ritter, our research group recently prepared RF aerogels at low resorcinol concentrations (R:W = 0.006-0.013) and incorporating an acidification step into the synthetic procedure. Surprisingly, novel, highly flexible aerogels with an envelope density of 0.06-0.08 g·cm<sup>-3</sup> could be prepared [25]. The synthesis and work-up procedure did not cause significant shrinkage to the aerogel monoliths enabling us to demonstrate their use as part of a composite material with Nomex<sup>®</sup> honeycombs [26].

In separate studies, it could be demonstrated that a late additional acidification step can yield RF aerogels that retain the small diameters of particles (in the nanometer range) that Pekala had described earlier yet containing macropores. These large pores allow the intermediate aquagels to withstand the gradient of capillary forces present in the evaporative drying under ambient pressure [27, 28].

However, a detailed investigation of structure and properties of RF aerogels prepared by pH-adjustment of more concentrated resorcinol mixtures has hitherto been missing.

Therefore, we prepared several RF aerogels with higher solid fractions ( $R:W \geq 0.012$ ) and compared the properties of the resulting aerogels to conventional Pekala-type aerogels.

## 2. Experimental

### 2.1 Materials

Resorcinol (R) 98% and anhydrous sodium carbonate (C) were supplied from Aldrich, aqueous solution of formaldehyde (F) (24% w/w) from Merck. Nitric acid (2.0 N; standardized solution) was purchased by Alfa Aesar. Acetone (pure, technical grade) was purchased from Th. Geyer. For the synthesis deionized water (W) was used. Carbene dioxide 4.5 (purity  $\geq 99.995\%$ ) for supercritical drying was purchased by Praxair, Germany. Sealable containers for gelation (180 mL, polypropylene (PP) with screw-cap) and for washing (400 mL, PP, snap-cap) were purchased from VWR, Germany.

### 2.2 Synthesis

For this study we synthesized RF aerogels with constant ratios of reactants ( $R:F=0.5$ ) and catalyst ( $R:C=200$ ), respectively. The  $R:W$  molar ratio was varied in the range of 0.012-0.035. A total of 10 samples were prepared. For each sample resorcinol was dissolved in water at 20-22°C (room temperature, *rt*). Then, an aqueous solution of formaldehyde was added in one portion to the transparent solution followed by stirring at *rt* for 5 min. Solid sodium carbonate (0.5 mol-% with respect to resorcinol) was then added in one portion, and the resulting suspension was stirred for another 5 minutes. The resulting colorless solution was divided among two sealable polypropylene (PP) containers. These samples with unaltered  $pH=7.0-7.2$  we label  $RF_7$ . In contrast, the  $pH$ -

value of the second solution was adjusted to 6.5 by dropwise addition of an aqueous solution of nitric acid ( $c = 2\text{M}$ ). The stirring was also continued for 30 minutes at 150-300 rpm using a cross magnetic stirring bar. Such samples were labeled  $\text{RF}_{6.5}$ . After stirring for 30 min at *rt* the samples were placed in a sealable PP container and kept seven days at  $80^\circ\text{C}$  in an oven. During gelation and curing gels  $\text{RF}_{6.5}$  turned opaque, dark red whereas  $\text{RF}_7$  appeared transparent dark red. After one week, the wet gel was cooled down to *rt*, transferred to a 400 mL PP container filled with acetone, and left for three days during which the acetone was replaced five times. The supercritical drying was carried out with  $\text{CO}_2$  in an autoclave (Eurotechnica, Germany) at  $50^\circ\text{C}$  and 83 bars for 5 days. The temperature was increased to  $55^\circ\text{C}$  and the pressure was released slowly (rate:  $0.1 \text{ bar}\cdot\text{min}^{-1}$ ).

