



Ice-templating beet-root pectin foams: Controlling texture, mechanics and capillary properties

Sarah Christoph^a, Ahmed Hamraoui^{a,b}, Estelle Bonnin^c, Catherine Garnier^c, Thibaud Coradin^a, Francisco M. Fernandes^{a,*}

^a Sorbonne Université, CNRS, Laboratoire de Chimie Matière Condensée de Paris, LCMCP, F-75005 Paris, France

^b Université Paris Descartes, Faculté des Sciences Fondamentales et Biomédicales, 45 rue des Saints-Pères, 75006 Paris, France

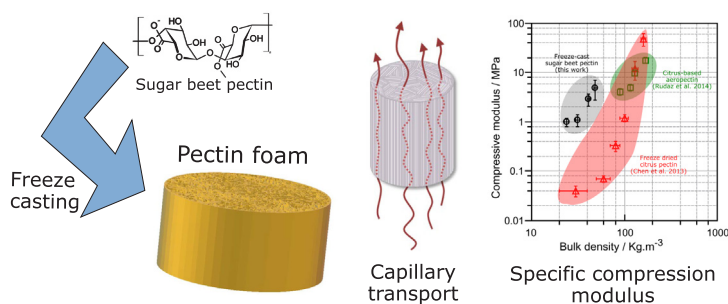
^c INRA UR 1268 – Biopolymères – Interactions – Assemblages, BP 71627, 44316 Nantes Cedex 03, France



HIGHLIGHTS

- Sugar beet pectin can be shaped into macroporous lightweight foams by freeze casting.
- Directional freezing enables enhanced liquid transport within pectin foams.
- Freeze cast pectin foams outperform previously reported low density pectin materials in compression testing.

GRAPHICAL ABSTRACT



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ABSTRACT

Sugar beet pectin is a byproduct of the sugar industry with a particularly low gelling power which hinders its application as gelling agent and thickener. Here we consider the use of freeze casting to shape sugar beet pectin into lightweight foams. Freeze casting processing conditions such as the applied thermal gradient and the polysaccharide concentration were explored to obtain macroporous lightweight foams with different textures. The precise control over the foams' texture and pore anisotropy was decisive for their performance as liquid transport devices by capillary ascension and for their mechanical performance. Overall, the obtained results show that the formation of highly anisotropic structures using freeze casting can be instrumental in the upcycling of polysaccharide industrial byproducts.

1. Introduction

Macroporous materials are omnipresent in everyday life. From natural examples such as trabecular bone, balsa wood or cork [1] to man-made materials used in transport applications [2], antifrost surfaces [3], thermal insulation materials [4] or water harvesting devices [5], we are surrounded by outstanding, lightweight, functional materials. To balance functionality and apparent density, Nature has relied

on highly specific – often cell-mediated – bottom-up processes to precisely shape the materials' porosity. Among these materials, a small portion, such as plant stems and tree trunks [6] or porcupine quills [7] displays highly anisotropic macropores. Two main reasons lie behind these aligned structures: mechanical performance [8–11] and/or fluid transport [12,13]. Several processing strategies are available to replicate such highly controlled porous structures [14–17], however few are as straightforward as freeze-casting, a technique based on oriented

* Corresponding author.

E-mail address: francisco.fernandes@upmc.fr (F.M. Fernandes).

ice templating that has gained considerable during the last decade [18]. Freeze-casting relies on the use of ice crystal growth to create porosity. The method presents the advantage of being easy to implement, cost effective and applicable to a wide range of materials [19]. In particular, since the technique relies on the use of low temperatures, it can be particularly relevant in the processing of materials prone to thermal denaturation such as biopolymers. The technique was first described in 1954 [20] for the processing of refractory powders and has been used since to shape ceramics [21], metals [22,23], clays [24], polymers [25,26] and composite materials [27,28].

