Carbon gels derived from natural resources
Geles de carbón de origen natural

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Abstract

Most carbon gels investigated so far and reported in the literature were prepared from resorcinol crosslinked with formaldehyde in water, and were generally dried with supercritical CO_2 before being pyrolysed. In the present paper, through some selected examples, we show how valuable carbon gels can be derived from other phenolic resources having a natural origin. Special emphasis is given to tannin and lignin, both derived from wood, as potential precursors of carbon aero- and cryogels. However, natural compounds not obeying the usual concepts of sol-gel chemistry may also be used for preparing carbon gels, such as cellulose, and even glucose. In the latter case, hydrothermal treatment forces the phase separation to occur, and leads to monoliths which can be advantageously converted into carbon aerogels by supercritical drying and subsequent pyrolysis.

Resumen

La mayoría de los geles de carbón investigados hasta ahora y citados en la literatura han sido preparados a partir de resorcinol reticulado con formaldehído en agua, y generalmente secados con CO_2 supercrítico antes de ser pirolizados. En este manuscrito, hemos seleccionado algunos ejemplos y mostramos como se pueden preparar excelentes geles de carbón a partir de compuestos fenólicos que tienen un origen natural. Especial mención merecen los taninos y ligninas, extraídos de la madera, como potenciales precursores de aero- y criogeles de carbón. Sin embargo, otros compuestos naturales que no obedecen al concepto habitual de la química de sol-gel también pueden ser usados para preparar geles de carbón, como la celulosa y la glucosa. En este último caso, el tratamiento hidrotermal fuerza la separación de fase, y conduce a monolitos que pueden ser convertidos en aerogeles de carbón por secado supercrítico y posterior pirólisis.

1. Introduction

Gels are, among other possible definitions that can be used for describing them, semisolid systems comprising two phases, solid and liquid, embedded in each other in such a way that the pores of the solid, filled with solvent, are of colloidal dimensions [1]. Removal of the liquid phase leads to a highly porous backbone, especially if supercritical of freeze drying has been carried out. The latter processes indeed prevent the shrinkage of the material (though never completely) and, therefore, the collapse of the pores induced by capillary forces can be minimized. Getting carbon gels is thus possible, as it is already the case for most carbonaceous solids, from the controlled pyrolysis of organic precursors, here organic gels, in non-oxidizing atmosphere.

From the simple aforementioned assertions, it can be concluded that using biopolymers or natural resources in general for preparing carbon gels involves several requirements. First, if the porous structure has to be maintained, the precursors should not melt when heated. Therefore, all chemical (i.e. crosslinked) gels might be used for that purpose, since chemical gels are insoluble, infusible, three-dimensional polymer networks. In contrast, jellies based on fruits and aspic based on gelatine, for example, are physical (i.e. coagulated) gels, and melt when heated. Then, the boiling and the pyrolysis of the resultant liquid lead to an ill-defined brittle residue, which is porous due to the evolution of gases, but which is certainly not a carbon gel. Nevertheless, infusible biopolymers which can be dissolved and next coagulated may also become precursors of carbon gels, provided that the porous structure made up by their entanglement can be maintained all along the drying and heat-treatment processes. This is the case of cellulose, whose carbon yield, however, is rather low.

Possible natural precursors for preparing carbon gels should thus be prone to gelation or at least to rigid entanglement, be infusible before or after being crosslinked, have a high carbon yield and be cheap. One advantage of using them is indeed, on top of their “greener” character, the correspondingly reduced cost of the resultant material. In the following, emphasis will be given to phenolic biopolymers such as tannin and lignin, especially well matching these requirements. They are described in section 2, and their use for preparing gels is developed in section 3 and partly in section 4. However, natural molecules not obeying the aforementioned requirements may, in some cases, also lead to carbon gels using special preparation processes such as hydrothermal treatment. Some examples are given in section 4.

2. Tannin and lignin as precursors of carbon gels

Tannin and lignin are both derived from plants, and especially from wood. There are fundamental differences between them, as explained below, but 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. Figure 1 shows the typical chemical structure of tannin and lignin, though that of lignin can just be a model, strongly depending on its vegetable origin and on the severity of its extraction process.

