RSC Advances

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

Journal Name

RSCPublishing

ARTICLE

A novel approach to alginate aerogels: carbon dioxide induced gelation

Cite this: DOI: 10.1039/x0xx00000x

P. Gurikov,*[a] S. P. Raman,[a] D. Weinrich,[b] M. Fricke[b] and I. Smirnova[a]

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

A novel technique for preparation of alginate aerogels, that utilizes high pressure CO_2, is presented. In pressurized carbon dioxide at 5 MPa and 298 K, a suspension of calcium carbonate dispersed in sodium alginate solution undergoes irreversible gelation without additional pH modifiers or crosslinkers. Solvent exchange to ethanol at ambient conditions followed by supercritical drying with carbon dioxide resulted in alginate aerogels with remarkable properties compared to the state of the art. They are very light with density down to 0.06 ± 0.02 g cm^{-3}, translucent and possess a fibrillar structure with both meso- and macroporosity. For selected samples, the surface area and mesopore volume are found to be 545 ± 77 m^2 g^{-1} and 6.98 cm^3 g^{-1}, respectively. Thermal conductivity measurements using the hot-wire method revealed excellent thermal insulation properties: thermal conductivity was determined to be in the range of (18–22) ± 2 mW m^{-1} K^{-1}. Although the initial aerogels are flexible to a certain extent, they can be classified as viscoplastic materials and their compression indicates improved flexibility and retained mesoporosity. Possible approach for the production of alginate aerogels in an integrated one-pot process – that combines gelation, solvent exchange and supercritical drying – is outlined.

Journal Name RSCPublishing

ARTICLE

A Introduction

Sodium alginate is a natural anionic polysaccharide copolymer of β-D-mannuronic acid and α-L-guluronic acid, which can be obtained both from brown algae and bacterial sources.[1] One remarkable feature of alginate chains is their ability to form gels in reactions with divalent metal ions and other cross-linkers. Owing to excellent biocompatibility and biodegradability, well-developed derivatization techniques[2] and variety of natural sources, the alginate hydrogels are widely adopted for food,[3] biomedical,[4] pharmaceutical[5] and other applications.[6,7]

Direct mixing of cations and alginate leads to inhomogeneous gels due to rapid and irreversible binding.[1,2] To perform controllable gelation two fundamental techniques have been developed: the diffusion method and the internal setting method. In the diffusion method, cations diffuse from bulk solution into an alginate droplet or layer. Gelation occurs at first in the thin layer on the outside followed by further diffusion-controlled propagation towards the center.[1,2] In the internal setting method, a cross-linking cation releases into the alginate solution from the dispersed insoluble precursor initiated mainly by changing of pH, *e.g.* $CaCO_3$ as a precursor in presence of slowly hydrolyzing D-glucono-δ-lactone, GDL. Both methods allow for the production of hydrogels in form of monoliths, beads and microspheres.[8,9]

Due to a versatile combination of unique properties (ultra-low density, high surface area and pore volume, low thermal conductivity and sound velocity), aerogels are extensively studied in a number of fields such as aeronautics, energy conservation, biomedicine, drug delivery systems, electronics, photovoltaics, acoustics and many others (see ref. 10 and references therein). With aforementioned characteristics and applications, the transformation of alginate hydrogels into aerogels by supercritical drying (sc-drying) opens up a multitude of opportunities towards high value added materials.[8,10–12] Presently, aerogel production consists of multiple isolated steps including gelation, solvent exchange and sc-drying.[13] From the engineering perspective it would be beneficial to reduce the number of steps as far as possible.

In this work, we set a goal to investigate the use of CO_2 as an alternative catalyst for alginate gelation. The catalytic effect of pressurized CO_2 on silica sol that allows to combine gelation and sc-drying, has been demonstrated by Loy *et al.*[14], and further investigated by many others.[15–17] The usage of sc-CO_2 as a continuous phase in particle production[18,19] and as a porogen to introduce macroporosity in polymers[20–22] has been also reported. To the best of our knowledge, only Partap *et al.*[21] showed that sodium alginate/$CaCO_3$ mixtures being dispersed in sc-CO_2 undergo gelation. Obtained hydrogels were found to be reversible and destabilized at ambient conditions within a few days presenting difficulties to use the hydrogels themselves.

In this work we expand the internal setting method for the gelation of alginate by using pressurized carbon dioxide instead of conventional pH reducers. The produced hydrogels serve as precursors for aerogels. A view on the CO_2 induced gelation as the first step in an integrated approach towards alginate aerogels, that combines gelation, solvent exchange and sc-drying, is presented.

B Experimental

B.1 Reagents

Sodium alginate (Alg) was purchased from Sigma Aldrich (suitable for immobilization of micro-organisms grade, catalogue no. 71238). Calcium carbonate (light, precipitated powder, particle size *ca.* 1 μm) was kindly provided by Magnesia GmbH (Germany). Ethanol 99.8 % was obtained from H. Möller GmbH (Germany). Carbon dioxide with a purity of 99.9 % was supplied by AGA Gas GmbH (Germany). All chemicals were used as received. Deionized water was used throughout the study.

