



Chitin and carbon aerogels from chitin alcogels

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ABSTRACT

Supercritical point drying of gels is a common technique for the production of a specific category of nano-porous materials called aerogels. We have successfully prepared chitin aerogels by extracting the solvent from the alcogels (gels with an alcohol as the solvent) with carbon dioxide under supercritical conditions. The produced nano-porous materials exhibit the typical properties of aerogels such as high porosity, high surface area, and low density, which make them quite attractive for many applications. The use of chitin, however, is of particular interest for the production of aerogels not only for being abundant and cheap but also because it has important inherent properties such as biocompatibility, non toxicity, thermal and chemical stability. In this work we examine the influence of different parameters on the porosity characteristics of the aerogels, such as the drying conditions (temperature and pressure), the nature of the solvent, and the gel concentration. Since these aerogels collapse in liquid medium, we also investigated the possibility of their utilization as carbon aerogel precursors.

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1. Introduction

The progress in nanotechnology in the last decades has a tremendous impact both on academic research and everyday life. A significant contribution to this progress comes from nano-porous materials. These materials can be used in a wide variety of applications such as advanced separation processes (gas separation for example), catalysis in chemical reactions, packaging and insulating materials, and for biomedical purposes (e.g., artificial skin or virus filtering) (Cooper, 2003). Aerogels is a category of nano-porous materials and exhibit unusual properties, such as low density, high surface area, transparency, low heat conductivity, and mechanical strength (Pierre & Pajonk, 2002). Applications of aerogels cover a wide range (including the applications of common nano-porous materials) from transparent super thermal and sound insulators to electronics, space and particle research (Pierre & Pajonk, 2002; Valentin, Bonelli, Garrone, Di Renzo, & Quignard, 2007).

Gels, in general, are colloidal dispersions of liquids in solid networks. They can be inorganic, organic, or organic–inorganic and are, usually, produced by the sol–gel process. In the case of aerogels more attention has been paid to the production of inorganic gels based on alumina and silica and to carbon aerogels (Pierre & Pajonk, 2002). Carbon aerogels due to electrical conductivity have great potential of applications (Pierre & Pajonk, 2002; Yamashita, Ojima, Shioya, Hatori, & Yamada, 2003; Moreno-Castilla & Maldonado-Hódar, 2005). With few exceptions (Pekala, 1989), organic polymeric aerogels have been studied relatively recently (Cai, Kim-

ura, Wada, Kuga, & Zhang, 2008; Fischer, Rigacci, Pirard, Berthon-Fabry, & Achard, 2006; Reverchon, Cardea, & Rapuano, 2008; Valentin et al., 2007), or have been used as precursors for producing carbon aerogels (Yamashita et al., 2003).

The supercritical point drying (SPD) is a widely used technique for the production of aerogels. The SPD is based on exposing the gel at conditions above the supercritical point of the solvent of the gel (homogeneous fluid system) in order to prevent the formation of a vapour–liquid interface. The interfacial tension of this interface can cause the collapse of the structure during solvent removal (e.g., when it is left to evaporate at ambient conditions), while the solvent removal under supercritical conditions (zero surface tension) retains the original structure of the wet gel (Pierre & Pajonk, 2002). This procedure is quite similar to the freeze-drying procedure, in which also the vapour–liquid interface is absent (the solvent in this case becomes vapour directly from a solid phase without passing through an intermediate liquid phase). Solid gels produced by freeze-drying are usually called cryogels and do not exhibit the attractive properties of aerogels (Pierre & Pajonk, 2002; Valentin et al., 2007).

Common solvents in gels are alcohols and acetone. The production of aerogels by SPD with these solvents requires high temperatures due to their high critical temperatures (>230 °C). Supercritical carbon dioxide (ScCO₂), on the other hand, is probably the most common supercritical fluid that has been used in polymer science and technology, due to its non flammability, low toxicity, low critical pressure and temperature (Pierre & Pajonk, 2002; Quirk, France, Shakesheff, & Howdle, 2004). Chemical synthesis/polymerization, production of polymeric foams and particles and encapsulation process are some of the applications of supercritical

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carbon dioxide (Pierre & Pajonk, 2002; Quirk et al., 2004). Another common approach then for gel drying (at low temperatures) is the replacement of the solvent in the gel with liquid carbon dioxide and the subsequent exposure of the gel at supercritical carbon dioxide (temperature above 31.2 °C and pressure above 73.8 bar) (Cai et al., 2008).