### 2.3 Methods

The pH was measured with a calibrated SevenEasy pH device with relative accuracy of  $\pm 0.01$ . The microstructure of aerogels was investigated using scanning electron micrographs (Zeiss Merlin, Germany). Due to the non-conductive property of RF aerogels they were coated with gold before microscopy. The Brunauer-Emmett-Teller (BET) surface area of aerogels was determined using a TriStarII from Micromeritics,. Envelope and skeletal density were measured on a Micromeritics GeoPyc 1360 analyzer and Micromeritics AccuPyc machine, respectively. Compression tests were performed using a Latzke universal testing machine and load cells of 5000 N. The compression was conducted at a rate of  $1 \text{ mm}\cdot\text{min}^{-1}$ . The thermal conductivity was measured with a Transient Plane Source (HotDisk TPS 2500S, Sweden) using the Kapton-coated sensor 5501 (radius: 6.4 mm). Measurements were conducted 3 times with at least 20 min of relaxation time between individual measurements.

### 3 Results and Discussion

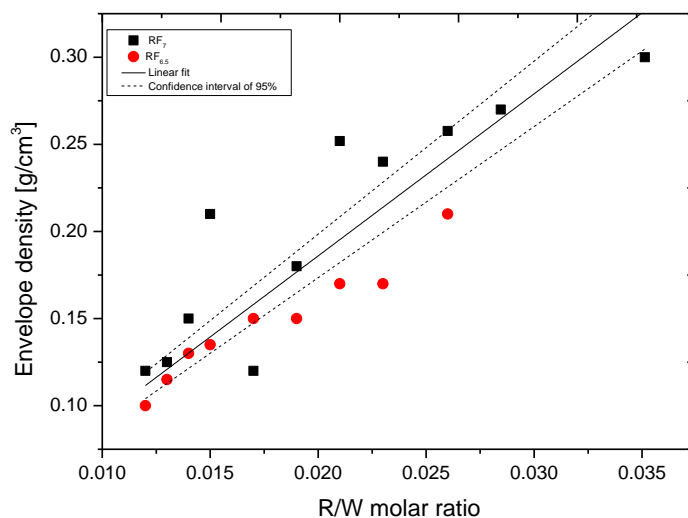
#### 3.1 Properties of RF aerogels

Aerogels prepared at pH 7 were obtained as described before by Pekala and others. They display a dark red to purple color, expose a hard and brittle surface, and show a translucence comparable to rough glass. When the pH was lowered to 6.5, however, the appearance of the resulting aerogels changed significantly: they are of (dark or light) brown color, are opaque, and exhibit haptics similar to smooth rubber. This difference in appearance is depicted in Figure 1.



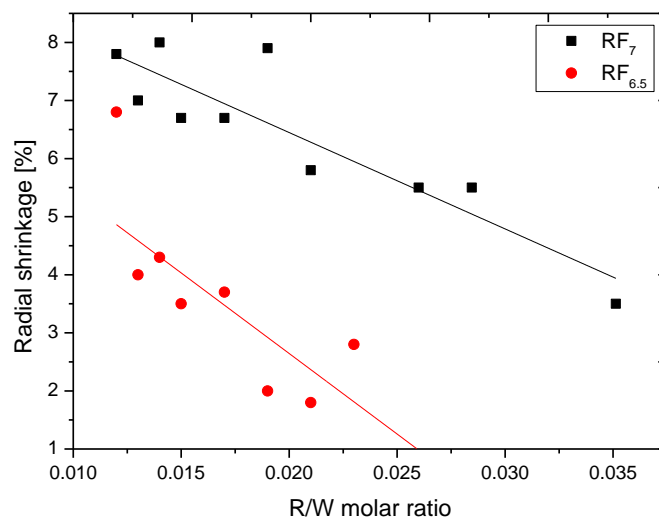
**Fig. 1.** Representative RF aerogels prepared at pH 7 (left) and pH 6.5 (right), respectively.

With regard to density, an increase of solid content in the synthetic procedure led to the expected increase in envelope density of the resulting aerogel as depicted in Figure 2 [29]. We observe some scatter in the data especially for aerogels prepared from solutions at a pH of 7.0 to 7.2. The source of this scatter is unclear at the moment.



