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Lignin–phenol–formaldehyde aerogels and cryogels

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ABSTRACT

Highly porous organic aerogels have been prepared for the first time from a mixed lignin–phenol–formaldehyde (LPF) resin. Six different P/L weight ratios and two (L + P)/F weight ratios have been tested, leading most of times to nice and reproducible hydrogels which were subsequently either supercritically of freeze-dried. A broad family of aerogels and cryogels, respectively, was thus obtained. These materials were thoroughly investigated in terms of porous structure, based on pycnometry, adsorption and electron microscopy studies. The pore-size distributions were found to depend strongly on the initial composition, but not on the method of drying. The thermal conductivity of aerogels and cryogels has been measured and found to be minimal in materials combining both high mesopore volume and ideal pore sizes.

1. Introduction

In 1989, Pekala developed the first resorcinol–formaldehyde (RF) aerogels [1]. Their synthesis, repeated by many researchers since then, became so famous that these materials quickly turned out to be synonymous of organic aerogels in general. Even today, RF aerogels remain widely investigated worldwide because of their interesting properties such as low bulk density, high surface area, high mesopore volume, and well-controlled porous structure. Such unique characteristics make them promising materials for various applications [2–5]. However, the resulting materials are quite expensive and are not yet commercially available. In order to increase the commercial viability of organic gels, many efforts have been made during the past 20 years, both for simplifying preparation methods and for using cheaper raw materials [6–11]. One of the possibilities for significantly decreasing the cost of organic gels is using natural resources derived from biomass.

The most common organic aerogels derived from natural precursors were made from cellulose [12]. However, either the cellulose was chemically modified in order to be crosslinked and thus to lead to chemical gels [13], or the cellulose was coagulated, leading to physical gels [14–16]. True chemical aerogels rather similar to those based on RF resin could also be prepared from natural phenolic molecules such as lignin [17,18] and tannin [19–23], and even using both together [24].

Lignin is of special interest since it is the second most abundant biopolymer after cellulose and, given its extremely low cost and phenolic nature, is one of the leading candidates for preparing aerogels. Lignin has a complex structure, composed of a highly branched phenylpropanoid network. Especially three repeat units, namely methoxylated coumaryl, coniferyl, and sinapyl alcohols, are very abundant in the polymer (see Fig. 1) [25–28]. Lignin has been extensively investigated by many research groups for different applications [29 and references therein] including the preparation of gels [17,18,30,31]. Lignin is indeed poorly valorised as a raw material, being mainly used as an energy source for pulp and paper industries, and is thus available in large amounts from paper and ethanol production processes. Nevertheless, previous studies have proved the interest of crosslinking lignin with phenol and formaldehyde for producing highly valuable lignin–phenol–formaldehyde resins [32–35]. Moreover, phenol is far cheaper than resorcinol and, despite its comparatively lower reactivity, it could be successfully used as precursor for producing gels [36,37]. It has indeed been recently postulated that adhesives can be easily converted into gels, provided that suitable changes are brought to their formulation [38].

Organic aerogels are usually produced by sol–gel reactions in aqueous solution, followed by solvent exchange and drying with supercritical carbon dioxide [1]. Supercritical extraction of the solvent indeed induces the vanishing of the liquid–vapour interface,

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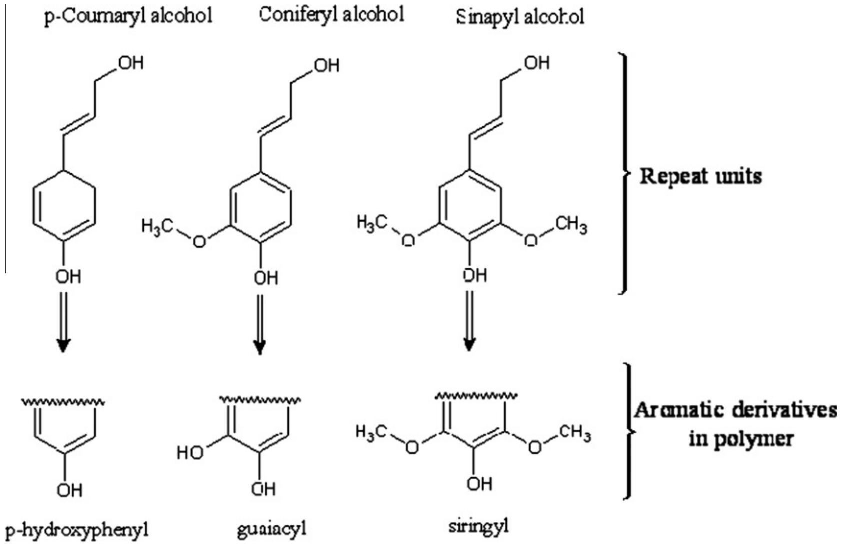