Chitin is a natural polymer (polysaccharide) found mainly in arthropods and it is one of the most abundant polymers in nature. It has gained much attention for biomedical applications due to its biocompatibility and restorative properties (Brugnerotto et al., 2001). The crystalline structure of chitin, due to intra- and inter-molecular hydrogen bonds, is to a great extent responsible for its thermal and chemical stability. However, the poor solubility in most organic solvents limits its utilization.

In our previous work (Tsiptsias & Panayiotou, 2008; Tsiptsias, Stefopoulos, Kokkinomalis, Papadopoulou, & Panayiotou, 2008) we observed that, when exposing chitin or cellulose “hydrogels” in high-pressure carbon dioxide, a porous structure was obtained rather easily. In the present study we continue this work and further investigate the factors affecting the production of porous structures from chitin gels by processing them with supercritical carbon dioxide. In contrast to our previous work (Tsiptsias & Panayiotou, 2008) with chitin hydrogels, now we focus on chitin alcogels (alcohol as the solvent), which are brought to conditions appropriate for supercritical point drying. In addition, the feasibility of producing carbon aerogels from chitin aerogels is investigated.

2. Experimental

2.1. Materials and instruments

Chitin (practical grade from crab shells, acetylation degree >75%) was purchased from Sigma–Aldrich. *N,N*-dimethylacetamide (DMA) (purity >98%) was purchased from Fluka. Lithium chloride (LiCl) (purity 99%) was purchased from Sigma–Aldrich. Carbon dioxide (purity >99.98%) and nitrogen (purity >99.99 %) were purchased from Air Liquide Mediterranee. Methanol (>99.8%) was purchased from Baker and ethanol, 1-propanol and 1-butanol (>99.8%) from Riedel-de Haen.

The apparatus used for the supercritical point drying is described in detail elsewhere (Tsivintzelis, Pavlidou, & Panayiotou, 2007). Briefly, it consists of a high-pressure cell of internal volume of 40 cm³, an ISCO syringe pump for pumping ScCO₂, and pressure and temperature controllers for keeping pressure and temperature constants at the desired values. A thermogravimetric analyzer (Shimadzu, model TGA-50) was used to examine the thermal stability of the produced materials. N₂ adsorption at 77 K was utilized to determine the specific surface areas and porosities of the prepared aerogel and carbon. A gas adsorption manometry apparatus was used for the N₂ adsorption experiments. The BET equation was used for the calculation of the specific surface area and the pore size distribution. Also, a Bio-Rad FTIR (model FTS 175) spectrometer was used, and measurements were carried out with a resolution of 2 cm^{−1} and 32 scans. For the preparation of the carbon aerogel a tubular fixed-bed reactor was used with 2-in. nominal diameter made of 316 stainless steel under constant nitrogen flow. Elemental analysis of the materials was conducted in a “FLASH EA T.M. 1112” ThermoFinnigan Elemental Analyser, and the carbon, hydrogen, nitrogen, sulphur and (by difference) the oxygen content of the samples were determined.

2.2. Preparation and characterisation of chitin aerogels

Chitin was dissolved in DMA + 6% (w/v) LiCl mixture at 20 °C under magnetic stirring overnight. It was dissolved in concentrations of 0.9% and 1.9% (w/v). The solutions were cast in petri dishes

and allowed to stay at room temperature overnight in order to provide with enough time for the gelation. The extensive washing of the gels containing DMA and LiCl with distilled water resulted in solid chitin hydrogels. The hydrogels were immersed in excess of methanol or 1-propanol many times to give chitin alcogels. Gels from the 1.9% initial solution were treated only with methanol. These gels were used to examine the influence of drying pressure and temperature on the final properties of aerogels. Gels from the 0.9% initial solution were treated with methanol or 1-propanol. These gels were used to examine the influence of the gel concentration (which arise from the different initial solution concentration 1.9% and 0.9%) and the nature (especially the molecular size) of the solvent.