**Fig. 2.** Increase of envelope density with higher resorcinol

To our delight, the shrinkage of gels prepared at pH 6.5 was significantly reduced when compared to aerogels obtained at pH 7. Figure 3 clearly indicates a steeper decrease of relative radial shrinkage as a function of solid content. Above R/W ratios of 0.019 an average shrinkage of less than 3% was found experimentally. Such a small degree of shrinkage can allow these aerogels to be used as part of composites such as aerogel-honeycombs [26].

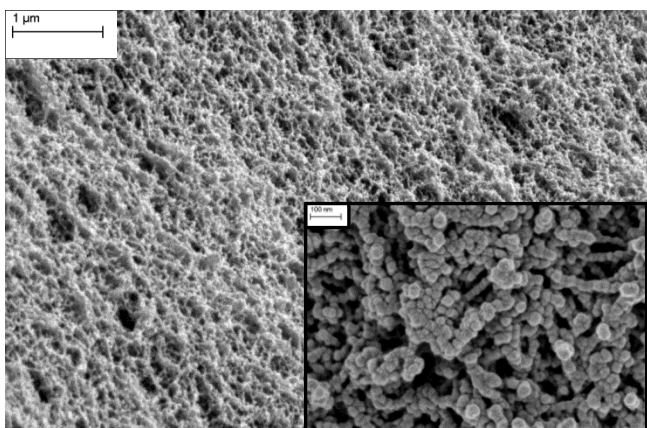


**Fig. 3.** Dependence of radial shrinkage on solid content. Acidified samples show less shrinkage than gels prepared at pH 7.

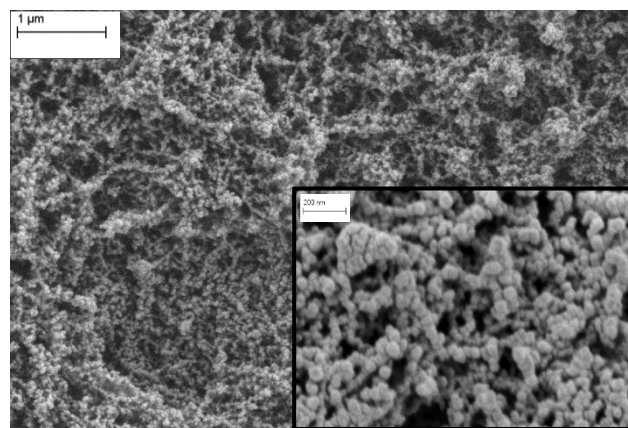
### 3.2 Microstructure of RF aerogels

The microstructure of the RF aerogels was investigated qualitatively by means of scanning electron microscopy. Fig. 4 depicts micrographs of aerogels produced varying both solid content (different R:W) and pH value (pH 7 vs. pH 6.5). A micrograph of an aerogel made at pH 7 is shown in Fig. 4-a. There, a highly homogeneous nanostructure with a large degree of crosslinking is visible. The network consists of small spherical particles which are connected in a string-of-pearl fashion. Particles of samples prepared at pH 6.5, on the other hand, (see Fig. 4-b) appear larger, their structure is less homogeneous, and pores are of different diameter. In general, the structure of samples prepared at pH6.5 involves larger pores and particles and shows fewer cross-links.