Fig. 1. Structure of repeat units of lignin and their derivatives (after [26]).

thus avoiding the significant shrinkage due to capillary forces, which may be considerable at the nanometre scale. This is especially the case with CO_2, for which moderate pressure and temperature are required. However, many attempts have been made to simplify the preparation process, mainly because supercritical drying is very expensive at large scale. Supercritical drying in organic solvents was shown to be feasible, but the procedure is only cheaper, not really easier [20 and references therein]. Freeze-drying was suggested as an alternative to supercritical drying [39], and was indeed shown to be an efficient way of preparing high-surface area carbon gels with controlled pore structure [40,41]. Such drying mode is also much cheaper.

In the present work, we successfully used lignin and phenol as inexpensive raw materials for preparing organic aerogels and cryogels. The aim of this study was to determine the conditions of gel formation, to observe the changes of porous structures depending on composition and drying mode, and to test the performances of the most promising materials in terms of thermal insulation. The results have been compared to those of Chen et al. [17,18], who prepared aerogels and cryogels from lignin–resorcinol–formaldehyde formulations. We show here that more lignin but also less formaldehyde can be incorporated into the gels when phenol is used instead of resorcinol, further decreasing the production costs at similar pore structure.

2. Experimental

2.1. Preparation of lignin–phenol–formaldehyde (LPF) hydrogels

Lignin was kindly supplied by Innventia and is presently commercialised by the company Metso under the name LignoBoost. It is a Kraft lignin that has been precipitated from softwood black liquor by injection of CO_2. The resultant precipitate has been filtered, re-dispersed, acidified again, filtered once more and finally washed. As a result, a much purer lignin than usual was obtained, having very low carbohydrate, sulphur and ash contents, typically 0.5–1.5, 1–3, and 0.2–1 wt.% on dry basis, respectively [42]. Additional information can be found elsewhere [43].

Fifty grams of this lignin were dissolved in 200 g of water heated and stirred at 85 °C during 1 h. In the meantime, 4.5 g of sodium hydroxide (on dry basis) was added very progressively in the form of 30 wt.% aqueous solution until the final pH was 12. A dark homogeneous solution, having a lignin concentration of 20 wt.% was obtained. After cooling at room temperature, this solution was used to prepare a number of hydrogels by addition of solid phenol and 37 wt.% aqueous solution formaldehyde, according to the different mass ratios (on dry basis) shown in Table 1. In all the cases, the amounts were adjusted for keeping the fraction of solid (sum of dry lignin + dry phenol + dry formaldehyde) always equal to 26 wt.%. After homogenisation, the final solutions had a pH close to 10, and were introduced into glass tubes which were immediately sealed and placed vertically during 5 days in an oven at 85 °C. The solutions were then frequently inspected in order to determine their gelation time. The latter was estimated visually as the moment at which the surface of the viscous liquid no longer flowed when the tubes were tilted at an angle of 45° [44].

2.2. Preparation of LPF aerogels and cryogels

After 5 days, the tubes were broken for removing the hydrogels, which were cut into cylindrical pieces of diameter and typical thickness 13 and 6 mm, respectively. Because water is highly undesirable in the drying process, a thorough solvent exchange was carried out as follows. The samples were immersed in pure, dry, solvent placed in a tightly closed flask, which was gently

Table 1
Synthesis conditions in the preparation of lignin–phenol–formaldehyde (LPF) hydrogels. NG means not gelled after 5 days at 85 °C.

Sample name	pH	Mass ratio (on dry basis)		Remarks
		P/L	(L + P)/F	
LPF 0.11/1.7	10.53	0.11	1.7	NG
LPF 0.25/1.7	10.23	0.25	1.7	
LPF 0.43/1.7	10.07	0.43	1.7	
LPF 0.67/1.7	10.02	0.67	1.7	
LPF 1.0/1.7	9.93	1.0	1.7	
LPF 1.5/1.7	9.85	1.5	1.7	
LPF 0.11/1.25	10.56	0.11	1.25	NG
LPF 0.25/1.25	10.35	0.25	1.25	NG
LPF 0.43/1.25	10.17	0.43	1.25	
LPF 0.67/1.25	10.04	0.67	1.25	
LPF 1.01.25	9.89	1.0	1.25	
LPF 1.5/1.25	9.65	1.5	1.25	