



Nano-fibrillated cellulose-zeolites based new hybrid composites aerogels with super thermal insulating properties

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ABSTRACT

Aerogel monoliths were prepared using combinations of cellulose microfibrils, cellulose nanofibers and nanozeolites. It was shown that these hybrid materials have tunable thermal conductivity and mechanical properties. Thermal conductivity value as low as $18 \text{ mW m}^{-1} \text{ K}^{-1}$ was obtained that confirms the super-insulation ability of these new fibrous aerogels. Synergism on the thermal conductivity properties was shown by adjunction of nanozeolites to cellulose microfibrils by reaching pore size lower than 100 nm that significantly reduces the thermal conductivity of the hybrid aerogels as predicted by Knudsen et al. In one hand, these properties seem to depend strongly on the interactions between the component and their relative fractions. On the other hand, the addition of nanofibrils to micrometric fibers based aerogel yields a significant increase of its stiffness. The higher improvement of the stiffness was obtained when nanofibrils with high surface charge are added. This study certainly opens a new investigation field to optimize the thermal conductivity properties of hybrid nanocellulose based aerogels.

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1. Introduction

Though Kristler discovered them since 1930, aerogels gain a great interest nowadays. Many research groups are working to develop new materials thanks to the variety of usable materials to form aerogels (organic, inorganic or hybrids) and the design of new extraction or preparation methods. The obtained aerogels, known to be structured with mesopores, are new materials having the best potential in many application fields: design fuel cells (Pekala et al., 1994), filtration and ultra-thin dust purification (Venkateswara et al., 2007; Tsou, 1995) and high performance thermal insulators (Baetens, 2011).

However, in order to design methods that may be perennially used in industry, research has to optimize fabrication and to use environmentally friendly processes. The increasing need of these new aerogels also requires a decrease of the processing cost and difficulties and the utilization of renewable and environmentally

friendly compounds. One of the most abundant materials on earth having the latter properties is cellulose under all its forms.

Aerogels can be either inorganic containing silica (Smith et al., 1999; Pekala, 1989a, 1989b; Pekala et al., 1990; Lu et al., 1995; Mackenzie et al., 1992), or organic for example resorcinol-formaldehyde (Pekala, 1989a, 1989b). They have a very low thermal conductivity and are often super-insulators, but they are relatively fragile (aerogel of silica; Pekala et al., 1990) or made of toxic molecules (organic aerogel; Lu et al., 1995). Mackenzie et al. (1992) first developed organics–inorganic hybrid aerogels. It consists of a silica matrix consolidated by incorporation in the sol–gel of silicone macromolecules. Although the mechanical characteristics are interesting, thermal conductivity is still high because of too important densities. Pajonk (2006) tested, starting from hybrid monomers, the synthesis of a very flexible material embedding too much macroporosity to be super-insulator. Aspen company was the first to produce industrial hybrid aerogels products with Space loft trademark (Aspen Aerogels, 2014) which are composites of aerogel with some kind of fibrous batting (Aerogel.org, 2014). Investigations on cellulose containing aerogels (and cellulose derivatives or other polysaccharides) were reported in the articles of Fischer et al. (2006), García-González et al. (2011), Guilminot et al. (2008) and Sescousse et al. (2011). A new way of research was recently carried

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out with an aim of developing super-insulators aerogels materials from bio-resources. The purpose of this article is to design new aerogels of cellulose with mineral loads that can be innovating solutions to manufacture biomaterials with high added value, in particular in the field of thermal insulation.

Pristine cellulose nanofibrils alone or in combination with other nanomaterials are showing very interesting mechanical and physical properties that open them new potential application fields as functional materials (Carlsson et al., 2012; Koga et al., 2013). Cellulose based aerogels where mechanical function is important are widely studied in literature. These materials characterized by their high porosity and low solid content have new potential applications in many specific high added value fields such as fire retardant and gas barrier functions (Liu et al., 2011; Liu and Berglund, 2013), biomedical application as wound and burn dressing material, and scaffolds for tissue regeneration (Borges et al., 2011; Gatenholm and Klemm, 2010), flexible magnetic aerogels (Olsson et al., 2010), catalysts support aerogel (Koga et al., 2012), etc. In the context of increased concern over risks associated with global warming, this newest generation of aerogels will certainly compete with the already existing aerogels based on inorganic or polymeric material owing to their precursors considered more eco-friendly making these aerogels most renewable.

The combination of cellulose nanofibrils and inorganic nanoparticles yield hybrid materials with expected synergistic effects obtained when the structure of the resulting hybrid material is controlled. This synergistic effect has been widely demonstrated while studying bulk materials. Liu et al. (Pekala, 1989b; Pekala et al., 1990) combined Montmorillonite clay and cellulose nanofibril to prepare nanopaper. The oxygen barrier properties of these hybrid materials in the dry state were very good with an oxygen transmission rate that was below the detection limit of the instrument. In addition, the use of a cellulose nanofiber matrix provided new deformation mechanisms so that ductility and toughness were quite high, despite an inorganic content as high as 89 wt%. For other functional applications, O. Carlsson et al. (Smith et al., 1999) prepared flexible magnetic aerogels and stiff magnetic nanopaper using cellulose nanofibrils as templates. The obtained materials exhibit large coercivities and moderately strong saturation magnetization per ferrite volume. Koga et al. (Aspen Aerogels, 2014) combined nanofibrillated cellulose and carbon nanotube to prepare Transparent, Conductive, and Printable Composites. The surface of anionic cellulose nanofibrils had reinforcing and nanodispersing effects on the CNTs both in water used as the dispersed medium and in the dried composite film, providing highly conductive and printable nanocomposites with a small amount of CNTs.

