

# Suitability of convective air drying for the production of porous resorcinol-formaldehyde and carbon xerogels

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*Keywords:* A. Carbon xerogels; Porous carbon; C. Transmission electron microscopy; D. Texture.

Production of carbon aerogels by CO<sub>2</sub> supercritical drying of resorcinol-formaldehyde (RF) hydrogels followed by pyrolysis in inert atmosphere has been extensively described in the scientific literature, since their introduction by Pekala in 1989 [1]. Supercritical conditions suppress the liquid-vapor interface, avoiding shrinkage and cracking of the material during solvent removal and preserving the porous texture. As supercritical drying remains difficult to apply at an industrial scale because of its expensive and potentially dangerous character, other softer drying techniques have been tested in order to produce an aerogel-like mesoporous texture: freeze-drying [2], vacuum drying [3], microwave drying [4], solvent exchange followed by freeze drying [5] or drying under nitrogen in tube furnace [6],... Quite surprisingly, it appears that conventional convective drying, with controlled air temperature, velocity and humidity, has never been used in order to produce RF xerogels. As this technique is well known and largely used in the industry, it seemed interesting to study its suitability: would this technique enable us to obtain porous RF (and carbon after pyrolysis) xerogels?

Hydrogels have been prepared following the method described by Job et al. [3]. The molar ratio  $R/F$  and the dilution ratio  $D$ , as defined by these latter, were fixed at 0.5 and 5.7 respectively. Three initial values of the pH of the precursors solution were chosen: 6. 6.5 and 7 ( $\pm 0.05$ ). Cylindrical

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samples were obtained by casting 5 ml solution into sealed glass moulds ( $\varnothing = 22$  mm) and putting them for gelation in an oven at  $85^{\circ}\text{C}$  during 72 h. After gelation, the samples had a mass comprised between 4.2 and 5.1 g. They have been dried in a classical convective rig, with air at ambient humidity, at a temperature of  $70^{\circ}\text{C}$  and a superficial velocity of 2 m/s, i.e. quite severe drying conditions. Fig. 1a shows the drying curves, i.e. the evolution of mass with time, for the three samples. In each case, mass stabilization occurs after approximately 4 to 5 hours, indicating the end of the drying process. In comparison with vacuum drying, the drying duration is about 40 times shorter [3]. The three samples reached a final mass close to 1.45 g and kept their monolithic form. Volumetric shrinkage was negligible when  $\text{pH} = 6$  (orange xerogel), reached 21% when  $\text{pH} = 6.5$  (light brown xerogel) and 60% when  $\text{pH} = 7$  (dark brown xerogel). At high pH, a large shrinkage is observed even with supercritical drying, because of the ‘polymeric’ character of the gel [7].

