SCALE-UP OF SUPERCRITICAL DRYING OF AEROGELS FOR DIFFERENT APPLICATIONS

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ABSTRACT

Aerogels have been extensively studied over the last decades due to their remarkable properties and versatile application potential. Although sol-gel chemistry is crucial to achieve a material with required thermal, mechanical or chemical properties, its drying might be equally important for keeping the previously obtained nanostructure intact. However, most of these works have stayed at laboratory scale, while industrial production often leads to xerogel materials rather than aerogels, offering inferior performance.

Herein is presented an overview of existing drying methods and as a solution, supercritical drying scale-up of various aerogel materials for diverse applications. Advantages and drawbacks of the different routes are discussed in order to comprehend the different challenges for manufacturing these nanoporous materials.

SOL – GEL CHEMISTRY

Aerogels, low-density open-porous solid materials, are produced by sol-gel chemistry. The aerogel structure consists in a porous solid where majority of pores are between 2 and 50 nm in diameter (mesopores). Based on this, exceptional properties such as high porosity (~95%), high specific surface area (up to 1,000 m^2/g), low thermal conductivity (~0.01 W/ m.K), low refractive index (~1.05), and high optical transmission (90%) might be achieved [1] .

Sol-gel chemistry is based on transformation of molecular colloidal into a cross-linked gel. Depending on the precursors nature, aerogels might be inorganic (i.e. oxides from silicium-, zirconium-, titanium-based precursors), organic (i.e. polymers from resorcinol-formaldehyde or polyurethane precursors) or hybrid (if obtained from organic-mineral precursors) [2].

Inorganic aerogels are prepared by hydrolysis and condensation of silica or metal based precursors. The first silica aerogel reported in the literature was prepared by Kistler in 1931, using sodium metasilicate, Na_2SiO_3 [3]. Nowadays, silica aerogels are prepared mostly using alkoxides of $Si(OR)_4$ type, in which R and OR designate alkyl and alkoxide groups, respectively. Progress of sol-gel chemistry over the last decades has promoted innovative alkoxide-derived precursors such as methyltrimethoxysilane (MTMS) [4, 5], polyethoxydisiloxane (PEDS) [6, 7], perfluoroalkylsilane (PFAS) [8], 3-(2-aminoethylamino) propyltrimethoxysilane (EDAS) [9], etc; all rely on existence of ≡Si-O polar covalent bond that allows a random 3D-network, while additionally including built-in chemical functionality.

Organic aerogel are predominantly based on natural sources (ex. cellulose) or synthetic polymers such as formaldehyde-resorcinol, formaldehyde-melamine, polyurethanes and polyisocyanurates. Several methods for cellulose aerogels production are described in the literature [10-14]. The first cellulose aerogels were prepared by Tan et al. [15] using cellulose acetate and cellulose acetate

butyrate, while "aero-cellulose" material was prepared by dissolving cellulose in aqueous NaOH or *N*-methyl-morpholine-*N*-oxide (NMMO) monohydrate.

Alike to cellulose-based aerogels are polyurethane aerogels that are obtained by polycondensation of polyols with polyisocyanates, where urethane groups –O-CO-NH- form a tridimensional network [16, 17]. Polyurethane aerogels exhibit low densities and very interesting thermal properties. Moreover, resorcinol-formaldehyde (RF) aerogels have been intensely studied since they are an important class of organic aerogels, although there are other types available, not only formaldehyde-based (phenol-formaldehyde, melamine-formaldehyde) but also polyimides, polyacrylates or polystyrenes [18]. Recent studies have shown that some of these materials could yield very low thermal conductivity values [19] combined with mechanical properties superior to silica aerogels [20] and a tendency to reduce dust release.

Organic aerogels can be transformed into **carbon aerogels** by pyrolysis under inert atmosphere. Carbon aerogels do not only exhibit exceptionally high stiffness, strength and resilience, but also possess unusual chemical and structural properties. Chemically inert pure carbon structure, with high surface area and electrical conductivity, might be used as electrical double-layer capacitors [21], electrode and catalyst support in PEM fuel cells [22], advanced catalyst supports [23, 24] and adsorbents [25].

A new class of **composite or hybrid aerogels** has been elaborated when combining inorganic and organic precursor. Eepoxy-based composites have been extensively studied[26]. Moreover, addition of biopolymers (ex. chitosan, cellulose and pectin) has significantly enhanced chemical and mechanical properties of silica based aerogels [27-29]. Zheng et al. [30] showed that cross-linked polyvinyl alcohol – cellulose nanofibril (PVA-CNF) hybrid organic aerogels exhibit excellent elasticity and mechanical durability, while demonstrating exceptional absorption performance. Novel material achieved by combining carbon nanotubes and polyaniline (SWCNT/PANI) nano-ribbons can be applied as lithium ion battery electrodes due to their high capacity (185 mAh/g) and good cycle performance (up to 200 times) [31].