a) R:W=0.012, pH 7

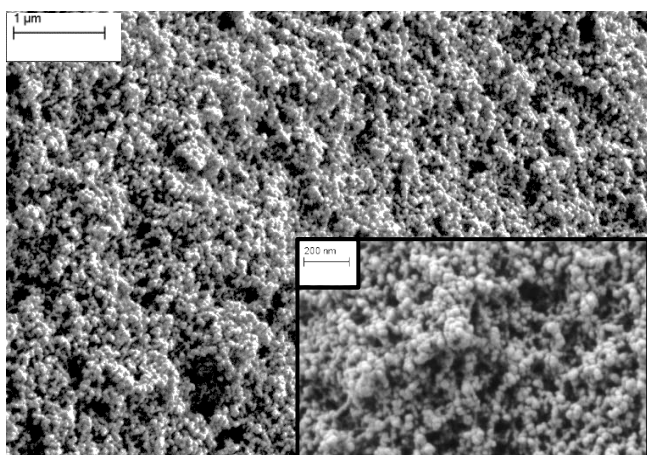


b) R:W=0.012, pH 6.5

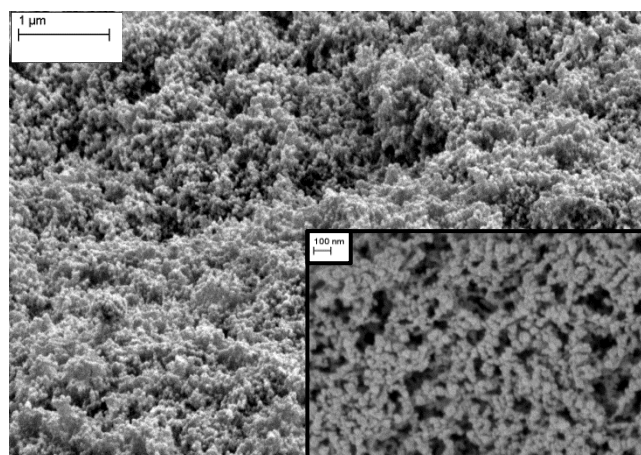




c) R:W=0.019, pH 7



d) R:W=0.019, pH 6.5



**Fig. 4.** Microstructure of aerogels prepared *via* conventional base catalysis (a and c) and base-acid catalysis (b and d).

A higher concentration of resorcinol and formaldehyde (i.e. increasing the R:W molar ratio) leads to an increase in particle size as visualized in Fig. 4 (c and d). One can see larger particles, but smaller pores, and the structures are denser and highly cross-linked. To quantify our observations we calculated the pore sizes of four aerogels using Equations (1) – (3) [30]. The porosity  $\Phi$  was calculated from envelope and skeletal densities ( $\rho_e$  and  $\rho_s$ ):

$$\Phi = 1 - \frac{\rho_e}{\rho_s} \quad (1)$$

Since, the specific pore volume  $v_{pore}$  is given by

$$v_{pore} = \frac{1}{\rho_e} - \frac{1}{\rho_s}, \quad (2)$$

the average pore size  $d_{av}$  can be calculated using

$$d_{pore} = \frac{4 \cdot v_{pore}}{S_{BET}} \quad (3)$$

Using the envelope density  $\rho_e$  the average particle size  $d_{part}$  follows from

$$d_{part} = \frac{6 \cdot (1 - \Phi)}{S_{BET} \cdot \rho_e} \quad (4)$$

The results are given in Table 1. Pores of aerogels prepared at pH 6.5 are almost two times larger than those of Pekala-type aerogels prepared at pH 7, and the pore size decreases with increasing amount of resorcinol-formaldehyde.

In the Pekala-type gel synthesis the high pH value is kept until gelation. There, condensation is much slower, and addition reactions dominate leading to the formation of many resole-type molecules that nucleate to form particles. Such small particles condense as “string of pearls” cross-linking eventually to form a three-dimensional network. Gels adjusted to pH 6.5, on the other hand, are formed after an accelerated condensation of resorcinol subunits at lower pH values, thus resulting in fewer - yet bigger- particles growing together. Along with an increase in particle size, the pore diameter decreases (see Table 1) [27]. The particle size of aerogels prepared at pH 7 is smaller than those prepared at higher pH value, confirming our estimates from SEM figures using the linear intercept method of Heyn [31, 32].