Zeolites are inorganic crystalline micro porous polymers. These molecules are hydrated aluminosilicate. It consists on a 3D network of tetrahedral AlO_4 and SiO_4 quadri-connected through the exchange of an oxygen ion (oxide). This structure generates a system of cavities or pores that forms canals through the material. These pores enable the capture of smaller molecule inside the network. Many studies highlighted the high absorption capacity of specific zeolites. These absorption properties of the zeolite make them usable in a great number of fields such as agriculture, medicine, oil industry, civil engineering and waste treatment. Notably, they are able to fix heavy metal salts that may be in solution in wastewater (Bouziane, in press). In addition to the usage of the adsorption properties, zeolites can also be used as catalysts, ion exchange materials or thermal isolators. Moreover, zeolites are less expensive and environmentally friendly compare to most of the actual materials on the market. However, it is still difficult to regenerate them because of the thermal regeneration process.

In order to fabricate porous materials, it exists various methods: fiber bonding (Ana et al., 2009), freeze-drying (Sudheesh et al., 2011), supercritical fluid technology (Hyun and Tae, 2007),

compression molding and salt leaching (Qingpu et al., 2003), gas foaming (Wenchuan et al., 2012), rapid prototyping (Huisuk et al., 2007) and electro spinning (Fei et al., 2011). Freeze-drying is a method consisting in freezing the material forming the matrix below its glass transition temperature or melting point. The temperature and the pressure are such that the solvents are eliminated by sublimation. The elimination of the solvent results in the formation of interconnected porous network (Liu, 2006). Compare to other methods, the advantages of this process are that no toxic organic solvents are used and, because of the low temperature, the activity of biological macromolecules or pharmaceutical compounds can be longer. Moreover, this technique allows having low surface tension, which helps to maintain the porous structure in time. Therefore, it was planned to prepare the cellulosic aerogels by freeze-drying. This should give opportunity to develop new material structures by combining the nanoporosity of the constituents (NZs, o-NFC) and a microporosity coming from freeze-drying, which can be tuned by optimizing the freeze-drying process (Lei and Haifei, 2011).

Several groups T. Butova, Fischer, Rigaci et al. (Budtova and Gavillon, 2008; Koga et al., 2013) have shown that aerogels are able to strongly decrease the thermal conductivity of materials to reach λ values lower than λ_{air} $25 \text{ mW m}^{-1} \text{ K}^{-1}$. These materials are consequently so-called super-insulators based on the Knudsen effect. In aerogels, the total thermal conductivity can be described by a simple addition of the gaseous thermal conductivity λ_g , the solid thermal conductivity, λ_s , and the radiative thermal conductivity λ_r . Since typical aerogels have pore size in the range of 1–100 nm, the mean free path of gas molecules in air, around 70 nm at 1 bar, is comparable. The gaseous conductivity is therefore suppressed whereas solid and radiative conductivities are maintained at a lower state thanks to the 95% air in the aerogels. In order to minimize the thermal conductivity of aerogels, one has to know how the porosity and the skeletal structure of the aerogels influence this property.

In the present work, we propose a preparation method to obtain nanoporous hybrid aerogels based on cellulose nanofibers and nanozeolite particles to achieve lower thermal conductivity of these materials. To the best of our knowledge only few studies (Silva et al., 2012; Yuan et al., 2014) in the literature dealt with the application NFC based aerogels as thermal super-insulator. The mechanical properties are also important to design the materials for various industrial applications. The preliminary results are very promising to realize partially bio-based thermal insulator with controlled mechanical and thermal properties.

2. Experimental

2.1. Materials

The rachis of date palm tree (*Phoenix dactylifera* L.) was used in this work as the original source of cellulose. Cellulose was extracted from the rachis following the procedure well described in our previous work (Jin et al., 2013) and the extracted cellulose will be mentioned in the coming text as white paste (WP).

TEMPO, sodium bromide, sodium hypochlorite solution (15%), HCl, and NaOH were purchased from Sigma–Aldrich and used without further purification. The general procedure and reagent ratios used by Sbiai et al. (Wu et al., 2012) were utilized for TEMPO-mediated oxidation of cellulose fibers. About 2 g i.e. 2.136 mmol of equivalent anhydroglucose unit (AGU) of cellulose were suspended in water (200 ml) and sonicated with a Branson Sonifier for 5 min. TEMPO (32 mg, 0.065 mmol) and NaBr (0.636 g, 1.9 mmol) were added to the suspension. An additional amount of the NaOCl solution, corresponding to 40.5 ml was versed dropwise in the cellulose

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