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CELLULOSIC AEROGELS FOR ENERGY APPLICATIONS

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Introduction

Coming from soft chemistry (e.g. sol-gel), chemical nature and nanostructuration of aerogels can be *softly* tailored. Moreover, they can be lightweight and they can present very high specific area (larger than 1000 m²/g) with narrow (or even broad) pore size distribution. Such structural characteristics make them potentially interesting for various applications.[1]

A large majority of the studies dedicated to aerogels are dealing with inorganics (SiO_2, TiO_2, ZrO_2…).[2] Anyway, some class of organic aerogels are known to present high interest. Such materials are particularly considered as organic precursors for new nanostructured carbons. Most of the corresponding samples are coming from Resorcinol-Formaldehyde (RF) systems.[3] During the past decade, further studies on organic aerogels for thermal insulation have addressed other kinds of aerogels, mainly based on polyurethane[4,5] and very recently polydicyclopentadiene systems.[6] Within these sphere, except original works of Kistler,[7] only very few works concern use of natural products. Knowing that cellulose is one of the most abundant natural materials, one can guess that combining sol-gel science and cellulose could be of high interest. Some works on elaboration of porous cellulose *via* drying of physical cellulose-based gels can be found but they are dealing with macroporous foams not *really* aerogels.[8,9] Some years ago, one of the first aerogel attempt with cellulose derivatives has been published.[10] On this basis, we have developed a softer route (*i.e.* using a non toxic isocyanate).[11] We have then examined the pyrolysis impact on the resulting carbonaceous *green* materials and evaluated its use as catalyst support for PEM fuel cell electrodes.[12] Here is presented a very brief overview of the related studies we have performed since then.

Experimental

Materials. All reagents were used without further purification. Cellulose acetate was purchased from Aldrich. Two grades presenting similar acetyl average substitution degree (2.4) but differing by their number-average molecular weight M_n (30 000 and 50 000) - and consequently by their number-average degree of polymerisation DP_n (respectively equal to 110 and 190) - were used. Polymethylene polyphenylpolyisocyanate (PMDI, Lupranat® M20S, presenting a NCO content equal to 31.8 wt%) was purchased from BASF. Dibutyltin dilaurate (DBTL, 95%) and Pyridine (99%) were purchased from Aldrich as well as the solvent (anhydrous acetone 99.8%). 1,4-diazabicyclo[2.2.2]octane (DABCO® TMR) was purchased from Air Products. CO_2 was purchased from Air Liquide.

Synthesis. Gels were prepared at room temperature through a sol-gel route based on the formation of urethane bonding by polycondensation reactions between cellulose acetate (CA) and isocyanate (I) as schematically represented in **Figure 1**. CA was dissolved in acetone for 15 hours until solution becomes translucent then stirred with a magnetic bar. Catalyst was added (DBTD, DABCO or Pyridine) then PMDI, dissolved in acetone, was rapidly mixed with this solution under mechanical stirring for 10 min. The resulting sol was cast in the gelation moulds. After sol-gel transition occurred, gels were covered with an excess of acetone and washed with acetone to remove unreacted species.

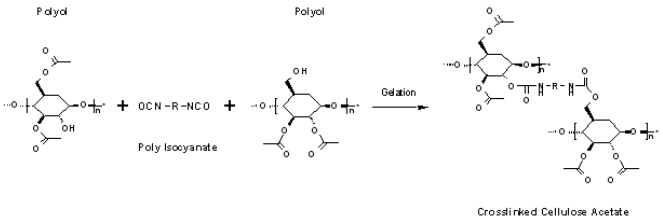

Figure 1. Scheme of urethane crosslinking of cellulose acetate.

In a PARR Instrument autoclave, the gels were then washed with superctitical CO_2 (85 bars and 40°C). When the whole acetone was replaced, CO_2 was vented out slowly (0.1 bar/min) and isothermally (40°C).

Instrumentation. FTIR and UV-VIS spectroscopy were respectively realised on Nicolet 510P and Philips PU8730 apparatus. Scanning electron microscopy (SEM) was performed with MEB FEG Ultra 55 (CMTC-INPG Grenoble, France). Helium pycnometry and mercury porosimetry were respectively performed with Micromeritics Accupyc 1330 apparatus and Carlo-Erba 2000 porosimeter (LGC, Liège University, Belgium). Specific BET and BJH porous characteristics were obtained on a Sorptomatic 1990 apparatus (Saft R&D, Bordeaux, France).