B.2 Preparation of the starting mixtures

Alginate solution was prepared by gentle stirring of sodium alginate powder with an appropriate amount of water overnight and stored at 278 K. Calcium carbonate was suspended in water by vigorous mixing (Heidolph DX900) for 5 min. While mixing, a certain part of the suspension was bled off and immediately transferred into the alginate solution (0.25; 0.5; 1.0; 2.0 and 3.0 wt%) to reach the target Alg/$CaCO_3$ ratio (Table 2). Obtained suspensions were again mixed (Heidolph DX900) for 2 min until they became homogeneous. These suspensions were found to be stable for at least 2 h even for lowest alginate concentrations. All prepared suspensions were transferred into Petri dishes and placed into a 25 L autoclave for subsequent gelation. Sodium alginate content in the final mixtures is listed in Table 2.

To study the influence of the crosslinking degree (q), Alg/$CaCO_3$ ratios of 1 : 0.091 and 1 : 0.183 (w/w), denoted as q = 0.5 and q = 1.0, respectively, were used. Selected samples with q = 1.5, 2.0 and 3.0 were also prepared.

B.3 Gelation procedure

Petri dishes were filled with a starting mixture and placed into a high-pressure 25 L autoclave (Fig. 1). The autoclave was pressurized with gaseous carbon dioxide up to 5 MPa at 298 K. The pressure was maintained for 12 h and then slowly released (0.02 MPa/min). Hydrogels formed were either transparent or translucent. Due to shrinkage, the diameters of the gel monoliths were less than the diameter of the employed dishes, and the gels were found to be in water ejected from the gel. The hydrogels were left in the air until formation of bubbles ceased, then washed several times with water. Finally gels were transferred into ethanol/water mixture to perform solvent exchange as described below.

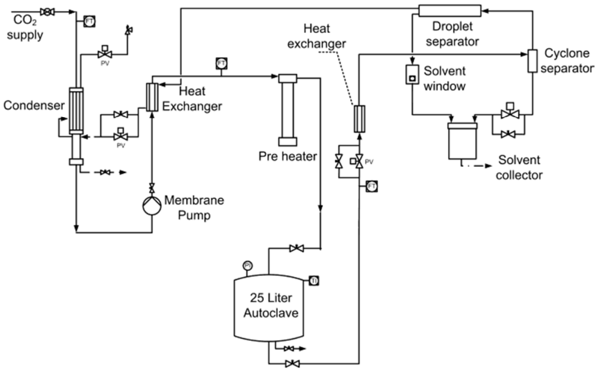


Fig. 1 Schematic diagram of the 25 L high-pressure autoclave used for CO_2 induced gelation and sc-drying.

B.4 Solvent exchange

Due to the low solubility of water in sc-CO_2, hydrogels needed to be converted into alcogels prior to sc-drying. However, direct soaking in a bath with pure ethanol or other organic solvents would lead to significant irreversible shrinkage.[8,23] To avoid this drawback stepwise solvent exchange was performed. Gels were successively immersed in ethanol/water mixtures with concentrations of 10, 30, 50, 70, 90 and 100 wt% for 12 h each. Soaking in 100 wt% ethanol was performed twice to ensure more than 98 wt% solvent purity in the final alcogels.

B.5 Supercritical drying

Alcogels were packed into filter paper parcels, placed into the preheated autoclave (313 K) and covered by ethanol to prevent premature solvent evaporation from the gel. Supercritical drying was performed using the same autoclave as for gelation (Fig. 1). The autoclave was sealed and filled with CO_2 by a membrane pump. Once pressure of 12 MPa was reached, the outlet was opened and constant flow was set for 6 h keeping the pressure constant such that 6 – 7 residence volumes of CO_2 were used. Then system was depressurized in 1 h followed by cooling down to room temperature.

B.6 Solvent exchange integrated with sc-drying

Alginate hydrogels were prepared from 0.75 wt% Alg and q = 1.5 by CO_2 induced gelation as described in Section B.3. Immediately after gelation hydrogels were demolded and placed into a 250 ml high pressure autoclave with a viewing window[24] preheated to 318 K. The autoclave was charged with sc-CO_2 to reach 12 MPa. Then 30 wt% ethanol/water mixture was introduced to cover the gels completely. The autoclave was left for 2.5 h with occasional shaking. During this time small portions (5 ml) of the ethanol/water mixture were taken to measure ethanol content (using a density meter DMA 4500). After 2.5 h the ethanol/water mixture was completely withdrawn from the autoclave by opening the outlet valve. The solvent exchange to 60 and 90 wt% ethanol was done in the same way (2.5 h each). During these steps pressure was kept at 12 ± 1 MPa. Then anhydrous ethanol (8 ml min^{-1}) and sc-CO_2 (20 g min^{-1}) were premixed and supplied into the autoclave to remove water from the gels (3 h). Finally, sc-drying was carried out with pure sc-CO_2 to remove ethanol (3 h, see Section B.5).

B.7 Characterization

Linear shrinkage (LS) was controlled after each step (gelation, solvent exchange, sc-drying) and was calculated as follows: $LS\% = (1 - d_i/d_0) \times 100\%$, d_i is the diameter of the gel at the current step, d_0 is the diameter of the mold for gelation. Contributions of each step to the overall shrinkage were calculated as the difference between LS at the current and preceding step. Reported values were averaged over three measurements.

