## TANNIN AS A KEY PRECURSOR OF NEW POROUS CARBON MATERIALS

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### Introduction

Condensed polyflavonoid tannins are natural oligomers extracted from vegetable resources, especially from tree barks, by an ecological process only based on hot water. Due to their polyphenolic nature, they can undergo some of the typical reactions of phenol such as reaction with formaldehyde, or other aldehydes, under acid and alkaline conditions. Therefore, high-quality thermoset resins can be prepared, having a high carbon yield after pyrolysis. These advantages, combined to their low cost, renewable and nontoxic character, definitely make tannin an essential precursor of new carbon materials able to compete with precursors based on more expensive, synthetic, phenolic molecules.

Depending on their origin, different kinds of condensed tannins are available. Those commercialized for leatherwork, namely mimosa (Acacia mearnsii) bark tannin extract or quebracho (Schinopsis lorentzii and Schinopsis balansae) wood tannin extract, are mainly composed of profisetinidin and porobinetinidin oligomeric chains (Fig. 1). For mimosa tannin, resorcinol A-ring and pyrogallol B-ring (i.e. a robinetinidin flavonoid unit) are the main patterns at about 90% of the phenolic content of the tannin itself [1]. For quebracho tannin, resorcinol A-ring and catechol B-ring (i.e. fisetinidin flavonoid unit) are the main patterns constituting more than 80% of the phenolic content of the tannin itself [1]. Tannins derived from softwood (pine, spruce and other conifer species) have a slightly different structure than those described above. They are indeed based on a phloroglucinol A-ring and a catechol B-ring (i.e. they are procyanidin type tannin) or on a phloroglucinol A-ring and a pyrogallol Bring (i.e. they are prodelphinidin-type tannin) (Fig. 1). Consequently, the A-rings of these condensed tannins are far more reactive than the A-rings of mimosa and quebrachotype tannins, namely about 6 - 7 times more reactive [1].



**Fig. 1** Repeating units in profisetinidin (quebracho) type tannin, prorobinetinidin (mimosa) type tannin, and prodelphinidin and procyanidin (pine) type tannin.

In this abstract, our very last results are reported, unambiguously demonstrating the interest of polyflavonoid tannins for preparing valuable porous carbons such as gels, foams, and porous monoliths. Different kinds of condensed tannins have been successfully tested, whose different reactivity required significant changes in the formulations, further broadening the resultant range of porous carbons. Only materials derived from mimosa tannin, however, are described below.

## New carbon gels

The first tannin-formaldehyde - based carbon aerogels obtained by our group in 2011 already presented a broader spectrum of porous textures than what is allowed by conventional resorcinol-formaldehyde formulations [2]. This finding is related to the wider range of pH, from 2 to 10, which can be used for gelling tannin. However, at that time, the effect of dilution had not been taken into account. A high initial dilution of the precursor resin indeed leads to high pore volumes, but the solid backbone is so weak that a significant part of the porosity is lost during drying and/or subsequent pyrolysis. In contrast, less diluted gels have a lower initial porosity whose major part can be maintained because they are stiffer, and hence may finally present much more developed porous structures. Mechanical strength is indeed a very important parameter, directly related to porosity which can be controlled by initial dilution, pH and amount of crosslinker. There exists an optimum for each of these experimental parameters. Additionally, some values that these parameters may take can be in favour, or in contrast hinder and even prevent, gelation [3].

Therefore, better understanding of new, biosourced, phenolic systems, requires building phase diagrams. This has just been done for tannin – formaldehyde aqueous solutions [4]. The situation is more complicated when more than one phenolic molecule is present, such as in tannin – lignin [5] or lignin - phenol [6] systems. In the latter cases, some parameters must be fixed for avoiding multidimensional diagrams that would be impossible to represent. Fig. 2 illustrates tannin – formaldehyde and tannin – lignin – formaldehyde diagrams as a function of a limited number of parameters. The existence of areas within which no gelation occurs, or within which reversible (physical) gels are obtained, not able to lead to carbon gels having the same structure, is evidenced.



N - Not gelled; PG - Physical gelation (orange - red) O - Opaque (reddish-brown); T - Transparent (orange - red) ST - Semi-transparent (burgundy); T(LR) - Transparent (light red) T(DR) - Transparent (dark red)



**Fig. 2** Phase diagrams of: (a) tannin – formaldehyde (TF) and (b) tannin – lignin – formaldehyde (TLF) solutions, showing the kinds of materials obtained, depending on a limited number of experimental parameters (for TF: pH and dilution at constant T/F ratio = 1.35; for TLF: T/L proportions and amount of formaldehyde at fixed dilution = 26% and constant pH = 10).