DRYING OF AEROGEL

Drying process is based on solvent elimination from the gel pores while keeping the nanoporous structure intact. Several processes have been developed concerning drying and their remarkable impact on the final material properties [32] and cost [33, 34].

Figure 1 shows three possible ways to dry an aerogel. Different type and quality porous materials can be achieved due to those processes which have been intensively studied:

    a. Cryogel – obtained by sublimation of the solvent below the triple point (Freeze Drying);

    b. Xerogel – obtained by evaporation of the solvent through the liquid-gas interphase line (Ambient Pressure Drying);

    c. Aerogel – obtained through supercritical state of the solvent, crossing around its critical point (Supercritical Drying).
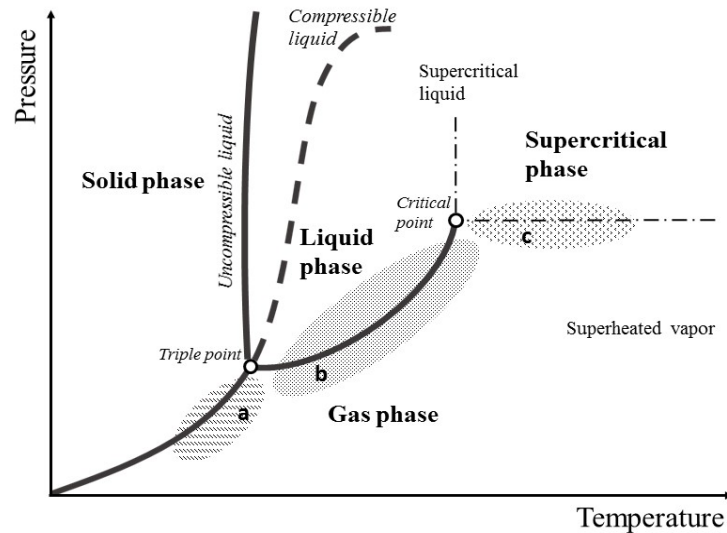
Figure 1. Phase transition routes.

Freeze-drying (FD) is direct transformation of a solvent from solid to gas phase by sublimation, when high-vacuum is applied. It avoids liquid phase meniscus stress, obtaining crack-free materials with high porosity [2].

Freeze-drying has become an important method for processing gels sensitive to higher temperatures or moisture (e.g. cellulose). However, it is time and energy consuming to reach the required lyophilization cycle [35] and different freezing/ sublimation ratios which can promote microcrystalline salt structures formulation within the samples [36].

Major efforts have been performed in order to optimize cryogenic production of monolithic nanoporous materials, since this process generates manly granular and powder materials [37]. Among others, exchange of the soaked solvent with higher melting temperature solvent leads to high porosity monolithic materials [38, 39]. The final structure of the material is highly influenced by solvent nature which effects freezing rate and sublimation temperature.

Ambient Pressure Drying (APD) is based on bringing solvent over its bubble point in order to be evacuated in gas form However, liquid evaporation from gels results in large capillary pressure within the pores (up to 100 - 200 bar) [40] which influences material density and porosity or may damage the structure. These deformations additionally influence either mechanical, thermal or optical properties of final material.

Ambient pressure drying provides manly xerogels in granular and impregnated-mat shape. The process itself is limited and not feasible for achieving higher quality material, such as an aerogel, although the novel synthesis routes and structural modifications of material have been intensively investigated in order to overcome those limitations.

Supercritical Drying (SCD) is based on pressurizing and heating the liquid solvent in the gel over its critical point, until it becomes supercritical. At this point, the supercritical fluid can be removed from the material pores by depressurizing the fluid under isothermal conditions without creating capillary stress within the structure [2]. There are two possible ways: i) venting the solvent from its supercritical state (High Temperature Supercritical Drying – HTSCD) or ii) solvent exchange with a second solvent, generally carbon dioxide (CO_2), which completely dissolves the previous one, and venting CO_2 from its supercritical state (Low Temperature Supercritical Drying – LTSCD).