Specific surface area (S_{BET}) and pore volume (V_p) were determined by Brunauer-Emmet-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively, using low-temperature nitrogen adsorption-desorption analysis (Quantachrome Nova 3000e). Prior to the measurements, the samples were degassed at 348 K for 24 h. The BET surface area was averaged over at least three independent runs. Bulk density (ρ) was calculated from the sample diameter and thickness measured with Vernier calipers. SEM pictures were recorded in a scanning electron microscope (Leo Gemini 1530) after sputtering with gold (Baltec Sputter Coater SCD 050). Thermal conductivity of the selected samples was determined by the hot-wire method[25] at ambient pressure and room temperature at ZAE Bayern (Germany).

C Results and discussion

C.1 Gelation

Due to geological and environmental implications, the system $CaCO_3/CO_2/H_2O$ has been abundantly studied at various temperatures and pressures.[26–28] Solubility of carbon dioxide increases with rising pressure along with lowering of pH down to 3.[29] Solubility of calcium carbonate also increases with pressure resulting in release of calcium ions. At conditions used in this study for gelation (5 MPa, 298 K), solubility of $CaCO_3$ is much higher (2.9 g L^{-1})[26] than at ambient conditions (≤ 0.01g L^{-1}).[30] Concentration of $CaCO_3$ in the final mixtures lies between 0.23 and 4.4 g L^{-1}. Hence more than half of introduced calcium carbonate is dissolved at equilibrium conditions and available to crosslink alginate chains.

Hydrogels produced with this method at q = 0.5 and q = 1.0 were transparent and colorless. After the solvent exchange and sc-drying they showed typical net-like structure (Fig. 2a, b). Gelation of alginate with higher $CaCO_3$ amount (q = 3.0) resulted in milky-white hydrogels with a clear sign of unreacted and precipitated $CaCO_3$ crystals (Fig. 2c). In some cases transparent hydrogels with shell-like voids were produced. To produce void-free hydrogels, the thickness of the samples was kept in the range of 10 – 12 mm at depressurization rate of 0.02 MPa min^{-1}. Void formation is most likely caused by slow diffusion of carbon dioxide through the hydrogel in combination with a considerable pressure gradient between the gel and the gas phase. Additional experiments with thicker samples (40 mm) at constant release rate (0.02 MPa min^{-1}) led to the scores of voids and thus further substantiated this supposition. Foaming by rapid gas decompression is described in the literature for various biopolymer hydrogels.[31–33] Combination of both gelation and foaming reported here may be an advantageous method for the production of dual porous alginate matrices without templating agents.

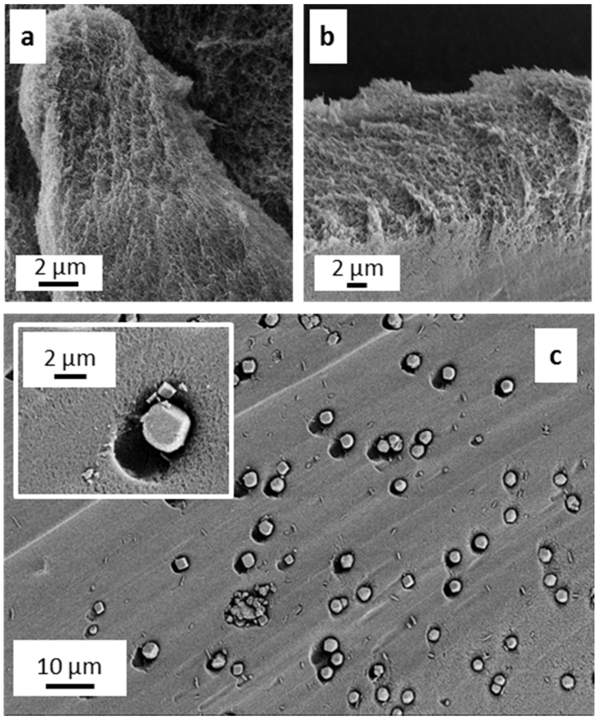


Fig. 2 Fibrillar structure of aerogels AA-2-2 (a) and AA-2-1 (b). Composition of the samples AA-2-2 and AA-2-1 are defined in Table 2. (c) Crystals of $CaCO_3$ precipitated in the aerogel produced with $q = 3.0$.

Partap *et al.*[21] reported that alginate/Ca mixture (with sodium citrate and a surfactant) treated with sc-CO_2 (10 MPa, 323 K) yields reversible hydrogels, which can be reinforced by immersion in a solution with free calcium ions. These findings were based on higher alginate concentrations (8% w/v) and hydrogels were found to be destabilized within 48 h. The hydrogels obtained using CO_2 induced gelation could be prepared with concentrations as low as 0.05 wt% while being stable at ambient conditions and can be stored in pure water for weeks without visible degradation (in presence of a preservative).