Supercritical, freeze-, or subcritical drying and pyrolysis of such gels leads to a very broad range of carbon gels, whose complete investigation is far from being accomplished. As an example, the broad range of surface areas of carbon aerogels derived from the tannin - formaldehyde systems of Fig. 2(a) is shown in Fig. 3.



**Fig. 3** BET surface area of tannin-formaldehyde – based carbon cryogels as a function of their synthesis parameters.

The structure of such carbon aerogels was strictly controlled through the first, systematic, study of the impact of the parameters of the supercritical drying process: pressure in the autoclave, nature of the supercritical solvent, and depressurizing rate after supercritical drying [7]. The latter parameter was shown to have a dramatic impact on the shrinkage, and hence on the porosity of the resultant aerogels (Fig. 4). We thus suggested that, for obtaining repeatable carbon aerogels, such experimental conditions had to be always controlled and made explicit, whereas they are almost never reported in the literature [7].

We have shown that, in a general way, any formulation for cold-setting adhesive, i.e. having a gel point above which a hard material is formed and for which the lowest porosity as possible should be desired, may be modified and diluted in order to obtain carbon aerogels. This was experimentally proved, not only with tannin and mixed tannin – natural polyphenol systems, but also with "blue glue", a phenol - resorcinol - formaldehyde system branched



**Fig. 4** Volume shrinkage of identical diluted gel samples submitted to supercritical drying in  $CO_2$  and in acetone at 10 and 14 MPa, respectively. Data from [8] are given for comparison.

with urea [9]. The corresponding aerogels had BET surface areas as high as  $1300 \text{ m}^2/\text{g}$ , and presented very narrow mesopore size distributions controlled by the initial pH.

The porous structure of tannin-based cryogels was always found to be different from that of their aerogel counterparts [10] for two reasons. The first one is related to shrinkage during drying. Freeze-dried diluted gels had a much lower shrinkage than what was observed when using any other supercritical solvent. As a consequence, extremely high porosities, but correspondingly low mechanical properties, were obtained. Such weak materials then suffered a serious pore collapse during pyrolysis, leading to materials that were finally less porous than their aerogel counterparts, whose mechanical properties were higher due to lower amounts of very wide pores. This phenomenon was observed for diluted tannin – formaldehyde carbon cryogels, indeed presenting a minimum of BET surface area at pH at which a maximum was observed for carbon aerogels [10].

The second reason for differences of porosity between aero- and cryogels is related to the nature of the solvent that has been used for freeze-drying. *Tert*-butanol is most frequently used, but is able to crystallise inside the porosity of the gels, leading to acicular crystallites, thus deeply modifying the resultant porosity. Fig. 5 shows the example of carbon cryogel particles prepared from tannin and formaldehyde using an emulsion polymerization process, and within which needle-like pores are easily seen.



**Fig. 5** Needle-like macroporosity exhibited by carbon cryogels made from a tannin-formaldehyde solution gelled, freeze-dried in *tert*-butanol and pyrolysed at 900°C.

Generally speaking, the porous structure of carbon cryogels is coarser than that of their aerogel or xerogel counterparts [11]. Accordingly, TF carbon cryogels presented a dual macro-microporosity, with a low fraction of mesoporosity. When used as electrodes of electrochemical double-layer capacitors, such materials presented specific capacitances close to 100 F/g, i.e. near those of standard carbon aerogels. The square shape of the voltammograms at low scan rate suggested a pure electrostatic attraction, and hence an ideal capacitive behaviour of TF carbon cryogels. Due to their special porous structure, micropores unambiguously controlled the capacitance, with a dominant role of ultramicropores and supermicropores at low and high scan rates, respectively [10].

Finally, unique carbon xerogels could also be obtained, based on soft-templating of tannin by Pluronic F127®, an amphiphilic surfactant made of triblock PEO-PPO-PEO chains. The xerogels, simply dried in room conditions, not only presented exceptionally low volume shrinkages, very similar to those of standard aerogels, but had truly unimodal pore-size distributions. Whereas those made with a tannin / Pluronic (T/P) weight ratio of 2 were purely macroporous, those made at T/P = 0.5 were purely mesoporous (Fig. 6) [12]. In the latter case, no ordered mesoporous structure could be observed as for other recent tannin-Pluronic – based carbon materials [13], probably because of the formation of spherical micelles leading to randomly dispersed spherical holes, as suggested by Fig. 7.

