



Properties of bio-based gum Arabic/clay aerogels



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ABSTRACT

Lightweight bio-based aerogels from sustainable gum Arabic (GA) and sodium montmorillonite (Na⁺-MMT) clay were prepared by means of a simple freeze-drying process. GA/clay aerogels showed high porosity (87.9%–94.9%) of mainly open type and the mechanical properties were improved by the clay. When 40% of clay was added to pure GA, the specific modulus and the absorbed energy of resultant aerogels increased by 1.6 and 4.2 times respectively. On the other hand, the exponent value for modulus in the power-law model for cellular materials increased from 1.95 to 3.28 due to the more anisotropic structures induced by the presence of the clay. In terms of thermal stability and flame retardancy, clay content played a dominant role. With 50% of clay loading, the initial decomposition temperature increased by nearly 16 °C and the peak of heat release rate was 3-fold reduced.

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1. Introduction

Increasing concern on environmental protection requires the limitation of usage of petroleum-based synthetic plastics and the development of new ecological solutions to replace them in order to reduce pollution, wastes and green-house gases. Foams are one of the common forms for polymers with applications including thermal insulation, packaging or cushioning to mention a few (Oertel, 1994). The majority of the low-density foams existing in the market are derived from petroleum and are not biodegradable. Therefore, alternatives based on polymers derived from renewable resources (bio-based polymers) are attracting an increasing attention. Among the different bio-based polymers, namely polyesters, proteins and polysaccharides, the latter have a great potential to be transformed into aerogels, a porous, lightweight foam-like material (Mikkonen et al., 2013).

Plastic foams are formed by a solid matrix skeleton and a gaseous phase which is derived from a blowing agent, and where the foaming process is carried out by applying mechanical, physical or chemical procedures to the solid material. In contrast, aerogels are created when the liquid contained in a wet gel is replaced by air. Aerogels are mainly obtained through supercritical drying (SCD) and contain a network of interconnected mesopores (2–50 nm). Due to their high surface area, they are used as drug carrier, catalyst, adsorbent or in insulating applications. García-González

et al. (2011) summarized the fundamental processing parameters and methods for preparing different polysaccharide-based aerogels through SCD, showing that polysaccharides can be used as an alternative to silica-based aerogels for drug delivery. Quignard et al. (2008) also employed this technique to prepare different marine polysaccharide aerogels for heterogeneous catalyst supports based on alginates, carrageenan and chitosan. Those aerogels presented a high specific surface area (200–570 m²/g) and were stable in most organic solvents. Superabsorbent alginate aerogels were prepared by Mallepally et al. (2013). In their work, the aerogels were capable of absorbing about 120 times their weight in saline water in 24 h. The observed behavior was attributed to the large pore volume and high specific surface area (~500 m²/g) of the aerogels as well as the polymer increasing in charge in the presence of salt ions. Finally, Rudaz et al. (2014) reported the preparation of superinsulating mechanically strong aerogels from pectin having a thermal conductivity as low as 0.016–0.020 W/(m K) which was attributed to the low density (<0.15 g/cm³) and nanometric dimensions of pores, leading to a decrease of conduction in the gas phase.

In contrast to SCD, freeze-drying applied to polysaccharide solutions usually yields structures having micron-sized pores. The nucleation and ice growth destroy the gel network, creating large pores and thus having considerably lower specific surface area. The aerogel structure is the result of the ice sublimation and is composed of a solid phase and a large fraction of air, which correspond to the volumes occupied by the biopolymer and ice in the frozen gel, respectively. In this process, the water solubility, swelling and gel-forming capability of polysaccharides contribute to the stability of the so-formed aerogels (Quignard et al., 2008).

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Several polysaccharide-based aerogels have been prepared through freeze-drying. [Sehaqui et al. \(2010\)](#) produced high porosity foam-like materials based on cellulose nanofibers. Due to its high affinity with cellulose, xyloglucan was employed to increase the strength and stiffness of the resultant micro-porous aerogels. [Bendahou et al. \(2014\)](#) combined extracted cellulose, cellulose nanofibers and nanozeolite particles to create hybrid aerogel monoliths. The thermal conductivity of cellulose nanofibers aerogels was found to decrease with nanozeolite content whereas it remained almost constant in the case of extracted cellulose aerogels. This was attributed to the different microstructures and the embedment of nanozeolite in cellulose nanofibers. [Valentin et al. \(2003\)](#) compared SCD with freeze-drying in chitosan aerogels, finding that SCD yields considerably higher porosity although freeze-dried aerogels showed even lower density than the ones dried with supercritical carbon dioxide. In general, these open cell freeze-dried bio-aerogels exhibit the properties of the precursor polymer but usually have low Young's modulus and reduced load-bearing capacity. Nevertheless, different approaches such as crosslinking ([Pojanavaraphan et al., 2010](#)) or filler reinforcement ([Svagan et al., 2008](#)) can be followed to improve aerogel performance. Among these methods, clay addition has been proved to be an economic and straightforward way to enhance both the thermal and mechanical properties and to expand the range of its potential applications. Following this approach, [Chen et al. \(2012\)](#) used a combination of alginate and sodium montmorillonite clay to create low flammability robust aerogels with mechanical properties close to that of balsa wood. Calcium cation crosslinking increased the solution viscosity leading to a finer network structure and to a further enhancement of mechanical properties. In another approach, xanthan gum/clay aerogels were produced by [Wang et al. \(2014\)](#). The increase of the content of xanthan gum lead to a network structure which increased the mechanical properties. However, a synergic effect was found by the introduction of agar. In the presence of both polysaccharides, the resultant aerogels displayed a significant improvement in mechanical properties as compared to those containing a single biopolymer. [Chen et al. \(2013a\)](#) combined clay and cation crosslinking to form pectin/clay aerogels with enhanced mechanical properties and thermal resistance. The introduction of clay generated a much rougher microstructure and also contributed to increase the decomposition temperature due to the thermal insulation and mass-transport barrier created by the clay layers. Among the different polysaccharides, gum Arabic (GA) exhibits a very high solubility in water. Unlike other gums, GA can be dissolved even at high concentrations (up to 50% w/v) without showing a remarkable increase in viscosity. These characteristics make GA a very attractive precursor for producing GA/clay hybrid aerogels.