Table 1 Shrinkage of the hydrogels occurred at different processing steps and the overall shrinkage

Sample	Composition	Linear shrinkage ± SD (%)			
		gelation	solvent exchange	sc-drying	Overall
HG-2-1	Alg 0.5 wt% $q = 1.0$	11.5 ± 0.7	20.2 ± 0.8	17.8 ± 0.4	49.5 ± 0.1
HG-2-2	Alg 0.5 wt% $q = 2.0$	21.2 ± 0.8	7 ± 1	14 ± 2	42 ± 2
HG-1-2	Alg 0.25 wt% $q = 2.0$	21.9 ± 0.1	9.4 ± 0.4	15.8 ± 0.7	47.1 ± 0.6

All hydrogel except those prepared from 0.25 wt% alginate solutions (AA-1-1, AA-2-1 and AA-1-2, Table 2) were strong enough to maintain their shape without breakage during the transfer from the mold into a container for the subsequent solvent exchange.

C.2 Solvent exchange

As mentioned previously, prior to supercritical drying, solvent exchange to an organic solvent is required, since water cannot be washed out from the pores using nonpolar sc-CO_2.[8] The hydrogel backbone can be affected during the exchange of the watery environment to less polar solvent leading to the gel shrinkage.

It is interesting to reveal the contribution of the gelation by CO_2, solvent exchange and sc-drying to the overall shrinkage (Table 1). The linear shrinkage after gelation lies in the range of 11 – 22 %. Formation of the intra-cluster associated multimeres is responsible for the shrinkage of alginate hydrogels, which becomes more evident at higher calcium concentrations.[34] Indeed, the shrinkage after gelation was twice as large for the samples with $q = 2.0$. However, these samples are more resistant against the solvent exchange showing moderate shrinkage of 7 – 9 %. At constant concentration of alginate (0.5 wt%) the crosslinking degree (q) influences the overall shrinkage: shrinkage was reduced by 15 % with doubled amount of $CaCO_3$. Even though the overall shrinkage is rather high, the bulk densities of the aerogels are low (0.06 – 0.24 g cm^{-3}, Table 2) showing that the structure of the wet gel is mainly retained in the aerogels. Further optimization of the solvent exchange (number of steps, duration, and nature of the solvent) is required to reduce the shrinkage. Recently published studies embark on studying these issues.[8,23]

The solvent exchange was carried out at ambient conditions in order to observe shrinkage behavior. However, there are no obstacles to perform solvent exchange in the same autoclave in pressurized CO_2 and thus couple gelation and sc-drying. First step of such an integrated process is described in Section C.5.

C.3 Supercritical drying

Supercritical drying was performed in the same autoclave (Fig. 1) that was used for gelation. Supercritical drying can be regarded as another solvent exchange, which also causes shrinkage to some extent. Shrinkage after sc-drying seems to be constant among studied formulations (15 %, Table 1). All aerogels produced by CO_2 induced gelation were milky-white, translucent and flexible to certain extent (Fig. 3a). This combination of properties differs significantly to that of alginate aerogels reported in the literature. Translucent samples were observed for sodium alginate concentrations of 0.25% and 0.5%. The degree of translucency and flexibility decreases with increasing calcium content. As shown in Fig. 2, aerogels retain fibrillar morphology with distinct macroporosity found previously for both alginate hydrogels and sc-dried aerogels.[35,36] Thus we can conclude CO_2 induced gelation results in hydrogels with secondary fibrillar structures similar to the diffusion gelation method.[36] Plausible reason for distinct translucency and flexibility of the aerogels reported here is the ratio between meso and macroporosity (Secion C.4).

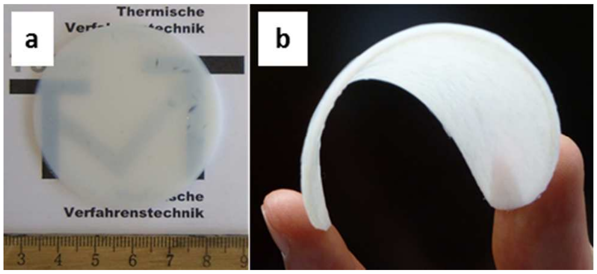


Fig. 3 (a) Translucent monolithic alginate aerogel (sample AA-2-2) as synthesized. (b) Aerogel after compression under a pressure of 10 kN m^{-2} becomes flexible.

Table 2 Textural properties of the alginate aerogels

Sample	c(Alg) (wt%)	q	ρ (g cm^{-3})	S$_{BET}$ †) (m^2 g^{-1})	V$_p$ (cm^3 g^{-1})
AA-1-1	0.25	0.5	– ‡)	545±77	4.24
AA-2-1	0.49	0.5	– ‡)	473±90	5.68
AA-4-1	0.98	0.5	0.13±0.01	413±18	3.20
AA-8-1	1.93	0.5	0.19±0.04	358±29	2.70
AA-12-1	2.84	0.5	0.24±0.03	264±19	1.68
AA-1-2	0.25	1.0	– ‡)	436±96	4.34
AA-2-2	0.49	1.0	0.06±0.02	479±67	6.98
AA-4-2	0.97	1.0	0.10±0.01	487±67	4.55
AA-8-2	1.86	1.0	0.16±0.04	448±22	3.85
AA-16-2	2.70	1.0	0.19±0.03	434±125	2.63
HP SE	0.75	1.5	0.016±0.003	538±37	5.96

† Confidence interval reported at 95 % confidence level.
‡ Samples obtained in the form of irregular pieces, thus, no density measured.