Results and Discussion

Preliminary results. Previoulsy published results[11] have shown that monolithic cellulose-acetate aerogels presenting a pearl-necklace structure (e.g. a branched polymeric network formed by spheroid aggregates) are obtained through this *simple* route as illustrated in **Figure 2**. The materials can be as light as 0.250 g/cm³ and present S_{BET} of 250 m²/g and porous specific volume around 3.30 cm³/g. Most of the densification occurred during the supercritical CO_2 drying step because of *poor* solubility of the polymeric network (Hildebrand parameter δ around 20 $MPa^{½}$) in CO_2 ($\delta \sim 4.9$ $MPa^{½}$ at 80 bars and 40°C)[13]. The total reversibility of the drying shrinkage when aerogels are re-impregnated by acetone confirms this assumption.

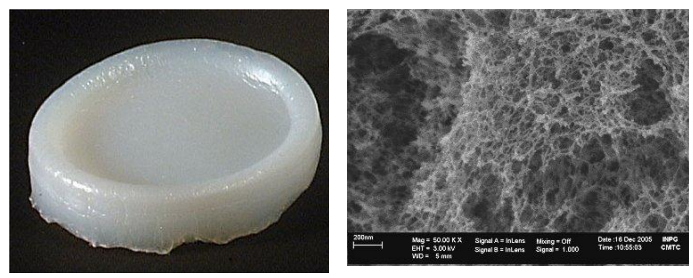

Figure 2. Aerogel (left) and its SEM-FEG micrograph (right).

Allophanate bridging. These preliminary studies have been continued paying a particular attention to aerogels elaborated with a CA/I ratio greater than the theoretical stoichiometric value (CA/I = 3.3). On the contrary of samples synthesized with low crosslinking conditions (CA/I = 10), the aerogels prepared with a large excess of isocyanate (CA/I = 1) experiment rather *constant* textural properties (bulk density ρ_b, porous volume V_{sp}, mean mesopore size d_{Hg}, mesoporous volume fraction $\%V_{Hg}$ and pore size distribution as shown in **Figure 3**) whatever acetate cellulose concentration %CA (defined as the CA and acetone mass ratio) and DP_n. As an illustration, when %CA varies from 5 to 10%, ρ_b, V_{sp}, d_{Hg} and $\%V_{Hg}$ remain close to 0.70 g/cm³ ± 0.05, 0.7 cm³/g ± 0.1, 13 nm ± 1 and 0.85 ± 0.05.

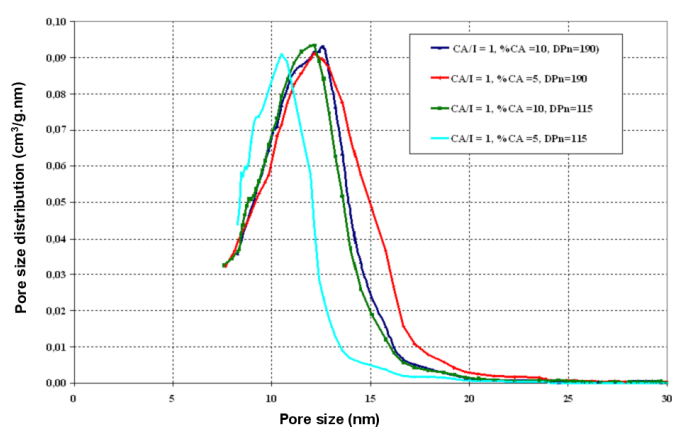

Figure 3. Pore-size distributions of aerogels prepared with CA/I = 1 characterizd by non-intrusive Hg porosimetry[14] with k_f = 28 nm.MPa¼ (d_{Hg} and $\%V_{Hg}$ were also characterized with this technique).

The excess of isocyanate was not detected by UV-Vis spectroscopy in the acetone washing baths. Besides elementary analysis have also proven that all the isocyanate initially dissolved in the sol have remained in the final aerogel. Is PMDI physically trapped or covalently bounded to the solid skeleton ? IR spectroscopy of aerogels showed that the characteristic isocyanate peak at 2250 cm^{-1} is not observable (as underlined at **Figure 4**). This result suggests that secondary reactions have occurred in the polymer.