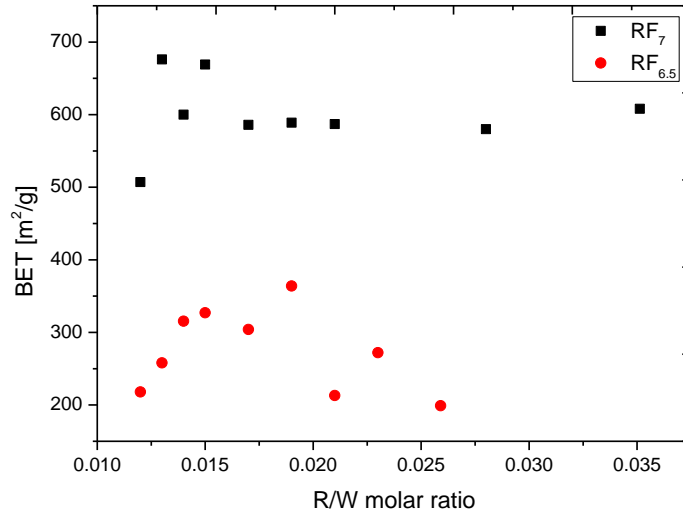
**Table 1**

Densities, porosity and pore size of RF aerogels as a function of resorcinol amount and pH value

R:W molar ratio	pH	Skeletal density [g·cm <sup>-3</sup> ]	Envelope density [g·cm <sup>-3</sup> ]	Porosity [%]	Pore volume [cm <sup>3</sup> ·g <sup>-1</sup> ]	BET area [m <sup>2</sup> ·g <sup>-1</sup> ]	Average pore diameter [nm]	Average particle size [nm]
0.012	6.5	1.49	0.10	93.3	9.3	218	171	18 <sup>a</sup> ; 32 <sup>b</sup>
0.012	7	1.44	0.12	91.7	7.6	507	60	8 <sup>a</sup> ; 20 <sup>b</sup>
0.019	6.5	1.52	0.15	90.1	6.0	364	66	11 <sup>a</sup> ; 31 <sup>b</sup>
0.019	7	1.42	0.18	87.3	4.9	589	33	7 <sup>a</sup> ; 26 <sup>b</sup>

<sup>a</sup> calculated with Equation 4; <sup>b</sup> calculated from SEM images with linear intercepts of particle boundaries

A clear trend is visible for the effect of pH adjustment on the internal surface area as determined by BET analysis: Irrespective of solid content, aerogels prepared using the additional acidification possess an internal surface area that is about  $300 \text{ m}^2\cdot\text{g}^{-1}$  lower than that of gels prepared by the route at pH 7.



**Fig. 5.** Specific surface area measured by nitrogen adsorption of RF aerogels. Upon acidification the average surface area drops from  $500\text{-}680 \text{ m}^2\cdot\text{g}^{-1}$  to  $200\text{-}380 \text{ m}^2\cdot\text{g}^{-1}$ .

### 3.3 Thermal and mechanical properties

For samples of RF aerogels prepared at pH 6.5 thermal conductivities in a range of  $0.023\text{-}0.032 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  were determined. These values are similar to Pekala-type aerogels prepared at pH 7 which ranged between  $0.021$  and  $0.034 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ . A general trend is that a higher R:W ratio leads to higher thermal conductivity due to the higher contribution of solid conductivity when the solid backbone of the aerogel increases [15]. There are, however, some inconsistent data points within this experimental row as for some of the pH 7 samples thermal conductivities were about twice as high as Pekala, Fricke and others had reported (R:W 0.014: density ca.  $0.15 \text{ g}\cdot\text{cm}^{-3}$ ,  $\lambda \approx 0.023 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ). These higher values might be attributed to the measurement method used: in our

