J. of Supercritical Fluids 107 (2016) 201–208

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

New soft and spongy resorcinol–formaldehyde aerogels

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ARTICLE INFO

Article history:
Received 17 March 2015
Received in revised form
10 September 2015
Accepted 11 September 2015
Available online 15 September 2015

Keywords:
Aerogels
Sol–gel process
Flexible aerogels
Supercritical drying
Compressive modulus
Shrinkage

ABSTRACT

Novel super-flexible resorcinol–formaldehyde (RF) aerogels were synthesized via a sol–gel process followed by supercritical drying. These aerogels are soft and are reversibly deformable up to 25%. Low density of 0.06 g cm^{-3} and low Young's modulus of about 116 kPa distinguish these sponge-like aerogels from conventional RF-aerogels made especially by ambient drying. The synthesis occurs from a very diluted sol-solution and demands high accuracy during preparation. Formation of small particles and relatively big pores allow bending of pore walls without breaking and establish microstructural conditions of flexibility. The experiments show the microstructure formation leading to superflexible RF-aerogels is a very sensitive process and depends on the homogeneity of the sol and its pH value. Shrinkage during for instance ambient dyring induces a collapse of the pore structure and reduces flexibility. Additionally, a definition and calculation of the term "flexibility" is presented and discussed in this study.

1. Introduction

Aerogels are open-porous materials synthesized via sol–gel processing. Due to their high porosity (>80%), aerogels exhibit densities in the range of 0.05–1.0 g cm^{-3} and surface areas of about 400–1200 m^2 g^{-1} [1–3]. The huge surface area is mainly due to the solid backbone of necklace-like nanosized particles connected in three dimensions. The high porosity together with the small particles and the even smaller connecting points between them make most aerogels very fragile and sensitive to especially inhomogeneous stresses. The fragility issue imposes serious limitations to applications of monolithic materials.

Since the first aerogels were produced in 1932 [4], the synthesis and properties have been continuously optimized and improved. Numerous attempts have been carried out to strengthen the three dimensional network. Most progress has been done on silica aerogels and include polymer crosslinking [5], flexibilisation of aerogels [6], or synthetic modification using trifunctional precursors [7]. To overcome the problem with handling, filling of a sandwich structure with granular silica aerogel was suggested by Joshi [8].

For organic resorcinol–formaldehyde (RF) aerogels several methods to reinforce the nanoparticle network have been suggested. Saliger et al. [9] developed conditions of synthesis followed by ambient drying. They observed that high resorcinol-to-catalyst (sodium carbonate) molar ratio e.g. 1000–1500 (high resorcinol amount) leads to formation of a strong 3D network, which can withstand the high capillary forces during drying under ambient conditions. This time- and energy-saving procedure yields aerogels with high Young's modulus, but also a fairly high bulk density in the region of 0.35–0.5 g cm^{-3} with particle sizes of about 0.1–1 μm. Composites consisting of RF and cellulose aerogels have been developed and resulted in a 51% higher Young's modulus [10]. Well known are polyimide flexible and foldable aerogels dried with supercritical CO_2 [11,12]. The group of Leventis reported about polyurea and polyurethane highly flexible aerogels [13–15]. They observed that macroscopic flexibility is indirectly affected by the molecular properties of the monomers. We recently reported the synthesis of low-flexible RF aerogels dried under ambient conditions [16]. Such aerogels are elastically deformable up to 16% and have a very low Young's modulus of about 65–150 kPa. They exhibit densities of 0.06–0.1 g cm^{-3}, which is very low for ambiently dried aerogels. They possess a coarse-porous microstructure (pore size of about 10–20 μm), which is crucial in order to achieve flexibility.

A further considerable improvement can be made by modifying the processing. Here, we report on the discovery of a novel soft, spongy super-flexible resorcinol–formaldehyde aerogel. A modified synthetisis route combined with supercritical drying leads to aerogels with lower Young's modulus and reversible deformation in uniaxial compression. Essential parameters in processing are stirring time of the solution, development of pH value during processing until gelation and the drying technique, ambient versus supercritical. Novel super-flexible RF aerogels possess almost two

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http://dx.doi.org/10.1016/j.supflu.2015.09.010
0896-8446/

times higher flexibility compared to low-flexible aerogels reported recently.

2. Experimental

2.1. Materials

Resorcinol 98% and anhydrous sodium carbonate were purchased from Aldrich, aqueous solution of formaldehyde (37% w/w, stabilized with 10% methanol) from Merck. Nitric acid (2.0 N; standardized solution) was supplied by Alfa Aesar. Acetone (pure, technical grade) was purchased from Th. Geyer. Deionized water was used for synthesis. Carbon dioxide 4.5 (purity ≥ 99.995%) for supercritical drying was purchased by Praxair, Germany. Sealable containers for gelation (180 mL, PP with screw top) and for washing (400 mL, PP, press-on lid) were purchased from VWR, Germany.

