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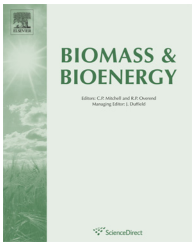

Tannin-based xerogels with distinctive porous structures

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ABSTRACT

Highly porous organic materials have been obtained from the gelation of a tannin-based resin at different pHs in the presence of F-127 Pluronic® surfactant. After subcritical drying in ambient conditions, and without the need of any solvent exchange step, the resultant xerogels had bulk densities typical of most organic aerogels. Their porous structures revealed unique features, depending on the initial pH, such as the possibility of getting either purely macroporous materials with narrow pore size distributions, or bimodal textures having a significant amount of mesoporosity. Correlations between porous texture and gelation time were clearly evidenced. On top of being easy to prepare, these xerogels are based on a cheap, renewable and abundant resource making them valuable precursors of porous carbon materials for a broad range of applications.

1. Introduction

Producing crack-free blocks of organic materials is the most important step before obtaining monolithic carbon materials by controlled pyrolysis. Easy and cheap processes leading to minimal shrinkage and loss of porosity are thus highly sought after, as well as precursors being both inexpensive and renewable. Carbon aerogels are examples of highly porous, monolithic, materials which have been suggested for a broad range of applications. Their high surface area, typically several hundreds of $m^2\ g^{-1}$, make them suitable adsorbents both in the gaseous and in the liquid phases, e.g. for separation or storage of permanent gases, adsorption and detection of condensable vapours, and adsorption of organic compounds, halides or metals dissolved in water [1]. Additionally, their chemical stability allows additional uses such as catalysis [2] and energy storage and conversion such as electrodes for battery, capacitor or fuel cells, electrochemical applications being possible through the excellent electrical conductivity of carbon aerogels [1].

However, preparing carbon aerogels is a costly process, requiring the supercritical drying of precursor aquagels before

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they can be pyrolysed. Such drying process indeed minimizes the capillary forces which are very high at the nanometre scale, unavoidably leading to the shrinkage of the material and hence to a loss of porosity and surface area. Various solvents can be used for that purpose [3], but supercritical CO_2, despite its high cost, remains the preferred solvent due to its moderate critical point ($T_c = 304$ K; $P_c = 7.4$ MPa), thus leading to a very low shrinkage. Replacing such supercritical drying step by a simple, subcritical, drying would be much cheaper and easier, but a significant loss of porosity still has to be avoided.

Many published papers have reported on materials improperly called "aerogels" whereas they were true xerogels, i.e. porous solids obtained after subcritical drying either in room conditions [4–7] or in an oven [8–14]. Such kind of materials indeed presented rather high surface areas and were found to be efficient adsorbents [15–20], catalyst supports [21], or electrodes for fuel cells [22], Li-ion batteries [23] or supercapacitors [4,5,7–9,12,13,24,25] for example. Strategies for minimizing shrinkage consisted in making very stiff aquagels by preparing them from a rather concentrated resin, with a typical mass fraction of solid in the solution of 40% in most published works, and/or exposing the water-filled gels to a dilute acid solution to further enhance crosslinking [10,26]. Templating aquagels or alcogels by small molecules able to preserve the mesoporosity has also been suggested [27], as well as, in many cases, exchanging water with a solvent of lower surface tension, such as acetone, with which shrinkage was indeed minimized [8,9].

As noticed by Job et al. [28], xerogels having very developed porous textures can be obtained, provided that the operating variables are correctly chosen. In other words, subcritical drying does not necessarily lead to a dramatic collapse of the porosity, especially when convective or vacuum drying conditions are used [29,30]. One may regret, however, that finding optimal parameters require long and meticulous studies which, furthermore, depend on synthesis parameters such as pH, which has a significant impact on the final pore size. Shrinkage is indeed strongly correlated to pore size, narrower pores leading to higher capillary stresses and hence to higher volume losses upon drying. Besides, the total pore volume of the resultant xerogels might be limited by all the aforementioned conditions required to get a shrinkage as low as possible. The last strategy for minimizing shrinkage thus consists in using surfactants. Surfactants not only decrease the surface tension of the solution to be evaporated, but may also form micelles above a critical concentration, thus introducing additional porosity [31]. So far, anionic [31], cationic [32] and non ionic [33] surfactants have been used for producing gels having various porous structures.

In the recent years, our team successfully prepared gels derived from natural resources, especially from condensated tannins [34–39], lignin [40], or both together [41]. Tannin and lignin are both derived from plants, and especially from wood. Such precursors are phenolic molecules so their behaviour is similar to that of very well known resorcinol – or phenol – formaldehyde systems from the point of view of their reactivity with aldehydes, their gelation and their drying. Besides, both share valuable characteristics such as very aromatic character, hence leading to a high carbon yield, around 45%, and ability of being easily crosslinked thanks to their number of reactive hydroxyl groups. Condensed tannin is of uppermost interest, since already a commercial product of constant quality, available in high purity and huge amounts, and made of much less complex oligomers than lignin. Condensed tannins are extractible molecules, industrially exploited from wattle, pine and quebracho trees, for example. They are based on the repetition of the unit shown in Fig. 1, whose exact structure depends on the origin. For instance, wattle tannin has OH groups in positions 3, 7, 3′, 4′ and 5′, and the corresponding flavonoid units are mainly 4,6-linked, leading to water-soluble phenolic compounds with typical molecular weights ranging from 0.5 to 3.5 kDa [42]. Condensed tannins can be suitably crosslinked by aldehydes, such as formaldehyde, and are thus natural counterparts of resorcinol from which most carbon gels have been prepared and investigated. Tannin can thus be used either alone with formaldehyde for preparing organic gels and derived carbon gels [34,36,38], or in combination with other molecules such as resorcinol, proteins or lignin [35,37,41]. All these previous attempts were concerning aerogels and cryogels, since xerogels were all very dense and presented very poorly developped porosity.

In the present work, preparation and investigation of new organic xerogels made by crosslinking tannin in the presence of a surfactant, followed by subcritical drying in simple ambient conditions, were carried out without need of any solvent exchange step. This research was motivated by three observations: (i) articles describing organic xerogels, i.e. before pyrolysis, are extremely scarce in the literature, the main contribution originating from the group of Job et al. [28–30]; (ii) benefits of a simple drying method would be even enhanced if the precursor was also cheap, easy to handle, non toxic and renewable, such as condensed tannin is; (iii) subcritical drying of tannin-based gels containing a surfactant had never been tried so far.

2. Materials and methods

2.1. *Preparation of tannin-formaldehyde-surfactant xerogels*

The same commercial tannin extract powder as the one we already used in a previous work [36] was used in the present study. This raw material is sold under the name Tupafin and was kindly supplied by the company Silva-Chimica (St. Michele Mondovi, Italy). Tannin was extracted industrially in

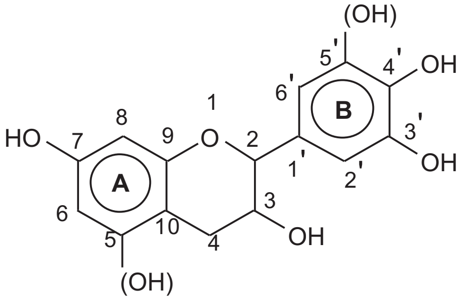

Fig. 1 – Chemical structure of the flavonoid unit of condensed tannins. In wattle tannin extract, the main compound is prorobinetinidin, having hydroxyl groups in positions 3, 7, 3′, 4′ and 5′.