C.4 Properties of alginate aerogels

Bulk density and pore volume. Bulk density and BJH pore volume were determined from linear dimensions and desorption branches of N$_2$ isotherms, respectively. Values of specific volume, calculated as a reciprocal to bulk density, lie between 4.17 – 16.7 cm^3 g^{-1} indicating that only 40 – 62 % of the overall porosity can be attributed to the volume of mesopores (pore size 2 – 50 nm). Thus both micro- and macroporosity may be present. The t-plot analysis of the N$_2$ adsorption data points indicates that the volume of micropores (pore size < 2 nm) is negligible within the experimental error for all samples. This observation is in agreement with the work of Robitzer *et al.*,[13] where no micropores were detected. Valentin *et al.*[35] have found micropore volume to only a small extent (≤ 0.014 cm^3 g^{-1}). Therefore, it can be concluded that only meso- and macropores are present in the alginate aerogels reported in this study.

Systematic study of macroporosity in aerogels produced by other gelation methods is not reported in the literature, to our knowledge. It seems that the internal setting method with GDL also leads to aerogels with dual meso and macroporosity. We have previously reported the density and pore volume for aerogels produced by the internal setting gelation with GDL.[37] Results of the work[37] show that only 24.7% of the overall pore volume is due to mesoporosity. Hence CO$_2$ induced gelation leads to the increase in mesopore volume approximately by factor 2. Moreover, absolute values of the BJH pore volume indicate that CO$_2$ induced gelation allows to reach higher overall pore volume compared to that produced by diffusion and internal diffusion methods. Polysaccharide-based aerogels usually possess lower pore volume compared to silica ones. To the best of our knowledge, the highest BJH pore volume of 4.10 ± 0.78 cm^3 g^{-1} for Ca-alginate aerogel has been reported by Alnaief *et al.*,[38] although typical values lie between 0.74 and 1.16 cm^3 g^{-1}.[12,39] The samples AA-2-2 and AA-2-1 show extremely high BJH pore volumes of 6.98 and 5.68 cm^3 g^{-1}, respectively, displaying values close to silica aerogels (typically around 6 cm^3 g^{-1}).[40,41]

BJH pore volume increases when sodium alginate concentration decreases and reaches a maximum around the concentration of 0.5 wt% (Table 2). To explain this behavior two factors affecting the pore volume have to be considered. First, pore volume increases when solution becomes more and more diluted since the volume of empty space encompassed by the aerogel, increases consequently. Secondly, the stiffness of the backbone decreases with decreasing alginate concentration. In turn it leads to diminished resistivity against solvent exchange/sc-drying and thus results in partial collapse of aerogel pore structure (Section C.2). The latter factor is probably applicable to gels derived from 0.25 wt% alginate. Thus sodium alginate concentration in the vicinity of 0.5 wt% appears to be optimal in terms of shrinkage minimization and allows for reaching the highest pore volume in the range of calcium content studied.

Specific surface area. Along with the pore volume, the specific surface area affects the potential adsorption capacity of aerogels. Typical values for alginate aerogels were observed between 151.8 and 570 m^2 g^{-1}.[11,12] To our knowledge, the highest surface area of 608 ± 60 m^2 g^{-1} has been reported by Alnaief *et al.*[38] The values obtained for samples AA-1-1, AA-2-1 and AA-4-2 are comparable with this result. Work[38] also reports the influence of sodium alginate concentration on the textural properties of alginate aerogels obtained by internal setting method. In contrast to the present work, both surface area and pore volume were found to increase with increasing alginate concentration within the range of 1.5 to 3.0 wt%. However, data given in Table 2 shows a monotonous decrease with increase in sodium alginate concentration for all samples with q = 0.5. For doubled calcium concentration (q = 1.0), a slight decrease of the surface area was also observed. This behavior is not yet fully understood and is currently under investigation.

Compressibility. One interesting property of alginate aerogels produced by CO$_2$ induced gelation is the compressibility. Even when compressed under a pressure of 10 kN m^{-2} to 20 % of their original thickness the samples retained almost the same surface area while BJH pore volume even increases (by *ca.* 10 %). It indicates that compression affects rather the macroporous than the mesoporous structure. Surprisingly, we found that compressed aerogels become flexible and could be many times reversibly bent by an angle of 180 ° (Fig. 3b) similar to folding a paper, although initial sample could not be bent by more than 30 – 40 ° without breaking. Tentative mechanical tests demonstrate that alginate aerogels produced by CO$_2$ induced gelation behave as viscoplastic materials. Thus it has been shown for the first time that biopolymer aerogels can be converted by compression into flexible materials retaining porous characteristics of the original aerogels at the meso-level. The aerogels also retained their translucency after compression. Furthermore, compressed aerogels did not swell in water during several days and floated on the water surface in contrast to uncompressed ones that swell within several hours. This finding may open up opportunities to use these alginate aerogels as high-capacity matrices in pharmaceutical applications,[37,42,43] adsorbents,[44] membranes[45] and others.[6,7]

Thermal conductivity. Low thermal conductivity is an attractive property of aerogels.[46] Gels listed in Table 1 were dried to obtain aerogels. Thermal conductivity measurements were conducted with the hot-wire method.[25] Thermal conductivity at ambient conditions was measured to be 22 ± 2, 18 ± 2 and 19 ± 2 mW m^{-1} K^{-1} for samples HG-2-1, HG-1-2 and HG-2-2, respectively. The latter value decreases in vacuum (0.08 mbar) to 6.3 ± 0.8 mW m^{-1} K^{-1} and reflects the contribution of both radiative (due to translucency) and backbone heat transfer. These values are within the range for other porous materials, such as carbon aerogels, fumed silica and others.[47] All tested samples showed a thermal conductivity lower than free air (26 mW m^{-1} K^{-1} at 300 K) and can be classified as superinsulators.