The obtained alcogels were weighted and then placed in the high-pressure cell at different conditions of pressure and temperature ranging from 80 to 300 bar and from 40 to 80 °C, respectively. The cell was preheated at the desired temperature while the pressure was reaching the set point value in less than 2 min after the sample was placed in the cell. The system initially was kept at static conditions for 90 min, and then the outlet valve was opened. The pressure was kept constant due to the continuous flow of carbon dioxide. The volumetric flow was different at each set of pressure and temperature in order to have a mass flow of carbon dioxide equal to 0.42 ± 0.09 g/min in all cases. The continuous extraction (drying) of the mixture from the gel was applied for at least 2 h. The mass proportion of the consumed carbon dioxide to the (initial) mass of alcohol in the gel was at least 170. The critical point of the mixtures was grossly estimated by the following mixing rule:

$$P_{\text{c,mix}} = x_{\text{CO}_2} \times P_{\text{c,CO}_2} + x_{\text{alc}} \times P_{\text{c,alc}} \quad (1)$$

$$T_{\text{c,mix}} = x_{\text{CO}_2} \times T_{\text{c,CO}_2} + x_{\text{alc}} \times T_{\text{c,alc}} \quad (2)$$

where P_c , T_c , x refer to critical pressure, critical temperature, and mole fraction, respectively, and the subscripts mix, CO₂ and alc refer to the mixture, carbon dioxide, and methanol or 1-propanol, respectively. The moles of carbon dioxide were estimated from the volume of the cell (40 cm³) and the density of carbon dioxide at these specific conditions (Nist Chemistry WebBook, 2008). The mole fraction of alcohols was less than 0.05 in all cases and, thus, the above simple mixing rule can be considered as an acceptable approximation for the calculation of the critical point in such dilute mixtures. In Table 1, the exact conditions of each experiment are presented and an identity number is given to each sample.

Phase inversion was applied to a methanogel at conditions below the critical point of the mixture and an air dried methanogel (regenerated non-porous chitin) was prepared for comparison. The surface area of aerogels was measured by the BET method.

The porosity of the materials was estimated by the following equation (Karageorgiou & Kaplan, 2005):

$$P = (1 - d_p/d_b) \times 100, \quad (3)$$

where d_p is the density of the porous material and d_b the density of the bulk material. The density of the bulk sample was measured

Table 1

Information for the samples prepared. All samples had methanol as the solvent (92% w/w) except if otherwise noted.

Sample identity	Conditions of drying	ΔP	ΔT
1	100 bar 40 °C	26	5
2	200 bar 40 °C	126	3
3	300 bar 40 °C	226	4
4	200 bar 80 °C	126	42
5	300 bar 40 °C, (methanol 94.7% w/w)	226	4
6	300 bar 40 °C, (1-propanol 93.8% w/w)	226	6
7	60 bar 40 °C,	−15	−15
8	Air dried	–	–

using the buoyancy method (ASTM D-792) with ethylene glycol as the liquid of known density. The density of the porous samples was calculated by measuring their mass and their dimensions.

Thermogravimetric analysis for chitin aerogels and air dried chitin, was done in an air atmosphere, at a rate of 10 °C/min until 80 °C, hold for 5 min, and then at a heating rate of 10 °C/min until 600 °C. The mass at 150 °C was set as the 100% mass.

2.3. Preparation and characterization of carbon aerogels from chitin aerogels

A prepared chitin aerogel (sample 5) was used as a precursor for the production of carbon aerogel. For this reason, a fixed amount of chitin aerogel was pyrolysed at 300 °C for 30 min under constant nitrogen flow. The carbonization was followed by activation with CO₂ at 800 °C for 2.5 h. The carbon produced, and the initial chitin aerogel (sample 5), were characterized by means of nitrogen adsorption for their specific surface area and pore volume distribution, elemental analysis and thermogravimetric analysis. Thermogravimetric analysis of these 2 samples was carried out in nitrogen atmosphere (at constant flow of 20 ml/min, with a heating rate of 10 °C/min until 800 °C). FTIR measurements of carbon aerogel and air dried chitin, were carried out with a resolution of 2 cm⁻¹ and 32 scans. The samples were powdered, mixed with KBr, and processed into pellets.