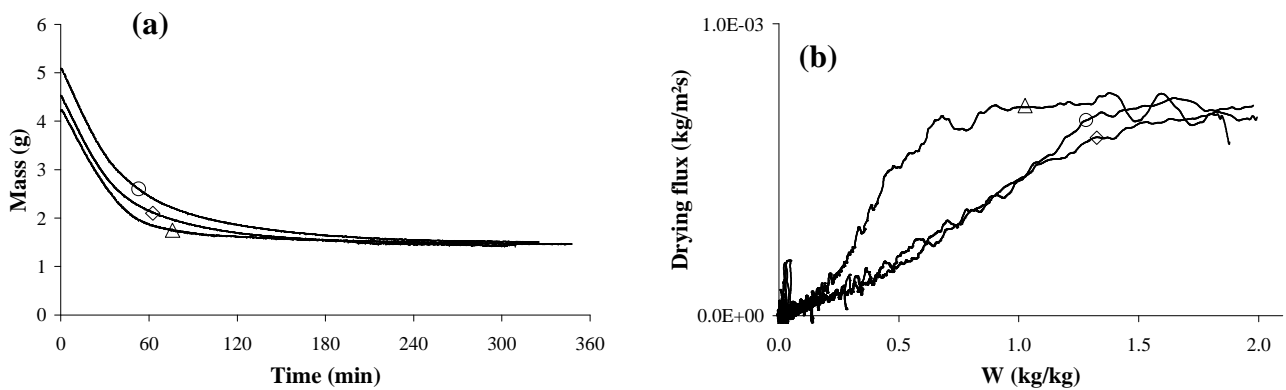


Fig. 1. (a) Drying curves of RF hydrogels: ( $\diamond$ )  $\text{pH} = 6$ ; ( $\circ$ )  $\text{pH} = 6.5$ ; ( $\triangle$ )  $\text{pH} = 7$  and (b) the corresponding drying kinetics ( $\diamond$ )  $\text{pH} = 6$ ; ( $\circ$ )  $\text{pH} = 6.5$ ; ( $\triangle$ )  $\text{pH} = 7$ .

The drying kinetics are represented in Fig. 1b by plotting the drying flux ( $\text{kg}/\text{m}^2\text{s}$ ) vs. the water content  $W$  ( $\text{kg}/\text{kg}$ ), expressed on a dry basis, as commonly encountered in the drying literature. A long constant drying phase is observed when  $\text{pH} = 7$  (up to  $W \cong 0.7$   $\text{kg}/\text{kg}$ ), while there is only a continuous decrease of the drying flux when  $\text{pH} = 6$ . A very short constant phase is observed when  $\text{pH} = 6.5$ . This can be related to the shrinkage behavior of the samples: during the constant rate period, the shrinkage is almost ideal, i.e. the volume reduction corresponds exactly to the volume of removed water. The external surface of the sample remains completely wet: external transfer

limitations prevail. Once shrinkage stops, internal diffusional limitations become predominant. A dried zone progressively develops, from the exterior to the inside of the sample [8].

As high microporous pyrolyzed xerogels are used in many applications, the effect of pyrolysis has been investigated on the gels dried with the proposed method. Pyrolysis has been performed under nitrogen flow in a tubular oven at 800°C, following the procedure of Job et al. [3]. Transmission electron microscopy (TEM) performed on all samples shows that the xerogels obtained by convective drying present the same structure as Pekala et al. [9] described for supercritical RF xerogels, i.e., a network composed by interconnected particles (“string of pearls”) of sizes between 10 and 30 nm (Fig. 2a). This structure remains after pyrolysis (Fig. 2b) but seems smoother and refined.

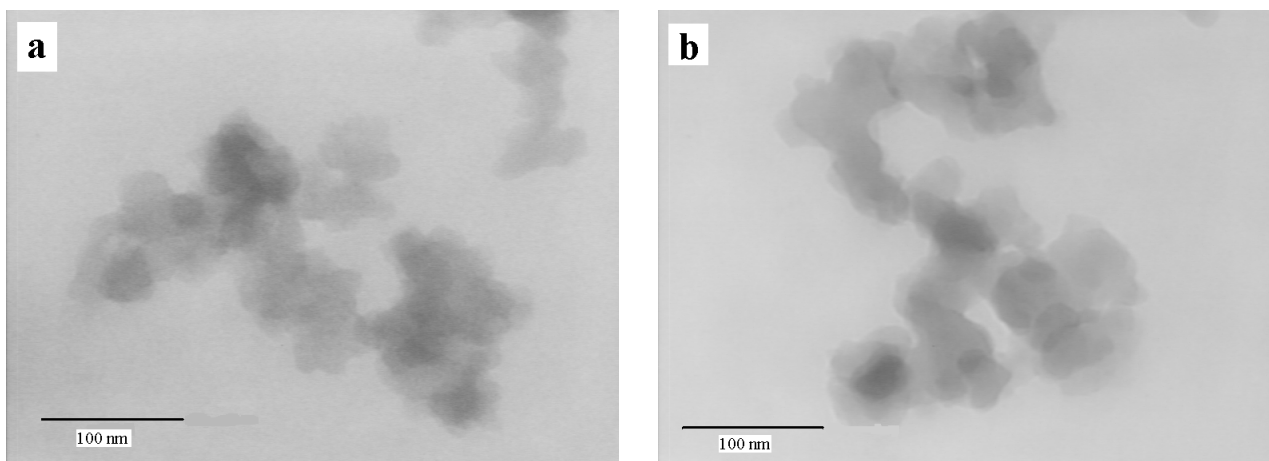


Fig. 2. TEM of gels synthesized with pH = 7 before (a) and after (b) pyrolysis.