Tannins are extractible molecules, industrially exploited from wattle, pine and quebracho trees, for example. They are oligomers based on the repetition of the unit shown in Figure 1a, whose exact structure depends on the origin. For instance, wattle tannin has OH groups in positions 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 [2]. Lignin is also a phenolic molecule, but is a three-dimensional, crosslinked, polymer. It is the most common natural polymer after cellulose, and its role in plant tissues is cementing cellulose fibres. It is based on three phenylpropanoid monomers, as shown in Figure 1b-d, connected with each others through various inter-unit linkages, thus resulting in a complex macromolecular structure [3,4]. Lignin is generally considered as a waste material from the pulp and paper industry, and is most often used as fuel for the energy balance of pulping process.

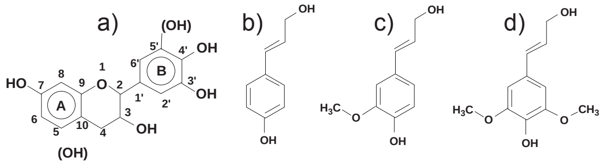

Figure 1. Chemical structure of: (a) the flavonoid unit of condensed tannins; (b)-(d) the structural units of lignin: (b) p-coumaryl alcohol; (c) coniferyl alcohol (guaiacyl); (d) sinapyl alcohol (syringyl).
Figura 1. Estructura química de: (a) la unidad flavonoide de taninos condensados; (b)-(d) las unidades estructurales de la lignina: (b) alcohol p-cumarílico; (c) alcohol coniferílico (guaiacilo); (d) alcohol sinapinílico (siringilo).

Tannin and lignin 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. However, tannin can be used either alone with formaldehyde for preparing organic gels and derived carbon gels [5], or in combination with other synthetic phenolic molecules such as phenol or resorcinol [6], whereas lignin can never be used alone. Whatever the way it is crosslinked, and as far as the authors know, lignin alone could never lead to homogeneous, stable, organic gels from which carbon gels might be prepared. Instead, hard precipitates are obtained. Nice, reproducible, gels could only be obtained by combining lignin with smaller phenolic molecules such as phenol [7], resorcinol [8] and tannin [9].

3. Carbon gels from tannin and lignin: selected examples

As explained above, tannin easily gels in the presence of formaldehyde. Unlike what is known for resorcinol, a broad range of pH can be successfully used with tannin, leading to materials having different porous structures, as demonstrated below. The typical pH of a tannin solution is close to 4.5, at which the reactivity with formaldehyde is the lowest, the highest reactivity being found at pH lower than 3 and higher than 7. The pH can thus be advantageously increased or decreased through the use of any base or acid, respectively, abusively but very frequently referred to as "catalysts". As a consequence, the gelation time is strongly modified, and the highest BET surface areas of the resulting carbon aerogels, above 700 m^2/g, are found at pH 4 – 5, whereas the mesopore volumes increase with pH, up to 0.9 cm^3/g [5].

Carbon aerogels derived from tannin present a typical nodular structure, see Figure 2, and the average diameter of such nodules decreases when the pH increases. Such features are very usual for all other gels derived from phenolic precursors. The materials shown in Figure 2 were obtained by supercritical drying in acetone, which is as efficient as CO$_2$ for that purpose [10] but much cheaper. Combined with the fact that a very inexpensive precursor was used, tannin, these resultant carbon aerogels are 5 times cheaper than their resorcinol-based counterparts [5].

Instead of drying supercritically the monoliths before pyrolysis, freeze-drying can be carried out. The process is a bit longer, since it requires several steps of solvent exchange, but is cheaper. Carbon cryogels derived from mixtures of tannin and resorcinol were successfully prepared, in which both proportions of reactants and pH were changed. As a result, a much broader range of porous structures than those of typical resorcinol – formaldehyde gels could be obtained. Interestingly, pore size distributions (PSD) could be tuned through the pH for both tannin – formaldehyde (TF) carbon aerogels and tannin – resorcinol – formaldehyde (TRF) carbon cryogels, either shifting the PSD at rather constant mesopore volume (for TRF), or keeping the PSD centred on the same pore width but changing the mesopore volumes (for TF), see Figure 3 [5,6].