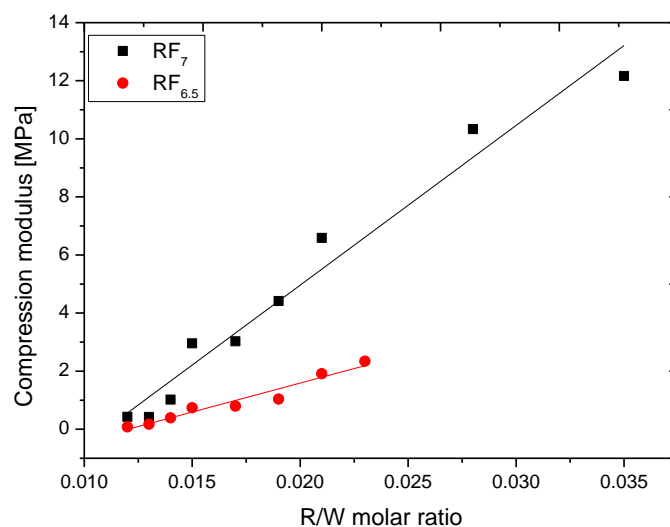
experience, for samples with thermal conductivities below  $0.03 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  the Hot Disk technique applied in these studies typically results in up to 20% higher values than those obtained by a guarded hot plate method.

**Table 2**

R:W molar ratio	Envelope density $\text{RF}_7$ [ $\text{g}\cdot\text{cm}^{-3}$ ]	Thermal conductivity $\text{RF}_7$ [ $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ]	Envelope density $\text{RF}_{6.5}$ [ $\text{g}\cdot\text{cm}^{-3}$ ]	Thermal conductivity $\text{RF}_{6.5}$ [ $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ ]
0.012	0.12	0.021	0.10	0.030
0.013	0.13	0.028	0.12	0.028
0.014	0.15	0.023	0.13	0.025
0.015	0.21	0.034	0.14	0.023
0.016	--	--	0.15	0.029
0.017	0.12	0.028	$0.15\pm 0.01^{[a]}$	$0.027\pm 0.002^{[a]}$
0.019	0.18	0.025	0.15	0.031
0.021	0.25	0.019	$0.17\pm 0.01^{[b]}$	$0.030\pm 0.001^{[b]}$
0.023	0.24	0.024	$0.17\pm 0.02^{[a]}$	$0.030\pm 0.002^{[a]}$
0.026	0.26	--	$0.21\pm 0.04^{[c]}$	$0.032\pm 0.004^{[c]}$
0.028	0.27	0.026	--	--
0.035	0.30	0.029	--	--

[a,b,c] Standard deviations were determined after multiple preparations of the samples: [a] 2x; [b] 7x; [c] 3x

Compression tests performed out-of-plane on aerogels prepared at pH 7 allowed us to reproduce values for the compressive modulus (ca. 8 MPa at a density of  $0.24 \text{ g}\cdot\text{cm}^{-3}$ ) reported by Pekala and Kong [11]. The measurements further revealed that our samples prepared from a solution at lower pH are less stiff than those prepared without acid catalysis. Also, the increase in stiffness as a function of solid content is much less pronounced with samples that were acidified during their synthesis (Fig.6). This lack of brittleness makes this kind of aerogel promising as part of a composite.



**Fig. 6.** Increase of compression modulus with higher R:W molar ratio.

#### 4 Conclusion

RF Aerogels prepared by pH adjustment were analyzed regarding their appearance, macro- and microscopic structure, and thermal and mechanical properties. They share with Pekala-type aerogels properties such as the low density, high porosity (around 90%), and the low conductivity of heat.

Yet, there are certain properties that differ significantly: The inner surface of RF aerogels made by pH adjustment to a lower value of 6.5 is much smaller ( $\approx 300 \text{ m}^2 \cdot \text{g}^{-1}$ ) whereas particles are slightly bigger and pores are about twice as wide.

Most significantly however, the new aerogels are more flexible than those prepared using only base catalysis as demonstrated by the compressive strength which is much smaller for aerogels made from solutions at pH 6.5. The shrinkage observed for the acidified monolithic samples after synthesis and work-up is negligible at R:W 0.019 and higher. Therefore, aerogels prepared by this route can be incorporated into composite materials such as honeycombs. Such studies are ongoing and will be published in due course.

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