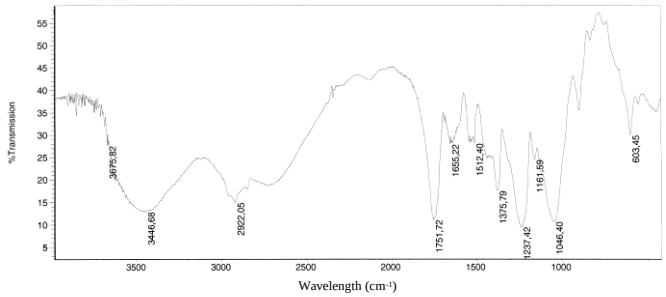

Figure 4. FTIR spectra of aerogels prepared with CA/I = 1 (pellets of KBr mixed with aerogel powder)

Taking into account the non-aromatic nature of the isocyanate, the absence of water and trimerisation catalyst associated to the fact that the whole process is performed at room temperature (which prevents the system from PMDI condensation), we assume that the secondary crosslinking network is based on allophanate bridging between isocyanate and urethane groups as shown in **Figure 5**.

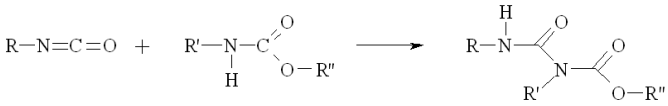

Figure 5. Schematic representation of allophanate crosslinking

Influences of catalyst nature and cellulose acetate concentration. One of the deals is now to extend easily the range of structural characteristics of these cellulosic materials. For this purpose, basic sol-gel parameters have been varied. Here are the results for %CA and catalysts (**Table 1**).

Whatever urethane catalyst nature, ρ_b increases with %CA, V_{Hg} and d_{BJH} decrease while $\%V_{BJH}$ displays a maximum at %CA = 10% (d_{BJH} and $\%V_{BJH}$ are respectively the mean pore size and the porous volume fraction determined *via* BJH treatment of N_2 sorption isotherms). Besides catalyst nature induces specific %CA influence. DBTL and Pyridine act similarly but differ from DABCO. In comparison with DBTL, DABCO leads to *i)* faster kinetics, *ii)* denser materials (as illustrated on SEM *clichés* at **Figure 6**) with lower specific area, mesoporous volume and fraction and *iii)* smaller mean mesopore size (d_{BJH}). Results show that a wide range of materials can be elaborated but studies are still in progress to explain such behaviours.

	%CA	t_g (min)	ρ_b (g/cm^3)	S_{BET} (m^2/g)	V_{Hg} (cm^3/g)	$\%V_{BJH}$	d_{BJH} (nm)
	3	190	0.18	240	4.25	35 %	60
DBTD	5	45	0.38	360	1.95	100 %	28
	10	30	0.56	250	1.00	85 %	18
	3	1	0.39	270	1.95	90 %	-
DABCO	5	3	0.73	215	0.60	100 %	11
	10	5	0.82	145	0.45	70 %	7
	3	*1 day*	0.16	205	5.80	15 %	-
Pyridine	5	240	0.62	345	0.85	100 %	12
	10	190	0.87	160	0.40	90 %	7

Table 1. Influence of %CA and catalyst nature on gelation time (t_g) and main structural characteristics of aerogels synthesized with CA/I = 5 (V_{Hg} appears similar to specific porous volume V_p calculated with ρ_b and $\rho_{skeleton}$ coming from He pycnometry and equal to 1.30 $g/cm^3 \pm 0.05$ for all the samples).

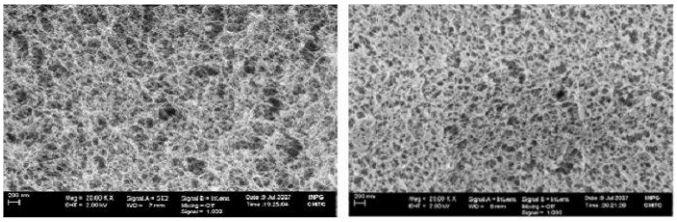

Figure 6 : SEM-FEG micrograph of acetate aerogels prepared with %CA = 3%, CA/I = 5 and DBTD (left) or DABCO catalyst (right)

Conclusions

This study has permitted to elaborate a new class of *greener* aerogels presenting interesting structural features that can be tailored through very basic sol-gel actions. Without any former optimization, these cellulose acetate aerogels have an effective thermal conductivity (lower than 0.030 W/m.K as measured with the well-known hot-wire method[15]) better than the available ecologic insulating materials. Of course, further works must now be focused on how to refine their nanostructuration to decrease this thermal conductivity below 0.020 W/m.K.

In parallel, first samples have been pyrolysed under N_2 at various T (< 1000 °C). During pyrolysis, the materials are bubbling because of melting of the organic network before its thermal degradation. The resulting carbonaceous matrices appear macroporous but a mesoporous fraction can be distinguished (0.5 cm^3/g). Finally, the corresponding samples have been studied as catalyst support for Proton Exchange Membrane Fuel-Cell electrodes. First results are promising.[12]

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