The porous structure of cryogels is different from that of aerogels of identical composition for two possible reasons. One is related to shrinkage during drying, which may be very different depending on the process. Thus, diluted gels can be freeze-dried with a much lower shrinkage than what can be observed when using supercritical solvents. As a consequence, extremely high porosities, but correspondingly low mechanical properties, are obtained. Such weak materials may then suffer a

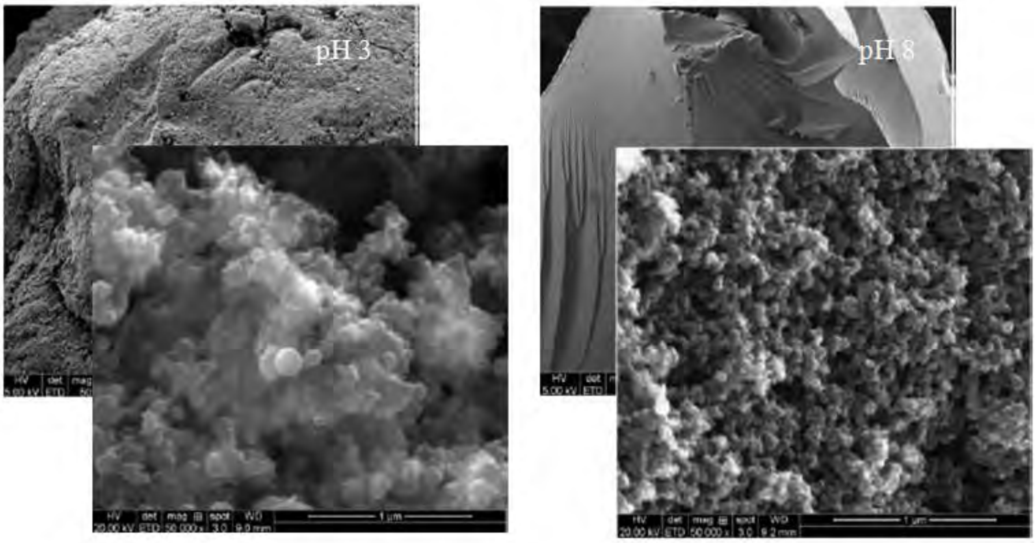

Figure 2. SEM pictures of tannin-based carbon aerogels prepared at two different pH. The effect of the pH on the porous structure is clearly seen even at low magnification (after [5]).
Figura 2. Fotografías MEB de aerogeles de carbón preparados a partir de tanino y a dos pH diferentes. El efecto del pH sobre la estructura porosa se ve claramente incluso al menor aumento (de [5]).

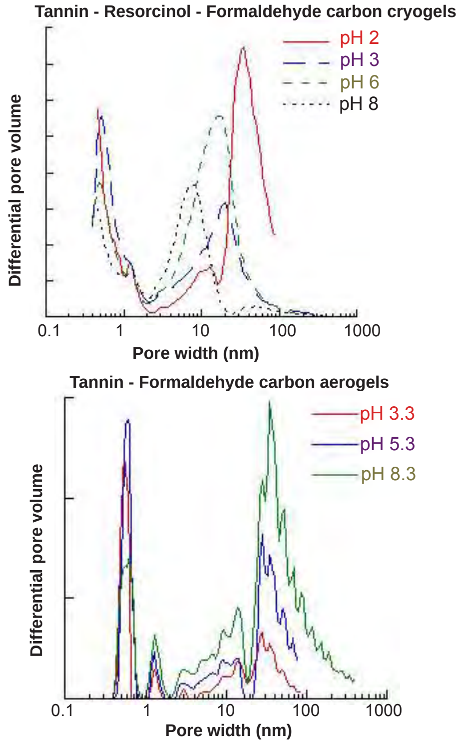

Figure 3. Pore size distributions of tannin – resorcinol – formaldehyde carbon cryogels (top) and tannin – formaldehyde carbon aerogels (bottom), showing the significant impact of the initial pH of the solution before gelation (after [5,6]).
Figura 3. Distribuciones de tamaño de poro en criogeles de carbón preparados a partir de tanino - resorcinol - formaldehído (arriba) y en aerogeles de carbón preparados a partir de tanino - formaldehído (abajo), mostrando el impacto significativo del pH inicial de la solución antes de la gelificación (de [5,6]).