**Fig. 6** SEM pictures and pore-size distributions of tannin-Pluronic (TP) – based carbon xerogels: (a) T/P = 2; (b) T/P = 0.5.



**Fig. 7** TEM picture of carbon xerogel (T/P = 0.5) and schematic representation of a spherical micelle of Pluronic F127®.

# New carbon foams

Tannin-based, cellular, carbon foams were reported for the first time in 2009 [14]. These are materials having densities close to those of the previous carbon aerogels, but whose typical pore size is 3 to 4 orders of magnitude higher. Most of their physical properties and textural characteristics have been extensively investigated in the past years. However, a few months ago, their homogeneity and the control of their porous structure have reached an incomparable level. As a consequence, such cellular materials based on vitreous carbon were suggested as models for solid-state physics and engineering science. The aim was solving a few questions which remain open in physics of disordered systems, through the achievement of new experiments carried out in unequalled conditions of control of the materials. The originality of the approach is based on the use of solid-state carbon chemistry for the preparation of perfectly controlled objects, allowing both rigorous physics studies and optimisation of applicative properties. Three examples are given below.

Organic tannin-based foams were prepared at different densities and pyrolysed at 7 heat-treatment temperatures (HTT) ranging from 200 to 1400°C. The elastic modulus and the compressive strength of around 200 samples ((green materials + 7 HTT) × more than 10 densities near the rigidity threshold × 2 directions of measurement)) were systematically measured, and the critical exponents were determined. That of the modulus nearly doubled, whereas that of the compressive strength remained constant. These results were interpreted as follows [15].

Through pyrolysis at different HTT, the resin was progressively converted into glassy carbon, therefore the mechanical properties drastically changed. So did the exponent of the elastic modulus, which strongly depends on the nature of elastic forces, changing from around 2 to about 4. According to percolation theory, such changes correspond to a shift from central forces to angle-changing forces [16], which is consistent with the expected hardening of the struts of the foams. In contrast, the exponent of the compressive strength remained constant, with a value slightly below 2. This finding is in agreement with what is expected from the theory of Gibson and Ashby in the case of foams whose cells are mainly open [17]. It is the first time that these theories were experimentally confirmed by so unquestionable experiments based on carbon foams [15].

Electromagnetic shielding efficiency (EM SE) was measured in the  $K_a$ -band of microwaves (26 – 37 GHz) for carbon foams having different cell sizes [18]. The materials were prepared in the form of 2 mm thick plates. Those having the highest density were those having the highest EM SE, around 23 dB at 24 GHz, mostly due to reflection of microwave signal (77%). The other contribution to SE was absorption (23%), transmission being negligible. Such performances of tannin-based carbon foams for EM shielding were found to be higher than those of epoxy – carbon nanotubes composites.

Acoustical properties of the same carbon foams were measured in the frequency range 50 - 4300 Hz. The sound absorption coefficient was determined, and found to be strongly dependent on foams' density. Two possible, different, behaviours were expected. Either the resistivity to

air was "high", and the material was poorly absorbing because of the reflection of the acoustic waves, or the resistivity was "low", enabling the attenuation of the waves inside the porosity, hence a good absorption of sound. Unlike reticulated vitreous carbon foams, for which the structure is mainly based on thin struts and whose acoustic behaviour is different [19], tannin-based carbon foams are cellular materials. Their high resistivity to air induced a rather low sound absorption coefficient, which increased when the density decreased. This finding, far from being disappointing, was overcome through the perforation of the carbon foams, thus producing a much lower resistivity and hence the easier penetration of the acoustic waves, as predicted by the theory [20]. Careful choice of the perforation diameters allowed increasing the sound absorption coefficient in targeted frequency ranges, as shown in Fig. 8 [19]. It was the first time that vitreous carbon foams were demonstrated to be so good soundabsorbing materials in a tuneable frequency range.



**Fig. 9** Sound absorption coefficient of a tannin-based carbon foam (sample called C3: density  $0.065 \text{ g/cm}^3$ , 90 pores per inch) with and without a perforation of radius 9 mm.

Such cellular tannin-based carbon foams were successfully converted into  $\beta$ -SiC foams by different routes [21]. The interest of using such precursors is related to their rather low cell size (100 – 500 µm), leading to microcellular ceramics. Indeed, there are only a few manufacturing techniques which are able to produce such kind of materials with exploitable properties, and even less if the ceramic material must be silicon carbide [22]. Optimization is still required for adjusting the stoichiometry and hence the oxidation resistance of the materials (Fig. 10) [21].