C.5 Integration of the solvent exchange and sc-drying

Production of biopolymer aerogels currently includes three separate steps: gelation, solvent exchange and sc-drying. Since gelation often takes place in water media, solvent exchange is needed due to the miscibility gap between sc-CO_2 and water.[48] One possible solution to eliminate the solvent exchange consists in continuous extraction of water with sc-CO_2/ethanol mixture. This process was exemplified by Brown *et al*. using agar hydrogels.[49] Our attempts to extract water from alginate hydrogels using various sc-CO_2/ethanol ratios were unsuccessful leading to significant shrinkage (Fig. 4a). Indeed, to avoid shrinkage, capillary forces should be eliminated and thus the system has to be exclusively in the single-phase region from the very beginning of the process. However, ternary mixture $CO_2/C_2H_5OH/H_2O$ shows single-phase behavior only above ethanol content of approximately 50 wt% (10 – 20 MPa, 313 K).[50] Thus, initially alginate hydrogels underwent the evaporative drying and only then the sc-drying. Moreover, alginate hydrogels seem to be much softer than agar used by Brown *et al*.[49] The combination of these factors is plausible explanation for such a pronounced shrinkage. This finding justifies that water has to be substituted by an organic solvent prior to (but not during) sc-drying, at least for soft hydrogels.

In this paper we present a proof-of-concept approach towards integration of the solvent exchange and sc-drying. Instead of immersing hydrogels in grades of ethanol at ambient conditions followed by sc-drying, we first exposed the alginate hydrogels to sc-CO_2 (12 MPa, 318 K) and then introduced ethanol/water mixtures (30, 60, 90 wt%) to cover gels completely. Preliminary study was carried out to find appropriate duration of the solvent exchange step. We found that each step require about 2.5 h (drop of ethanol concentration was less than 3 % after that time). Then the gels were flushed with sc-CO_2/ethanol mixture (*ca.* 25 wt% of ethanol, 3 h) to ensure complete water removal and finally dried with pure sc-CO_2.

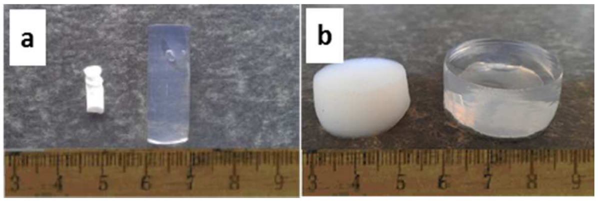


Fig. 4 (a) Collapsed gel (left) after the extraction of water from the parent hydrogel (right) with sc-CO_2/ethanol mixture. (b) Aerogel produced by CO_2 induced gelation and integrated solvent exchange and sc-drying (left); parent hydrogel (right).

High pressure viewing cell allowed to observe shrinkage during the course of the process. It was noticed that major shrinkage occurred at the flushing and sc-drying stages, but when covered by an ethanol/water mixture, the gels almost retained their initial sizes. This observation highlights that gels should be covered by the liquid phase till the point where the ethanol concentration is high enough so as the whole system is in a single phase.

Resulting aerogel had excellent textural properties with density of 0.021 ± 0.007 g cm^{-3}, BET surface area of 538 ± 37 m^2 g^{-1} and BJH pore volume of 5.96 cm^3 g^{-1} (sample HP SE, Table 2). Thus, solvent exchange at high pressure led to aerogels with only moderate shrinkage (Fig. 4b). Tentative results also show that solvent exchange is accelerated at high pressure. Comparative study of ambient and high pressure solvent exchange processes will be published elsewhere.

Conclusions

In this work, the possibility of using carbon dioxide to initiate the gelation of alginate solutions is demonstrated. We have revealed that pressurized carbon dioxide at 5 MPa and 298 K can act as a weak acid and results in the release of calcium ions from $CaCO_3$ suspended in the sodium alginate solution. Liberated calcium ions crosslink alginate resulting in the formation of hydrogels. Thus we have shown that internal setting method can be performed using pressurized carbon dioxide. Several features are associated with this process: (i) fast depressurization leads to macroporous foam-like hydrogels, whereas slow depressurization yielded macroscopically homogeneous hydrogels; (ii) bactericidal activity of pressurized CO_2 may simplify preparation of food and medical materials;[51] (iii) this process can potentially be applied to the gelation of other polysaccharides and alginate-based polymer blends.