serious pore collapse during pyrolysis, leading to materials that are finally less porous than their aerogel counterparts, whose mechanical properties were higher due to lower amount of very wide pores. This phenomenon was observed for diluted tannin – formaldehyde cryogels, presenting a minimum of BET surface area (400 m^2/g) at pH 4 – 5 [11], i.e. at the pH at which a maximum was observed for tannin – formaldehyde aerogels (see above). Surface areas and micropore volumes as high as 1400 m^2/g and 0.55 cm^3/g, respectively, were measured at pH 7.5. The fact that NaOH used for adjusting the pH at this value, remaining inside the porosity and acting as an activating agent during the pyrolysis, thus leading to somewhat activated carbon gels, can not be discarded. 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 and deeply modifying the resultant porosity. Figure 4 shows the example of carbon cryogels particles prepared from tannin and formaldehyde using the emulsion polymerization process formerly described by Yamamoto et al. [12], and in which needle-like pores are easily seen. Materials freeze-dried in water, whose ice volume is much bigger than that of the liquid phase, comprise even bigger pores. As a conclusion, foreseeing the kind of porosity that a carbon gel will have after drying and pyrolysis is totally impossible.

Preparing a chemical gel from any phenolic precursor assumes that the conditions of gelation are known and have been optimized. As explained above, high initial dilution of the precursor resin 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. Less diluted gels should thus be preferred, having a lower initial porosity, but whose major part will be maintained because they are stiffer, so they can finally present much more developed porous structure. 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.

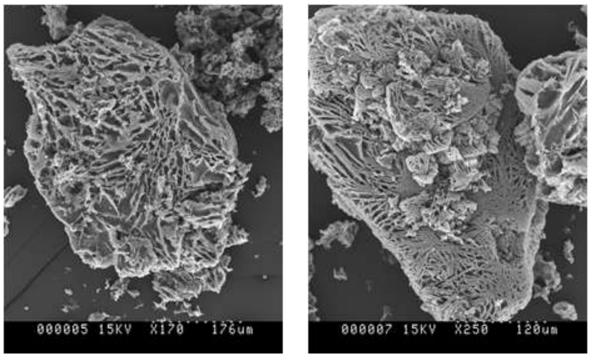

Figure 4. Needle-like macroporosity exhibited by carbon cryogel particles made by inverse emulsion polymerization of a tannin-formaldehyde solution, followed by freeze-drying in t-butanol and pyrolysis at 900°C.
Figura 4. Macroporosidad acicular que muestran las partículas de criogel de carbón sintetizadas por polimerización en emulsión inversa de una solución de tanino - formaldehído, seguida de liofilización en ter-butanol y pirólisis a 900°C.

Therefore, for better understanding phenolic systems, building a phase diagram may be of great interest. This has been recently done by our group in the case of tannin – formaldehyde aqueous solutions, see below. The situation is more complicated when more than one phenolic molecule is present, such as in lignin – tannin or lignin – phenol systems. In the latter cases, some parameters must be fixed for avoiding multi-dimensional diagrams that would be impossible to represent. Figure 5 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, is evidenced.

The organic gels presented in Figure 5, especially the aerogels, have been investigated recently [7,9] but still deserve additional studies. All stable chemical gels present the expected nodular structure, whatever the composition, and so do their carbonaceous derivatives. Both packing and average diameter of their nodules depend on the amount of crosslinker, pH and dilution of the resin. Pyrolysis leads to nice carbon aerogels, whose porous texture is still under investigation and will be published in the near future. The first results confirm the relevance of lignin as precursor of carbon gels, leading to surface areas higher than 500 m^2/g, just like for many other carbon gels derived from synthetic resources.

4. Carbon gels prepared from alternative methods or derived from other resources

The usual sol-gel chemistry used above is not necessarily involved for preparing organic monoliths from which carbon gels can be finally obtained. In other words, the classical scheme consisting in dissolving a precursor into a solvent, and whose