3. Results and discussion

3.1. Porosity characteristics of chitin aerogels

Samples 1–6 remained swollen after solvent removal. The solvent in all samples was methanol except sample 6 which had propanol as solvent. Sample 7 was extensively shrunk like the air dried sample 8. This could be attributed to the co-existence of vapour and liquid phases. N₂ adsorption at 77 K was measured in all porous samples and a representative isotherm is illustrated in Fig. 1. The isotherm exhibits the typical form of isotherms corresponding to physical sorption and can be classified as type II or IV according to IUPAC recommendations (Keller & Staudt, 2005), suggesting an essentially meso-porous structured material (pore sizes between 2 and 50 nm). Similar isotherms were obtained for all samples 1–6. From the isotherm and for relative pressures between 0.05 and 0.35 the surface area was found to be 275 ± 15 m²/g. From

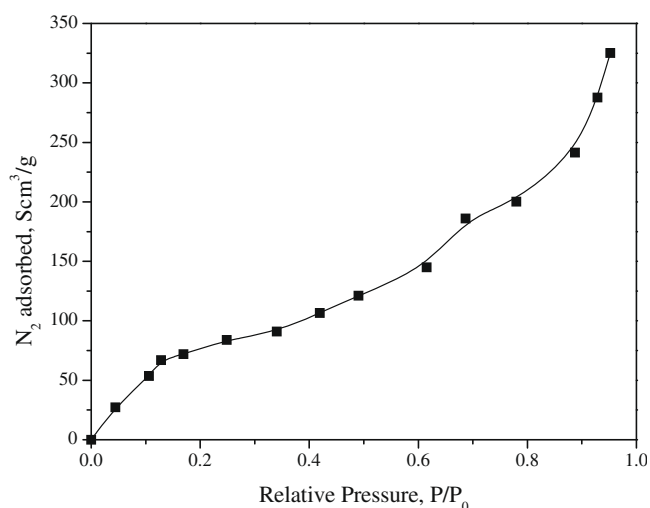


Fig. 1. Representative N₂ adsorption isotherm at 77 K of sample 2.

the density measurements and by using Eq. (3), the porosity of the material was found to be 88 ± 0.5%.

The porosity characteristics of all samples are summarized in Table 2. As can be seen, all samples exhibited porosity higher than 85%, surface area greater than 220 m²/g, and low density (<0.23 g/cm³). Samples 1–4, that were prepared at different pressures and temperatures, appear to have different characteristics. The surface area and the porosity increase (smaller pore size) by increasing pressure or decreasing temperature. However, the large uncertainty in the surface area of sample 4 and the small difference in the density and porosity of these samples does not allow for a safe conclusion. In general, the samples prepared under different conditions of temperature and pressure, do not exhibit significant changes in their characteristics despite the significant differences in the examined parameters.

Gel concentration seems to have a more pronounced influence on the porosity characteristics (samples 3 and 5). As described in the experimental section, two chitin solutions in DMA + LiCl were prepared. The difference of the initial concentration of chitin in the solutions resulted in gels with different solvent content (~95% and 92% w/w). However, this small change (3% w/w) was enough to significantly alter the density of the final material.

Another examined parameter was the nature of the solvent of the gel (samples 5 and 6). When using a solvent of larger molecular size (1-propanol instead of methanol), the porosity characteristics indicate larger pores. It should be stressed that these gels were prepared from the same less concentrated chitin solution in DMA + LiCl. However, the obtained gels exhibited a slightly different solvent content (94.73 ± 0.02% w/w in the case of the methanogel and 93.78 ± 0.03% w/w in the case of 1-propanogel). The difference (in the solvent content in the gel) might be attributed to both the molecular size and the interactions with chitin or water as it can be concluded from the partial solubility parameters (Table 3).

3.2. Thermal and chemical stability of chitin aerogels

As mentioned above, in general, aerogels can be used in a wide variety of applications due to their unusual properties. However, the existence of high surface area can possibly have a negative impact on certain properties such as thermal or chemical stability. By thermogravimetric analysis (TGA) we have examined the thermal stability of the aerogels and of the regenerated non-porous (air dried) chitin. The differential TGA curves of the aerogel with the highest surface area (sample 5) and of air dried chitin are shown in Fig. 2. As can be seen, the aerogel decomposes faster than the non-porous chitin. The temperature of highest decomposition rate is 308 °C for the aerogel and 331 °C for the non-porous chitin. At 280 °C the aerogel has 87.5% remaining mass versus 93.4% of air dried chitin. All aerogels had similar thermal behavior with only small differences (no more than 5 °C). However, despite the non-negligible reduction in the thermal stability in comparison to non-porous chitin, the produced chitin aerogels can be considered as thermally stable compared to other polymeric materials.

Table 2
Porosity characteristics of the prepared samples.