We have demonstrated that CO_2 induced gelation gives transparent and stable (in the humid atmosphere) hydrogels. The thickness of the samples was found to be critical to obtain bubble-free gels. Mixtures with thickness of 10 – 12 mm gave homogeneous hydrogels, whereas thicker samples were sponge-like containing bubbles of several millimetres in size. Stepwise solvent exchange and supercritical drying maintained fibrillar structure of the hydrogels and despite pronounced shrinkage led to translucent, low density (0.06 – 0.24 g cm^{-3}) aerogels with low thermal conductivity (as low as 18 ± 2 mW m^{-1} K^{-1}). Surprisingly, it was found that aerogels can be easily compressed into very flexible paper-like material. Solvent exchange can be performed in pressurized CO_2 and coupled with supercritical drying. This paper presents a first step towards such an integrated one pot-process, which is the purpose of our ongoing work.

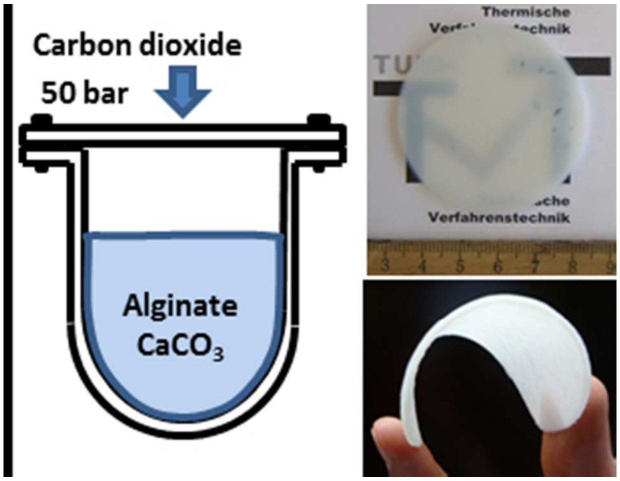
Acknowledgements

The authors are thankful to Dr. Gudrun Reichenauer, Lena Weigold and Dr. Matthias Wiener (Bavarian Centre for Applied Energy Research, Germany) for the measurements of thermal conductivity and Marianne Kammlott for her help with the nitrogen adsorption measurements. Pavel Gurikov acknowledges DAAD for supporting him through a postdoctoral fellowship. Financial support from DFG (project SM 82/8-2) is gratefully acknowledged.

Notes and references

[a] Hamburg University of Technology, Institute of Thermal Separation Processes, Eißendorfer Straße 38, 21073 Hamburg, Germany.
E-mail: pavel.gurikov@tuhh.de
Tel: +49 40 42878 4275; Fax: +49 40 42878 4072
[b] BASF Polyurethanes GmbH, GMU/LF - A10, 49448 Lemfoerde, Germany.