2.2. Synthesis of RF aerogels

At 20–22 °C (room temperature) 25.0 g (0.227 mol) of resorcinol (R) was dissolved in 487.6 g water (W), resorcinol to water molar ratio is 0.008. Then 36.9 g of aqueous solution of formaldehyde (F, 0.454 mol), R:F molar ratio 0.5, and 0.481 g sodium carbonate (C, 0.00454 mol), R:C = 50, were added under stirring. After 5 min stirring the pH was adjusted to 5.4–5.6 with 2 N nitric acid (ca. 4 mL). The stirring was continued for 60 min at room temperature with stirring velocity of 150 rpm with a cross magnetic stirring bar. The homogeneous, transparent solution was placed in a sealable polypropylene container for seven days at 80 °C in an oven. During gelation and curing the gel became beige or brown beige. After one week the wet gel was cooled down to room temperature and transferred into an acetone bath (400 mL polypropylene container) for three days to remove the residual chemicals and to exchange water with acetone being soluble in supercritical carbon dioxide. The acetone was refreshed six times.

Several sets of samples were prepared to study process parameters in manufacturing of soft flexible aerogels:

Set A: Variation of stirring time. The samples were synthesized as described above but with 5, 30, 45 and 60 min of stirring, respectively. The experiment was repeated four times; the average and standard deviation were calculated.

Set B: Variation of drying type. Samples were synthesized as described above and dried supercritically and subcritically. The supercritical drying was carried out with CO_2 in an autoclave of 12 L volume (Eurotechnica, Germany) at 50 °C and 83 bars for 5 days. In the first four days (on the whole circa 32 h) the extraction of acetone occurs. Periodically, three-four times per day the separated acetone was drained and fresh carbon dioxide was passed into autoclave. On day fourth no solvent anymore could be extracted, so that degassing was started on the fifth day. The degassing rate was adjusted to 0.1 bars per minute.

The subcritical drying took place in an oven at ambient pressure and 80 °C. Wet gels after washing with acetone were placed in a drying cabinet for 24 h. After one day the samples were dry.

2.3. Characterization

The microstructure of aerogels was investigated using a scanning electron microscope (Zeiss Merlin, Germany). Since resorcinol–formaldehyde aerogels are not electrically conducting they were coated with platinum before microscopy. The bulk density was calculated from measured volume and weight of the aerogel pieces. The pH was measured with SevenEasy pH device with relative accuracy of ±0.01 and the pH electrode InLab® Expert Pro (Mettler Toledo, Germany). Surface area and pore size distribution of the aerogels were measured by BET/BJH method (TriStar II, Micromeritics). The thermal conductivity was measured at room temperature and ambient pressure using HotDisk 2500 S based on the Transient Plane Source technique (HotDisk, Sweden) with a sensor 5501 (radius 6.403 mm) [17]. The compression tests were performed at room temperature with compression machine (Latzke, Germany) and load cells of 100 N for sf-RF and 5000 N for c-RF, with 1 mm min^{-1} speed of compression. For compression tests cylindrical samples (sf-RF: diameter 51.4 mm and height 12.9 mm and c-RF: diameter 40.8 mm and height 18.2 mm) were prepared. The skeletal density was measured by helium pycnometry with an AccuPyc (Micromeritics) helium pycnometer.

2.4. Calculation of buffer capacity

The determination of carbonate buffer capacity is based on the titration method given by Hecht [18]. We prepared, as described in "2.2. Synthesis of RF aerogel", a solution where resorcinol, formaldehyde, and sodium carbonate were dissolved in water. The addition of 2.0 N nitric acid was performed step wise 0.02 mL per minute. The pH was read every minute before next addition of acid. The experiment was stopped as the pH reached 5.24. The buffer capacity β was calculated using Eq. (1)

$$\beta = \frac{\Delta mol}{l \cdot \Delta pH} \tag{1}$$

where Δmol is acid amount per step, l the volume of solution titrated, and ΔpH is change of pH per step.

3. Results and discussion

The synthesis of soft spongy RF aerogels occurs in high diluted solutions with a high amount of catalyst and at a pH value in the region of 5.4–5.6. We studied the influences of several parameters leading to highly flexible aerogels. In a preceding paper we described a type of RF aerogel we referred to as "corky" aerogel. These aerogels can be transformed into the new, super-flexible ones described herein. Accordingly, we will first describe the effects of several processing parameters and describe "corky" RF aerogels before we describe the properties of the new super-flexible ones.

3.1. Influence of pH and stirring time on the gelation ratio

According to our investigation the sols prepared do not always gel completely, e.g. from 100 mL solution not always 100 mL gel body can be generated. Some sols gel only around 50–90%, while the rest of the sol could be seen on the top of the gel body as a clear solution. The volume of this solution was determined with a 10 mL graduated cylinder with accuracy of ±0.1 mL. We observed that only gels with 90–100% gelation volume resulted in highly flexible aerogels. It turns out that the stirring time and the temporal evolution of the pH-value is essential. We, therefore, investigated the influence of stirring time on the gelation. As shown in Fig. 1 increasing the stirring time raises the amount to which a solution gels.

The gelation ratio Φ_{Gel} was determined using the simple relation (Eq. (2)), where V_i is the volume of initial and V_u the clear, unreacted part of the solution.

$$\Phi_{Gel} = 1 - \frac{V_u}{V_i} \tag{2}$$

One can also observe, looking at the data of Fig. 1, that the standard deviation is very high at short stirring times, while it decreases at longer mixing times. In our opinion a sufficient stirring of the reactants is necessary to produce a homogeneous sol solution, leading then to a complete gelation (a more detailed explanation is given below).