Sample	S _{BET} (m ² /g)	Density (g/cm ³)	% Porosity
1	220 ± 15	0.226 ± 0.017	84.5 ± 1.5
2	275 ± 15	0.174 ± 0.006	88 ± 0.5
3	308 ± 47	0.171 ± 0.007	88 ± 0.5
4	259 ± 75	0.175 ± 0.011	88 ± 1
5	363 ± 41	0.124 ± 0.006	91.5 ± 0.5
6	327 ± 28	0.125 ± 0.007	91.5 ± 0.5
7,8	–	1.44 ± 0.05	–

Table 3

Gels concentration in chitin alcogels for different alcohols and solubility parameters (Hansen, 2000; Ravindra, Krovvidi, & Khan, 1998).

Substance	δ_d	δ_p	δ_h	% w/w in chitin gel
Chitin	23.9	18	22.3	–
Water	15.5	16	42.3	–
Methanol	15.1	12.3	22.3	94.73 ± 0.02
Ethanol	15.8	8.8	19.4	94.63 ± 0.02
1-propanol	16	6.8	17.4	93.78 ± 0.03
1-butanol	16	5.7	15.8	68.89 ± 0.2

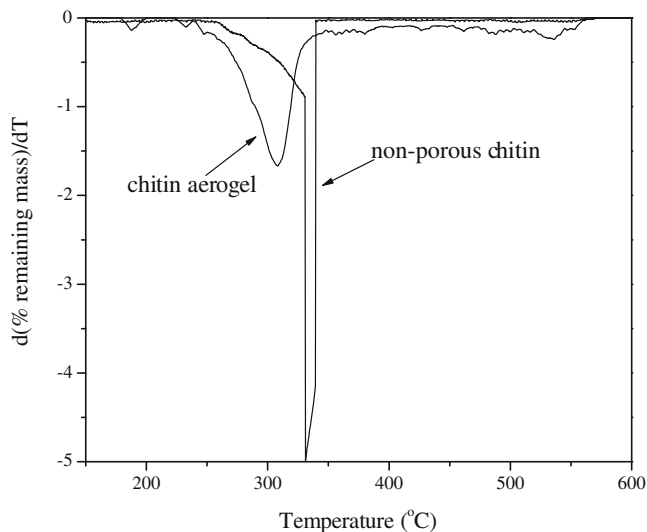


Fig. 2. Differential TGA curves for regenerated air dried (non-porous) chitin and chitin aerogel (sample 5).

Besides thermal stability, native and regenerated chitin exhibit also high chemical resistance, due to intra- and inter-molecular hydrogen bonds. Regenerated chitin (air dried and non-porous) can be swollen by water or aqueous solutions. After water removal shrinking occurs. Alcohols and non-polar liquids (e.g., dichloromethane) do not have a similar influence. In addition, redissolution of chitin is very difficult. Chitin aerogels exhibit the same poor solubility as non-porous chitin, but are strongly influenced by liquid substances. We noticed that if we immerse a chitin aerogel in some liquid, after air drying, extensive shrinking and macroscopical shape deformation of the aerogel occurs regardless of the liquid's nature (polar or non-polar). The fact that the porous network of chitin aerogels is destroyed in liquid medium undoubtedly limits the possible applications of chitin aerogels. Thus, we examine next the feasibility of utilizing them as carbon aerogels precursors.

3.3. Carbon aerogels

The conditions used in this work for the initial pyrolysis of chitin aerogel were based on its thermal decomposition profile (Fig. 3). During carbonization, a mass loss of 47% was observed while the specific surface area was reduced to 207 m²/g. The porous

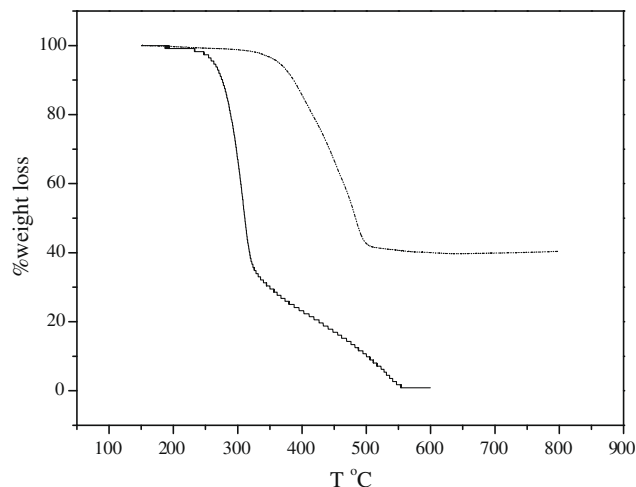


Fig. 3. TGA curves of chitin (–) and carbon (···) aerogel.