1 K. I. Draget, O. Smidsrød and G. Skjåk-Bræk, in *Polysaccharides and polyamides in the food industry: properties, production, and patents*, ed. A. Steinbüchel and S. K. Rhee, Wiley-VCH; John Wiley, Weinheim; Chichester, 2005.
2 S. N. Pawar and K. J. Edgar, *Biomaterials*, 2012, **33**, 3279.
3 D. Rassis, A. Nussinovitch and I. S. Saguy, *Int. J. Food Sci. Technol.*, 1997, **32**, 271.
4 W. R. Gombotz and S. F. Wee, *Adv. Drug Delivery Rev.*, 2012, **64**, 194.
5 H. H. Tønnesen and J. Karlsen, *Drug Dev. Ind. Pharm.*, 2002, **28**, 621.
6 A. I. Zouboulis and I. A. Katsoyiannis, *Ind. Eng. Chem. Res.*, 2002, **41**, 6149.
7 J. T. Delaney, A. R. Liberski, J. Perelaer and U. S. Schubert, *Soft Matter*, 2010, **6**, 866.
8 C. A. García-González, M. Alnaief and I. Smirnova, *Carbohydrate Polymers*, 2011, **86**, 1425.
9 C. L. Herran, Y. Huang and W. Chai, *Journal of Micromechanics and Microengineering*, 2012, **22**, 085025.
10 *Aerogels Handbook*, ed. M. A. Aegerter, N. Leventis and M. M. Koebel, Springer, 2011.
11 F. Quignard, R. Valentin and F. Di Renzo, *New Journal of Chemistry*, 2008, **32**, 1300.
12 A. Veronovski, Z. Novak and Z. Knez, *J. Biomater. Sci., Polym. Ed.*, 2012, **23**, 873.
13 M. Robitzer, L. David, C. Rochas, F. D. Renzo and F. Quignard, *Langmuir*, 2008, **24**, 12547.
14 D. A. Loy, E. M. Russick, S. A. Yamanaka, B. M. Baugher and K. J. Shea, *Chem. Mater.*, 1997, **9**, 2264.
15 M. Moner-Girona, A. Roig, E. Molins and J. Llibre, *J. Sol-Gel Sci. Technol.*, 2003, **26**, 645.
16 I. Smirnova and W. Arlt, *J. Sol-Gel Sci. Technol.*, 2003, **28**, 175.
17 R. Sui, A. S. Rizkalla and P. A. Charpentier, *J. Phys. Chem. B*, 2004, **108**, 11886.
18 K. N. Lee, H. J. Lee, J.-Y. Lee and J.-H. Kim, *J. Dispersion Sci. Technol.*, 2001, **22**, 79.
19 U. Fehrenbacher and M. Ballauff, *Macromolecules*, 2002, **35**, 3653.
20 A. I. Cooper, C. D. Wood and A. B. Holmes, *Ind. Eng. Chem. Res.*, 2000, **39**, 4741.
21 S. Partap, I. Rehman, J. R. Jones and J. A. Darr, *Advanced Materials*, 2006, **18**, 501.
22 E. Reverchon, S. Cardea and C. Rapuano, *Journal of Applied Polymer Science*, 2007, **104**, 3151.
23 C. Rudaz, Ph.D. Thesis, MINES ParisTech, 2013.
24 I. Smirnova, J. Mamic and W. Arlt, *Langmuir*, 2003, **19**, 8521.
25 H.-P. Ebert, V. Bock, O. Nilsson and J. Fricke, *High Temp. - High Pressures*, 1993, **25**, 391.
26 J. P. Miller, *American Journal of Science*, 1952, **250**, 161.
27 D. Buhmann and W. Dreybrodt, *Chemical Geology*, 1987, **64**, 89.
28 A. N. Palmer, *Geological Society of America Bulletin*, 1991, **103**, 1.
29 B. Meyssami, M. O. Balaban and A. A. Teixeira, *Biotechnol. Prog.*, 1992, **8**, 149.
30 J.-Y. Gal, J.-C. Bollinger, H. Tolosa and N. Gache, *Talanta*, 1996, **43**, 1497.
31 C. Tsioptsias, A. Stefopoulos, I. Kokkinomalis, L. Papadopoulou and C. Panayiotou, *Green Chemistry*, 2008, **10**, 965.
32 C. Tsioptsias and C. Panayiotou, *J. Supercrit. Fluids*, 2008, **47**, 302.
33 C. Tsioptsias, M. K. Paraskevopoulos, D. Christofilos, P. Andrieux and C. Panayiotou, *Polymer*, 2011, **52**, 2819.
34 Y. Fang, S. Al-Assaf, G. O. Phillips, K. Nishinari, T. Funami, P. A. Williams and L. Li, *J. Phys. Chem. B*, 2007, **111**, 2456.
35 R. Valentin, K. Molvinger, F. Quignard and F. Di Renzo, *Macromol. Symp.*, 2005, **222**, 93.
36 M. Robitzer, L. David, C. Rochas, F. Di Renzo and F. Quignard, *Macromol. Symp.*, 2008, **273**, 80.
37 T. Mehling, I. Smirnova, U. Guenther and R. H. H. Neubert, *Journal of Non-Crystalline Solids*, 2009, **355**, 2472.
38 M. Alnaief, M. A. Alzaitoun, C. A. García-González and I. Smirnova, *Carbohydrate Polymers*, 2011, **84**, 1011.
39 M. Robitzer, A. Tourrette, R. Horga, R. Valentin, M. Boissière, J. M. Devoisselle, F. Di Renzo and F. Quignard, *Carbohydrate Polymers*, **2011**, 85, 44.
40 Z. Knez and Z. Novak, *J. Chem. Eng. Data*, 2001, **46**, 858.
41 A. V. Rao, E. Nilsen and M. A. Einarsrud, *Journal of Non-Crystalline Solids*, 2001, **296**, 165.
42 P. Del Gaudio, G. Auriemma, T. Mencherini, G. D. Porta, E. Reverchon and R. P. Aquino, *Journal of Pharmaceutical Sciences*, 2013, **102**, 185.
43 A. Veronovski, Z. Knez and Z. Novak, *J. Supercrit. Fluids*, 2013, **79**, 209.
44 R. R. Mallepally, I. Bernard, M. A. Marin, K. R. Ward and M. A. McHugh, *J. Supercrit. Fluids*, 2013, **79**, 202.
45 F. J. Zhang, G. X. Cheng, Z. Gao and C. P. Li, *Macromol. Mater. Eng.*, 2006, **291**, 485.
46 H.-P. Ebert, in *Aerogels Handbook*, ed. M. A. Aegerter, N. Leventis and M. M. Koebel, Springer, 2011., ch. 23, pp. 537–564.
47 G. Reichenauer, U. Heinemann and H.-P. Ebert, *Colloids Surf., A*, 2007, **300**, 204.
48 A. Bamberger, G. Sieder and G. Maurer, *J. Supercrit. Fluids*, 2000, **17**, 97.
49 Z. K. Brown, P. J. Fryer, I. T. Norton and R. H. Bridson, *J. Supercrit. Fluids*, 2010, **54**, 89.
50 N. E. Durling, O. J. Catchpole, S. J. Tallon and J. B. Grey, *Fluid Phase Equilib.*, 2007, **252**, 103.
51 L. Garcia-Gonzalez, A. H. Geeraerd, S. Spilimbergo, K. Elst, L. Van Ginneken, J. Debevere, J. F. Van Impe and F. Devlieghere, *International Journal of Food Microbiology*, 2007, **117**, 1.



A novel process, carbon dioxide induced gelation, opens new pathways towards hydrogels and can be coupled with supercritical drying to produce aerogels
51x39mm (150 x 150 DPI)