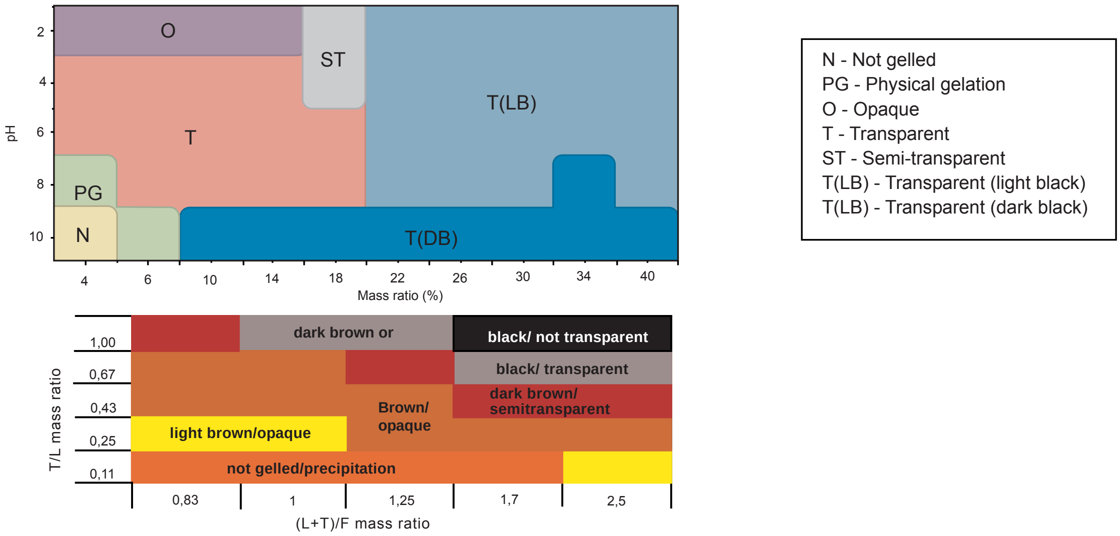

Figure 5. Phase diagrams of tannin – formaldehyde (TF, top) and tannin – lignin – formaldehyde (TLF, bottom, reprinted from [9] with permission) solutions, showing the kinds of materials obtained, depending on a limited number of experimental parameters (for TF: pH and dilution at constant T/F ratio = 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.

Figura 5. Diagramas de fase de las disoluciones tanino - formaldehído (TF, arriba) y tanino - lignina - formaldehído (TLF, abajo, reproducido de [9] con permiso), mostrando las clases de materiales obtenidos, según un número limitado de parámetros experimentales (para TF: pH y proporción de la dilución a T/F constante = 1.35; para TLF: Proporción de T/L y cantidad de formaldehído a dilución fija = 26 % y pH constante = 10). El secado supercrítico, por liofilización, o subcrítico de esos geles y su posterior pirólisis conduce a una muy amplia gama de geles de carbón, cuya investigación completa está lejos de haberse finalizado.

crosslinking will lead first to a sol, i.e. to a very fine suspension of solid, and next to a gel through the gradual clustering of the suspended particles, can be more or less modified, depending on both the synthesis protocols and on the precursors.

For example, the phase separation leading to the occurrence of polymer particles and hence to a gel can be forced when hydrothermal conditions are used. In this case, separation between gelation and precipitation is not always easy, and some experimental conditions lead to an overlapping of these two regimes. In a general way, it can be assumed that a gel is formed when the size of the constitutive nodules is both “small” (say, a few nm to a few tens of nm) and homogeneous, unlike precipitates whose particles have all possible dimensions, and can be much bigger. Figure 6 thus shows the materials which could be derived from wattle tannin dissolved in aqueous solutions of different pH and submitted to 180°C under 1MPa.

Gels obtained this way are, just like their counterparts prepared by conventional sol-gel chemistry, based on rather spherical nodules. However, using hydrothermal conditions, neither crosslinker nor supercritical drying was required. The porosity was indeed fully maintained after normal (i.e. subcritical) drying in air and subsequent pyrolysis at 900°C. Thus, the sample shown at the left of Figure 6 had a BET surface area of 495 m^2/g [13]. Additionally, and interestingly, if not pure water but concentrated ammonia solution is used instead, direct functionalization of the precursor can be achieved, leading to hydrothermal carbons having nitrogen contents as high as around 15 wt.%. However, even if the term “hydrothermal carbon” has been widely used in the literature, the materials obtained directly from the autoclave should never be considered as authentic carbons, since their elemental carbon content is around 60 wt.% only. Therefore, an additional pyrolysis step is required for increasing the carbon content above 80%. Doing so, the materials functionalized with nitrogen loose part of the latter, which is decreased to a value (a few %) which depends on the final temperature.