structure in the produced aerogel was based solely on physical interactions by exploiting the high hydrogen bonding capacity of the amide and hydroxyl groups. Since no additional chemical crosslinking agents were used, it was expected that, due to the thermal treatment, several of these bonds would be disrupted. This partial shrinkage and collapse of the porous structure along with the densification of the aerogel result in the reduced surface area (Yamashita et al., 2003).

In view of the above shrinkage, it was decided to proceed with further activation of the pyrolysed material by means of CO₂ in order to achieve increased surface area. Due to its small molecular size CO₂ creates porosity without completely disrupting the pre-existing aerogel structure. As shown in Table 4, the produced carbon possesses a surface area of 463 m²/g, which lies within the range of what is commonly accepted for carbon aerogels. The shape of the N₂ adsorption isotherm of chitin (continuous increase of adsorption with increase in pressure) indicates a material with extensive mesoporosity, (Fig. 4a). After activation, the produced carbon aerogel presents a narrow distribution in pore sizes in the range of micropores (sizes lower than 20 Å) as depicted by the sharp increase in adsorption at low relative pressures, Fig. 4a. These findings are further supported by the pore size distribution curves, Fig. 4b. As can be seen, the carbon aerogel presents a very narrow distribution of porosity with most pores having a pore radius of less than 10 Å, and a smaller percentage with pore radius up to 20 Å. The mean pore size is 13.1 Å. In Table 4, porosity characteristics of the two aerogels are summarized.

The results from elemental analysis, presented in Table 5, indicate that there are no considerable differences between the chemical composition of the chitin and carbon aerogel. In accordance to the elemental analysis results, the FTIR spectra of air dried chitin and carbon aerogel (Fig. 5), resemble remarkably, leading to the conclusion that the original structure of the aerogel is preserved to some extent. In particular, in both spectra appears the peak around 1100 cm^{−1} that corresponds to the saccharide structure (Wanjuna, Cunxin, & Donghua, 2005), the double peak in the area of 1500–1650 cm^{−1} attributed to amide groups (Jang, Kong, Jeong,

Table 4

Porosity characteristics of chitin (sample 5) and carbon aerogel.

Sample name	$V_{0.99}$ (cm ³ /g)	V_{tot} (cm ³ /g)	V_{μ} (cm ³ /g)	V_m (cm ³ /g)	S_{BET} (m ² /g)	R_p (Å)	% μ_p
Chitin aerogel	328	0.5084	0.133755	0.3746	362	28.1	26.3
Carbon aerogel	196.3	0.3043	0.2024	0.1019	463	13.1	66.5

V_{tot} , total pore volume, V_{μ} , micropores volume, V_m , mesopores + macropores volume, R_p , average pore radius, % μ_p , micropores percentage.

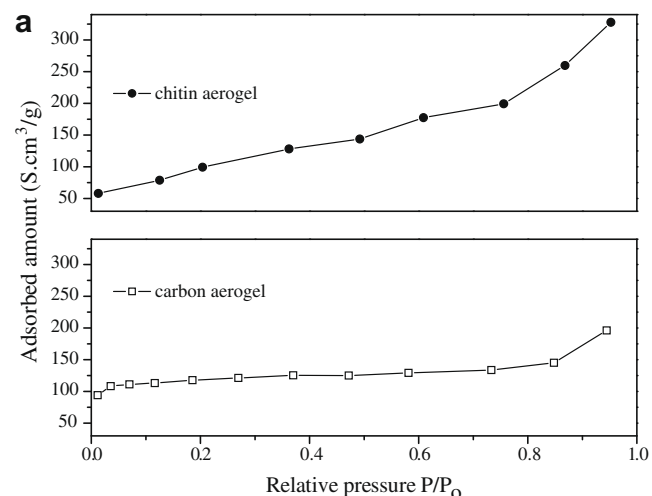
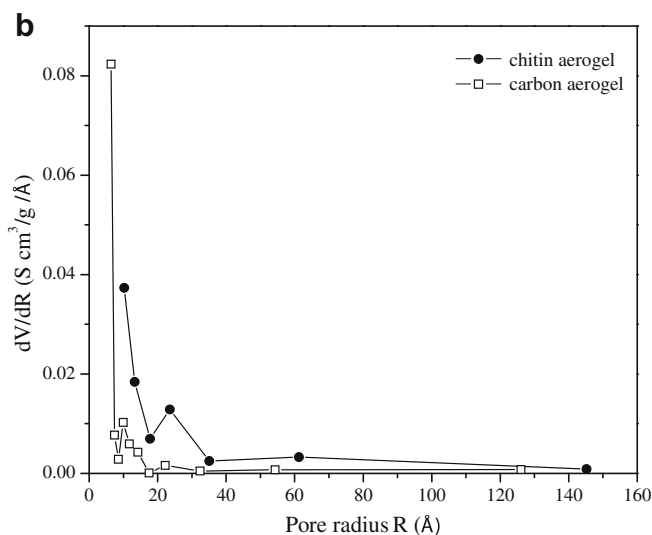