- High Temperature Supercritical Drying (HTSCD)

The materials dried by HTSCD generally reveal highly hydrophobic behaviour due to the high critical temperature of most organic solvents used in sol-gel chemistry (200-500 °C). High hydrophobicity level is achieved by replacing hydroxyl groups (OH) within the structure with hydrolytically stable organo-functional alkoxy groups (e.g. $R=CH_3$). However, the stability of this hydrophobic behaviour during time depends on precursor and solvent nature (e.g. TEOS silica aerogel dried through supercritical ethanol route loses its hydrophobicity over a couple of hours).

Although HTSCD minimizes shrinkage of the gel, temperature sensitive materials such as organic polymer [16] or cellulose-based [13] aerogels cannot be produced this way. Moreover, the solvents are highly volatile and flammable under elevated temperature and pressure, while supercritical ethanol causes corrosion of equipment and seals. Therefore, the process development has not become feasible at large scale due to specific safety requirements [41].

- Low Temperature Supercritical Drying (LTSCD)

The organic solvent within a gel can be replaced with liquid or supercritical carbon dioxide, followed by an isothermal depressurization from supercritical state that can take several hours depending on aerogel thickness, since both are controlled by diffusion [42].

The critical factors for the aerogel LTSCD are pressure and temperature that directly control the state of the CO_2-solvent mixture. Temperature changes have no significant influence on material although a minor variations in pressure can easily provoke shrinkage of the sample due to the expansion of the solvent or possible phase separation [43]. To avoid shrinkage, the $scCO_2$-organic solvent mixture shall remain in a homogenous phase during extraction.

The final material is hydrophilic (if there is no material surface modification during sol-gel chemistry), since LTSCD does not favour replacement of the hydroxyl groups (OH) by hydrolytically stable organo-functional alkoxy groups (e.g. $R=CH_3$).

It would be quite challenging to make a systematic comparison of the drying methods described above, but in general terms, all of these have advantages and limitations. FD involves special equipment to reach the low temperatures required for the solvent sublimation, whereas aerogel powder is produced rather than monolithic samples. APD does not require costly equipment, but it is an energetically intensive multi-step process, that employs huge quantities of volatile organic solvents. Moreover, gel nanostructure is affected since evaporation process generates strong capillary forces within. Besides the limited final properties, APD has been the most economical choice to be scaled up for high volume aerogel production along the last years. Nevertheless, higher quality aerogels can be achieved when using SCD. The main limitation of HTSCD is extremely high temperatures required to reach supercritical state of organic solvents, emphasizing the process safety. To overcome high temperature applied either for APD or HTSCD, LTSCD becomes the most pertinent method. By using $scCO_2$ as a solvent, LTSCD operates at near ambient conditions, and even if time is a drawback, energy consumption and organic solvent use are highly reduced. The optimization of LTSCD has been an intensive work for several industries in order to scale it up to large volume production. Different approaches and minor modifications to optimise the extraction process have been performed. The authors are confident that the use of this technology will bring a great opportunity in the manufacturing of aerogels materials at large scale since the production cost can be still lowered while obtaining the highest quality aerogel product.

APPLICATION

Due to our expertise, we have been involved in several FP7 European projects, namely AEROCOINS [44], HIPIN [45] and RESSEEPE [46] (building insulation) and AerSUS [47] (aerospace application). Various nanoporous insulation materials have been developed within these projects and their application will be described afterwards.

- AEROCOINs

The main drawbacks to apply aerogels based materials in building insulation are their mechanical properties and high cost. AEROCOINs project develops a new reinforced super-insulating aerogel hybrid material to overcome those issues. The synergy of both new synthesis approach and manufacturing concepts are studied to achieve:

- o Material: Obtain a reinforced aerogel-based thermally superinsulating material (<18 mW/ m.K) with improved mechanical properties.
- o Manufacturing: Development of a cost-effective pilot scale drying process (APD or LTSCD) and production of new building component.
- o Application: Demonstrate the thermal, structural and mechanical performance of the highly insulating component under real conditions.

Separex is involved in LTSCD development, producing aerogel materials as a quality reference for APD method enhance. Additionally, cost reduction and implementation of the supercritical drying was performed as well. At a pilot scale, the CO_2 dried aerogel-based solutions demonstrate reduced durst release, low thermal conductivity (<14mW/ m.K at room temperature) and low density (<100 Kg/ m³). Yet, the main benefit of Separex dried material is its tailored hydrophobicity offering a moisture-resistant grade, which avoids both degradation of properties with time and high flammability due to current surface treatments.