Gum Arabic is an exudate from the *Acacia* tree and its precise molecular structure is little known. It is recognized by many researchers that gum Arabic consists of a mixture of arabinogalactan polysaccharide (major component) and hydroxyproline protein (minor component) ([Idris et al., 1998](#); [Islam et al., 1997](#); [Randall et al., 1988](#)). The main structural feature of the major component is a β -(1 \rightarrow 3)-galactose backbone and 1,6-linked galactose side chains terminating in β -D glucuronic acid. Moreover, the properties of GA differ according to the botanical source ([Cozic et al., 2009](#)). Due to its unique emulsification, film-forming, and encapsulation properties, GA is extensively used in industry, such as food ([Krishnan et al., 2005](#)), paper ([Verbeke et al., 2003](#)) and pharmacy ([Ward, 2000](#)).

In the current work, bio-based light-weight GA aerogels were prepared using an environmentally-friendly freeze-drying process with the aim of providing alternatives to replace packaging materials traditionally prepared from non-biodegradable petrochemical products. Hybrid organic-inorganic aerogels were also created by adding sodium montmorillonite (Na^+ -MMT) clay to GA aqueous solution. The resultant aerogel composites were expected

Table 1
Physicochemical data and composition of gum Arabic powder.

Physicochemical data	Value	Composition	Value
Moisture content (%)	7	Galactose (%)	39.8
Ash content (%)	3.4	Arabinose (%)	58.1
Optical rotation (degrees)	-25	Rhamnose (%)	2.1
pH (25% w, 20 °C)	4.1–4.8	Glucuronic acid (%)	–
Intrinsic viscosity (cm^3/g)	23.7	Molecular weight (g/mol)	1.1×10^6

to show improved thermal and mechanical properties than the neat GA aerogels. The microstructures, compression properties, thermal stability and flame retardancy of aerogels were investigated, respectively.

2. Material and methods

2.1. Materials

Gum Arabic in powder form was bought from T3Q Quimica (Spain). Its physicochemical properties resulted from a preliminary characterization are reported in [Table 1](#). Sodium Montmorillonite (Na^+ -MMT, PGW grade) was purchased from Southern Clay (USA), having a density of 2.6 g/cm^3 and cation exchange capacity (CEC) of 145 meq/100 g. All materials were used as received.

2.2. Aerogel preparation

2.2.1. GA aerogels

GA powder was dissolved in deionized (DI) water at room temperature under magnetically stirring until achieving transparent solutions with different concentrations (5 wt%, 7.5 wt%, 10 wt% and 15 wt%). Then they were poured into cylinder vials (diameter: 30 mm) or square-shaped moulds ($100 \times 100 \text{ mm}^2$) before being frozen at -80°C in an ethanol/solid CO_2 bath for 30 min. Aerogel samples were obtained after ice sublimation in a lyophilizer (Telstar Lyoquest) for 96 h using a condenser temperature of -80°C and vacuum of 0.01 mbar.

2.2.2. GA/Clay aerogels

Clay suspensions were prepared by dispersing Na^+ -MMT clay nanoparticles in DI water using an IKA Ultra-turrax disperser. GA solutions were obtained using the previously mentioned procedure. Then they were blended and mixed to attain homogenous precursor suspensions containing 5 wt% clay and various GA concentrations (5 wt%, 7.5 wt%, 10 wt%, 15 wt%). Finally, the same freeze-drying process was applied to acquire GA/Clay aerogels.

Sample identification is GA or clay used followed by their respective concentration in precursor suspensions, i.e., GA5C5 represents a sample that was prepared from an aqueous suspension containing 5 wt% of gum Arabic and 5 wt% of clay.

2.3. Characterization

The sugar composition of the gum Arabic was determined by HPLC (Agilent 1100) using the procedure described by [Randall et al. \(1989\)](#). An ICsep ION-300 Interaction analysis column equipped with a refractive index detector was used. The sample ($20 \mu\text{dm}^3$) was injected into the column using 0.013 M H_2SO_4 solution as eluent at flow rate of $0.4 \text{ cm}^3/\text{min}$. The retention times were monitored using a Beckman 156 refractive index detector. Individual standards of glucuronic acid, arabinose, galactose and rhamnose were used.

To determine the intrinsic viscosity of gum powder solutions the method of [Solomon and Ciuta \(1962\)](#) was used. Gum powder was dissolved in distilled water to a concentration of 0.01 g/cm^3

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