Hydrothermal treatment is also a very interesting process for getting carbons from precursors whose carbon yield is intrinsically low when directly pyrolysed in standard conditions, and/or whose gelation does not occur according to the classical sol-gel chemistry. Hydrothermal process indeed partly prevents the evolution of gases based on light elements such as C and N, and forces the phase separation to occur. When a highly dispersed monolith, based on very fine particles, is obtained, i.e. a true gel, its drying and subsequent pyrolysis may lead to a carbon gel derived from *a priori* unexpected precursors. The best examples have been reported by the group of Antonietti, using glucose as the main starting compound. A rather fibrous carbon aerogel could indeed be prepared from the hydrothermal treatment of a mixture of glucose and ovalbumin, see Figure 7. BET surface area and mesopore volume higher than 300 m^2/g and 0.5 cm^3/g, respectively, were measured after pyrolysis at 900°C. Due to the presence of protein among the precursors, this carbon aerogel was naturally doped with around 6 wt.% of nitrogen [14].

Such materials could also be easily doped by sulphur by simply incorporating a S source in the form of low amounts of either S-(2-thienyl)-L cysteine or 2-thiophene carboxaldehyde, leading to similar carbon aerogels as above, after supercritical drying and pyrolysis, but presenting special catalytic properties related to their surface composition [15]. Finally, borax has been recently suggested as both catalyst and structure-directing agent, allowing the preparation of monoliths from glucose treated in hydrothermal conditions. After supercritical drying and pyrolysis, carbon aerogels having different porous textures could be obtained, depending on the amount of borax. The highest BET surface area and mesopore volume were around 360 m^2/g and 0.4 cm^3/g, respectively [16]. As found in many other works before, the size of the constitutive nodules changed with the pH, hence with the amount of borax in this special case.

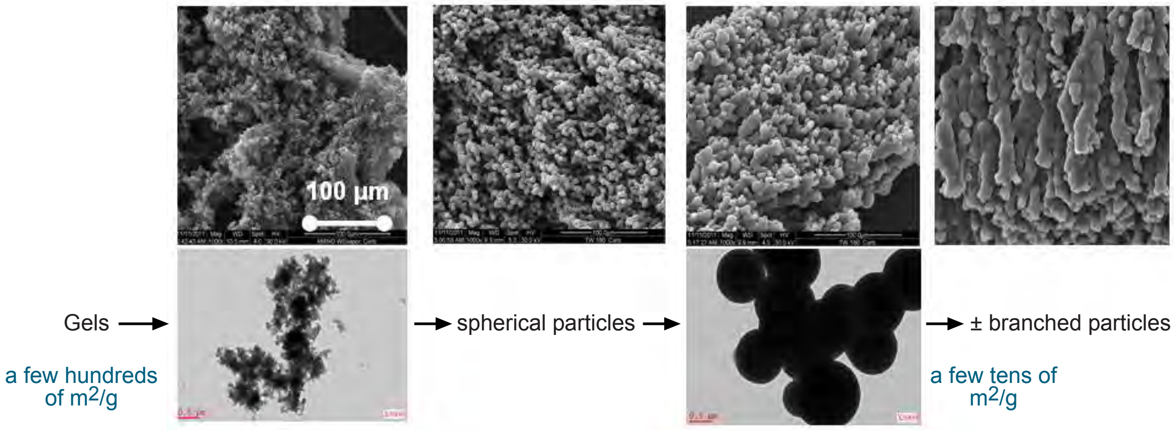

Figure 6. Various materials obtained by hydrothermal treatment of wattle tannin followed by pyrolysis at 900°C, using various pHs and conditions of dissolution. Those at the left are true carbon gels (after [13]). Even wider range of materials can be obtained by changing temperature, time and initial dilution.

Figura 6. Varios materiales obtenidos por tratamiento hidrotermal de tanino de acacia seguido de pirólisis a 900°C, usando varios pH y diluciones. A la izquierda, verdaderos geles de carbón (de [13]). Cambiando la temperatura, el tiempo y la dilución inicial se puede obtener una gama de materiales más amplia incluso.

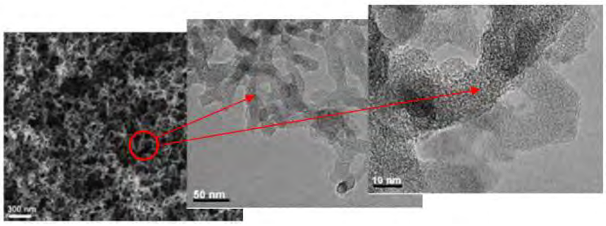

Figure 7. Fibrous carbon aerogels derived from the hydrothermal treatment of a mixture of glucose and ovalbumin (after [14], reproduced by permission of the Royal Society of Chemistry).