- AerSUS

Multi-Layer Insulation (MLI) materials are currently used for thermal protection of the hardware and diverse components of spacecraft. Their raw material is often subjected to access restriction. The AerSUS project aims to develop aerogel manufacturing technology for the next generation of thermal insulation in space. Its integration would be an advantage due to the excellent intrinsic properties of the open-nanoporous aerogels. The main objective of the project is creating a European supplier of aerogels with optimized low density and low bulk thermal conductivity for diverse thermal control systems of spacecraft, in particular in low pressure environment (e.g. launchers, re-entry, planetary probes, etc).

According to the space technology requirements, the weight of the different components is a critical factor. AerSUS technology is based on supercritical drying technology since LTSCD avoids densification of materials. Separex has optimized the drying procedure for the different solutions within the project, reaching density of 50 Kg/m³ and thermal conductivities below 5mW/ m.K (at 10^{-5} mbar).

- HIPIN

There is a huge potential market for a highly insulating material for cladding buildings with a coating thin enough to satisfy the needs of high density housing (to avoid space decrease with internal insulation).

The concept of HIPIN project is developing a sustainable and affordable technology to produce a nanostructured thermal insulating coating to improve thermal efficiency in new and retrofitting buildings. HIPIN developed materials shall have an added value such us self-cleaning, sound insulation and fire retardant properties. The innovative multi-functional materials are appropriate for either interior or exterior application in liquid or solid form. Their advantage over currently available solutions and optimization of LTSCD will allow an industrial scale production.

Separex has developed a new aerogel material using precursor tailored to obtain mechanically reinforced, low density aerogels. The final material will be applied in powder form for coating systems and as granular in render, plaster and composite panels.
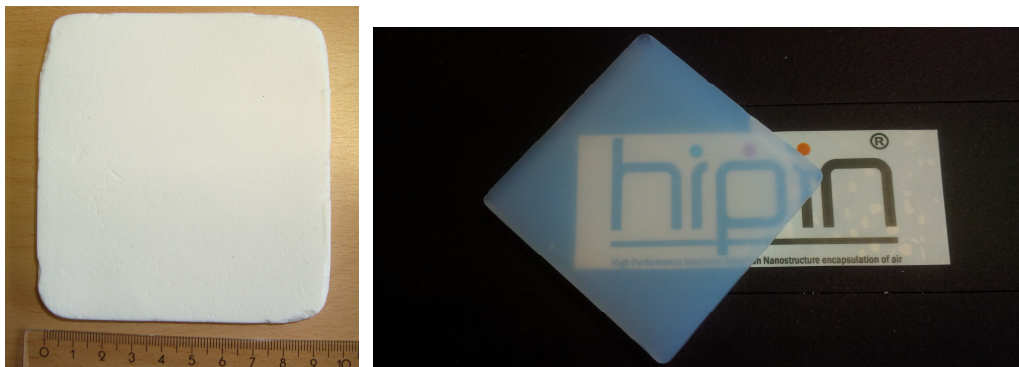

Figure 2. Cellulose based aerogel synthetized by Mines ParisTech in AEROCOINs project (left) and mechanically reinforced silica based aerogel from HIPIN project (right).

- RESSEEPE

The core idea of the RESSEEPE project is to technically advance, adapt, demonstrate and assess a number of innovative retrofit technologies. Reductions by 50% shall be achieved in terms of energy consumption. The principal idea is to identify and select the best possible retrofitting customized mix to reach particular requirements.

Separex develops an aerogel of different granulometry to be implemented in an optimized mortar formulation. LTSCD provides a super-hydrophobic material without damaging the internal surface, keeping thermal conductivity low. Physicochemical stability of the final aerogel formulation is a key parameter for the success of the retrofitting solution. Between the applied technologies, aerogel-based super-insulating mortar will be used for outer part façade among other applications.

FUTURE OVERVIEW

The commercial products currently available are generally based on silica. Two leading aerogel producers are North American companies, Cabot (manufacturing plant in Germany) and Aspen Aerogel, offering sodium silicate-based granular materials and alkoxysilane-based flexible blankets, respectively. Cabot has used both ambient and supercritical drying while Aspen is focusing on supercritical CO_2 drying.

General need for nanoporous materials with better performance and durability, yet versatility of its final use, has motivated us to improve existing LTSCD, developing an efficient drying process of aerogels. The main issues, such as process time and cost have been overcome. The new process takes

only a couple of hours and its total cost has been reduced up to 40 % when compared with the commercially existing processes.

These attractive results are just a spark for launching another industrial production of aerogels in Europe focused on innovation on aerogel materials (powder, granular, boards, monolithic plates, etc.) for large volume manufacturing. Its main target will be construction and renovation sector, but able to offer solutions for cosmetic, pharmaceutical, automotive or energy storage requirements.

AKNOWLEGMENT

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