The textural properties of the samples have been determined before and after pyrolysis by using classical characterization techniques ( $N_2$  adsorption-desorption isotherms, mercury porosimetry, pycnometry) and calculation methods [10], [11]. Results are summarized in Table 1 where  $S_{BET}$  is the BET specific surface area,  $V_{DUB}$  is the micropores volume calculated by the Dubinin–Radushkevich equation,  $V_p$  is the pore volume calculated from the adsorbed volume at saturation,  $V_{Hg}$  is the specific pore volume measured by mercury porosimetry,  $V_v$  is the total void volume obtained by combining mercury porosimetry and  $N_2$  adsorption results, and  $\rho_{bulk}$  is the apparent density. RF xerogels obtained in the investigated pH range exhibit specific surfaces and total void

volumes ranging respectively from 115 to 355 m<sup>2</sup>/g and 0.4 to 2.0 cm<sup>3</sup>/g. The corresponding carbon materials develop relatively high specific surfaces  $S_{\text{BET}}$  ranging from 430 to 630 m<sup>2</sup>/g and total void volumes  $V_v$  varying from 0.3 to 2.4 cm<sup>3</sup>/g. This is similar to results obtained with more sophisticated techniques [2], [3], [12]. It must be pointed out that the apparent density obtained at pH = 6 (0.35 g/cm<sup>3</sup>) corresponds exactly to the theoretical density when no shrinkage occurs during drying, as observed in this paper.

Table 1

Sample texture characterization

pH	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$V_{\text{DUB}}$ (cm <sup>3</sup> /g)	$V_p$ (cm <sup>3</sup> /g)	$V_{\text{Hg}}$ (cm <sup>3</sup> /g)	$V_v$ (cm <sup>3</sup> /g)	$\rho_{\text{bulk}}$ (g/cm <sup>3</sup> )	Type of pores
$\pm 0.05$	$\pm 5$	$\pm 0.01$	$\pm 0.05$	$\pm 0.05$	$\pm 0.1$	$\pm 0.02$	
After drying							
6	115	0.06	0.65	1.95	2.0	0.35	Micropores + macropores
6.5	245	0.11	1.35	1.15	1.3	0.63	Micropores + macropores
7	355	0.15	0.40	- <sup>a</sup>	0.4	1.05	Micropores + mesopores
After pyrolysis							
6	630	0.27	0.80	2.00	2.4	0.39	Micropores + macropores
6.5	615	0.27	1.25	1.20	1.5	0.61	Micropores + macropores
7	430	0.19	0.30	- <sup>a</sup>	0.3	1.34	Micropores + mesopores

<sup>a</sup> Not measured: sample containing micropores and mesopores only and whose pore volume measured at saturation by nitrogen adsorption  $V_p$  corresponds to the total void volume  $V_v$ .

These results show that it is possible to produce porous RF and carbon xerogels by using convective drying to remove the solvent, without any preliminary treatment. When synthesis conditions are adequate, the mechanical strength of the gel network is high enough to withstand capillary pressures, avoiding the collapse of the structure. As this technique presents several advantages in comparison with supercritical, vacuum or freeze drying methods (easy industrial implementation, well known, safe and non-expensive process,...), this preliminary research work will go further. The influence of drying conditions (air temperature, velocity and absolute humidity) on the textural properties of the gels is currently investigated, once synthesis conditions have been defined. Detailed mechanical and thermal characterization will also be performed. The change of drying

conditions but also the investigation of other synthesis conditions should lead to the production of carbon xerogels with higher mesopore volumes, closer to those observed in carbon aerogels.

### **Acknowledgements**

A. Léonard is grateful to the FNRS (National Fund for Scientific Research, Belgium) for a Postdoctoral Researcher position. Authors thank the Ministère de la Communauté française - Belgium (ARC 00/05-265) for its financial support.

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