**Fig. 10** Si-SiC (left) and C-SiC (right) composite foams prepared by liquid silicon infiltration and vapour silicon infiltration, respectively.

## New carbon polyHIPEs

Emulsion-templated porous monoliths are a new class of macroporous solids having an increasing number of potential applications in the fields of catalysis, chromatography, thermal or phonic insulation, drug delivery, tissue engineering, etc. Especially, polyHIPEs are polymerized High Internal Phase Emulsions, i.e. emulsions having a volume fraction of internal phase generally (but not necessarily) higher than 74%. This value indeed corresponds to the compacity of a close FCC packing of identical spheres, above which contact-induced polygonization of the internal phase's drops occurs. Leaching the internal phase is thus possible and is expected to lead to highly porous monoliths, once the external phase has been hardened.

So far, polymeric materials made this way were mainly based on synthetic, non-renewable and most of times toxic molecules, like those patented by Unilever in 1982 [23]. To date, very few natural polymers have been suggested as polyHIPE precursors, and carbon polyHIPEs have been reported only twice so far. We have used tannin for the first time as a base of the resin from which porous monoliths presenting a fully open and interconnected porosity were prepared. From these monoliths, carbon polyHIPEs of identical structure have been obtained by pyrolysis at 900°C.

Using different volume concentrations of internal phase (a vegetable oil), different concentrations of tannins, different amounts and kinds of surfactants, and different pH, a very broad range of porous monoliths was obtained. In a typical experiment, oil was incorporated progressively under stirring into an aqueous solution of tannin containing a crosslinker and a surfactant. Once the emulsion was done, hardening was carried out in an oven, followed by extraction of the oil by a solvent in a Soxhlet, drying and pyrolysis. Typical porous structures are given in Fig. 11. These materials present porosities within the range 75 - 98%, and very high mechanical properties. As an example, the material at the right of Fig. 11 has an elastic modulus and a compressive strength of 103 and 5.7 MPa, respectively, whereas its porosity is 93%. These values are significantly higher than those of the previous carbon foams: 30 and 1.5 MPa, respectively, at the same porosity.



**Fig. 11** Tannin-based carbon polyHIPEs prepared with different volume fractions of oil (70% at the left; 74% at the right), all other things being equal. The scale bar is  $100 \,\mu\text{m}$  long.

Interestingly, preparing highly porous monoliths was also possible without oil. The mechanical stirring which was required to do the emulsion produced, at very high mixing rate, a liquid foam which was fully stable due to the presence of the same surfactants. Such liquid foam was converted to solid foam after drying in an oven. In other words, compared to the previous protocol, we did *meringue* instead of doing *mayonnaise*. Pyrolysis of the resultant, very light, material, led to new kinds of vitreous carbon foams, whose porosity and cell sizes were easily adjusted through the changes of the initial tannin concentration (Fig. 12). These differences of pore structures were also clearly evidenced by micro computed X-ray tomography (Fig. 13).



**Fig. 12** Tannin-based carbon "meringues" prepared with different wt. % of tannin in the initial solution, all other things being equal: (a) 30%; (b) 40%; (c) 45; (d) 50%. The scale bar is 1 mm long.



**Fig. 13** Tomography pictures of the materials presented in Fig. 12(b) (left) and in Fig. 12(d) (right), in which the pores are seen as solid bodies. The side of the cubes is 2.95 mm.

#### Conclusion

Tannin was definitely proved to be an excellent precursor of many kinds of new porous carbons. Due to its reactivity, metastable structures such as organic gels, liquid foams, emulsions or micelle-templated structures readily turned solid. The resultant thermoset, insoluble and infusible, resin could always be successfully carbonized into vitreous, flawless, carbon materials having the same structure with a high yield, about 50%, thanks to the polyphenolic nature of tannin. Additionally, tannin is cheap and non-toxic. The broad range of pH within which tannin can be polymerized further widens the versatile family of carbon materials that can be obtained. Furthermore, tannin-based formulations can be adjusted for speeding up - or slowing down polymerization reactions, accounting for the significantly improved level of control of the structure which could be reached recently. As a consequence, some carbon foams were effectively tested as model solids for testing theories in solid-state physics, whereas others were converted into microcellular ceramics.

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