Figura 7. Aerogeles de carbón fibrosos preparados por tratamiento hidrotermal de una mezcla de glucosa y albúmina de clara de huevo (de [14], reproducido con el permiso de Royal Society of Chemistry).

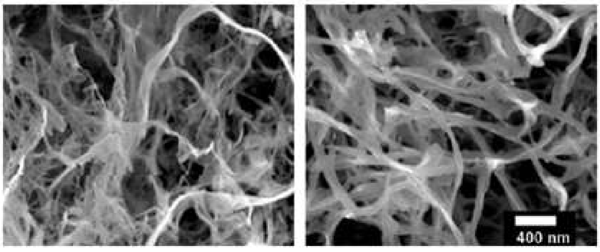

Figure 8. Fibrillar carbon cryogels derived from cellulose and pyrolysed at 600°C in nitrogen (left) and HCl (right). Reproduced from [20] with permission.

Figura 8. Criogeles de carbón fibrilares preparados a partir de celulosa y pirolizados a 600°C en nitrógeno (izquierda) y HCl (derecha). Reproducido de [20] con permiso.

Cellulose gels, aero- and cryogels, have been successfully prepared according to a number of techniques [17-21]. Cellulose could be used as such or as an ester: cellulose acetate. The former leads to physical (coagulated) gels, whereas the latter, through the use of isocyanate as crosslinker, leads to chemical gels. Both kinds of materials could be converted into carbon gels. Due to the fibrous nature of the precursor, the morphology of the resultant carbons was found to be fibrillar, thus was different from the traditional nodular structure most frequently reported so far. However, the characteristics of such gels are fully comparable with those based on phenolic precursors. For example, carbon aerogels derived from cellulose acetate (dried with supercritical CO_2) presented BET surface areas higher than 400 m^2/g [22] and mesopore volumes around 0.2 cm^3/g [23]. Because of such valuable characteristics, these materials could be successfully doped with noble metals and suggested as catalyst for PEM fuel cells [24]. From physical cellulose gels, fibrillar carbon cryogels have been obtained. These cryogels presented surface areas and mesopore volumes higher than 500 m^2/g and 0.6 cm^3/g, respectively [20]. Due to the low carbon yield of cellulose, these materials were advantageously pyrolysed in HCl, making the carbon yield increase from 15 to 30%, see Figure 8.

5. Conclusion

Producing carbon gels from natural resources, whether they are aerogels, cryogels or xerogels, was reported to be perfectly feasible, provided that the precursors are suitably chosen. Given that melting and extensive thermal decomposition should be absolutely avoided, most of the porous, organic, precursors are chemical gels of phenolic nature. However, other systems have been reported, whose main drawbacks, especially low carbon yield, could be got round through a preliminary hydrothermal treatment or through a pyrolysis in unusual atmospheres. Nevertheless, such methods are not enough when the precursor can not resist the pyrolysis step, such as materials mainly based on proteins. For example, soy-tannin aerogels recently reported could never be converted into their carbonaceous counterparts [25].

When compared to carbon gels made from synthetic molecules, biopolymer-derived carbon gels generally have very similar micropore volumes but possess higher macropore volumes and much broader mesopore size distributions. This finding is certainly related to the much higher molecular weight of structural units of bio-oligomers and biopolymers. Crosslinked phenolic biopolymers are indeed characterized by long polymer chains leading to steric hindrance, hence preventing the formation of very narrow pores related to high surface areas. This is well known for tannin oligomers, which are essentially branched and rigid, preventing the complete reactivity of all possible sites with formaldehyde. Additionally, the reaction with the crosslinker further provides a 3D-character to the polymer network, e.g. in the case of lignin, thus preventing the formation of very narrow pores. In contrast, organic and carbon gels based on smaller synthetic molecules, such as resorcinol, may present higher surface areas, higher mesopore volumes and narrower mesopore size distributions, but are significantly more expensive.

Anyway, and provided that their purity is high enough, carbon gels derived from natural resources are expected to have, and in some cases were already found to have, the same applications as those suggested for their synthetic counterparts, i.e., adsorbents, porous electrodes for electric double layer supercapacitors or secondary batteries, filling material for HPLC columns, catalyst supports, and heat insulators at high temperature.

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