Fig. 4. (a) N_2 adsorption isotherm at 77 K for carbon and chitin aerogel (sample 5), (b) pore size distribution for carbon aerogel and chitin aerogel (sample 5).

Table 5
Results of elemental analysis % by wt.

Sample name	% C	% H	% N	% S	% O
Chitin aerogel	40.85	6.12	7.19	0	45.84
Carbon aerogel	41.62	0.89	7.9	0	49.59

Lee, & Nah, 2004), and the broadened peak at 3500 cm^{-1} corresponding to the hydroxyl groups.

The TGA curves (Fig. 3) highlight the more thermally resistant nature of the produced carbon aerogel. The decomposition steps at 400 and 450°C are indicative of the decomposition of cyclic, polysaccharide-like structures or stable acetylated side-chains (Wanjuna et al., 2005) connected to the main carbon structure (Wu, Sasaki, Irie, & Sakurai, 2008). It should also be noted that almost 40% of the carbon aerogel structure is not liable to thermal decomposition at the studied temperatures, and possibly represents the stable graphite-like structure that was created by the carbonization and activation procedures.

4. Conclusions

Chitin aerogels were successfully prepared by supercritical point drying. The aerogels exhibited high porosity, high surface

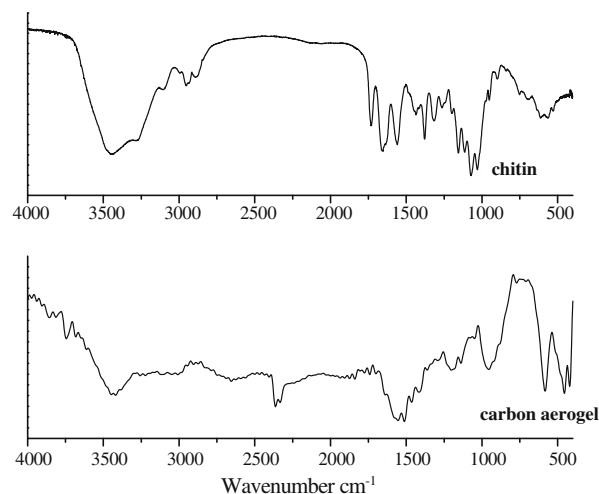


Fig. 5. FTIR spectra of chitin and carbon aerogel.

area, and low density compared to air dried chitin or chitin dried by phase inversion below the critical point of the mixture. The drying pressure and temperature does not have very significant influence on the properties of aerogels as does the gel concentration. The molecular size and nature of the solvent can influence gel concentration and, thus, the porosity. However, the porosity and related properties are responsible, to some extent, for the reduction of chitin's thermal stability. Also, the aerogels undertake irreversible changes in the macro- and micro-scale (such as shrinking) when they are in contact with liquids. This fact can be a limiting factor for the utilization of chitin aerogels as filters in liquid media, but the abundance, low cost, and biodegradability of chitin could turn these aerogels useful in other fields, such as thermal and sound insulation or carbon aerogel precursors.

The results presented regarding the production of carbon aerogels indicated that chitin aerogels are promising precursors. The materials obtained possess large surface area and highly developed narrow porosity with most pores in the micro-porous region, while interestingly they seem to partially maintain the structure of the original aerogel. Of course, further exploitation and optimization of the carbonization and activation conditions is needed in order to optimize the overall production process.

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