Pectin is a polysaccharide present in plant cell wall that finds extensive application as gelling and thickening agent [29]. The gelling properties of this heteropolysaccharide are strongly dependent on its source and extraction conditions [30]. Pectin from sugar beet – a source yielding pectin with particularly low gelling power – displays fewer direct industrial application without extensive chemical modification than high gelling ability sources such as citrus peel or apple pomace [31]. Such difference in gelling power is mainly due to the presence of acetyl esters on the galacturonic acid chain [32]. As a result, sugar beet pectin remains a largely undervalued material, often considered as a byproduct of the sugar industry with few valorization alternatives beyond the production of arabinose and galacturonic acid [33]. Designing new processing approaches that enable the application of sugar beet pectin represents an opportunity to upcycle a largely overlooked industrial resource. Here we report how ice templating techniques can shape pectin to obtain biobased materials with adjustable porosity. We demonstrate that control over pore size and pore morphology can provide pectin-based materials with interesting mechanical and liquid transport properties. In summary, the finely controlled porous structure imposed during the ice templating unveils the possibility to apply a wide variety of water-soluble industrial sub-products for their potential application as lightweight structural elements, insulation or liquid transport devices.

2. Material and methods

2.1. Materials

Sugar beet pectin powder was obtained from CP Kelco and used without further purification. Degrees of methylation and acetylation were 49.00 and 20.90 respectively. The detailed composition is presented in [Supplementary Information \(Table S1\)](#). Pectin aqueous solutions ranging from 10 to 50 g.L⁻¹ were prepared by dissolving the pectin powder in ultra-pure water followed by stirring under magnetic agitation for 24 h at room temperature.

2.2. Process

The macroporous pectin monoliths were shaped by growing ice crystals into aqueous pectin solutions, followed by freeze-drying in a Christ Alpha 2–4 LD freeze-dryer operating at 0.06 mbar for a 48 h period, in order to sublimate the ice crystals.

Four freezing conditions were investigated: two using laboratory freezers (–20 °C and –80 °C), one using a liquid nitrogen (LN) bath and one using a custom-made freeze-casting setup (FC) ([Fig. S1](#)). The samples frozen in the laboratory freezers (4 mL at 40 g.L⁻¹) were placed in PE cylindrical molds ($\varnothing = 19$ mm) and left overnight in the freezer either at –20 °C or –80 °C before freeze-drying. Samples obtained through ice templating in LN were first poured in similar 19 mm diameter molds at room temperature and subsequently plunged for 5 min into LN before freeze-drying. Various samples were obtained by freeze-casting, using a previously reported setup [34]. The device consists in a heat conductive copper rod partially immersed into LN. Temperature profiles at the top of the rod (interface between sample and copper rod) is set through a heating resistance controlled by a dedicated PID. The pectin solutions (3 mL) were placed at the top of the

copper rod in 15 mm diameter cylindrical molds. The samples were then cooled down from 20 °C to –60 °C at a controlled cooling rate of 10 °C.min⁻¹. To ascertain the impact of the pectin solution concentration on the final material properties, samples were prepared from initial pectin solutions ranging from 20 g.L⁻¹ to 50 g.L⁻¹.

2.3. Characterization

The cooling profiles for each freezing process were determined by inserting a K thermocouple at the center of 40 g.L⁻¹ pectin solutions before freezing. The temperature profiles for the samples frozen inside the freezers (–20 °C and –80 °C) and by plunging into LN were recorded until thermalization. For the freeze-cast samples, the temperature profile was determined at the center of the pectin solution and at the interface between the copper rod and the pectin solution.

Samples obtained after freeze drying were manually cut with new scalpel blades. Scanning electron microscopy observations were performed on Hitachi S-3400N SEM. The samples were sputter coated with 20 nm of gold and observed under 3–4 kV acceleration and 30 μ A probe current. SEM pictures were analyzed using the OrientationJ plugin [35] in ImageJ software for pore morphology characterization. The foams' pore dimensions and pore wall thickness were determined on 150 and 25 individual measurements, respectively.

Wetting behavior of the foams was assessed by capillary rise of a solution of Disperse Red at 0.2 g.L⁻¹ in ethanol. Cylindrical pectin foams (triplicates with height between 6 and 8 mm) were placed above a Disperse Red solution and the impregnation recorded on camera at 30 fps. The resulting footage was analyzed using the “Reslice” operation to deduce ascension profiles in ImageJ software. The surface tension of Disperse Red in ethanol was measured using the Wilhelmy plate method on a Krüss K11 model.

Mechanical behavior under compression was assessed using an Instron 5965 universal testing machine equipped with a 50 N load cell. Samples were cut into 1 cm³ cubes and compressed between stainless steel plates up to 50% strain at constant displacement rate of 1 mm.min⁻¹. The corresponding stress-strain curves were obtained for 5 replicas per sample.

3. Results and discussion

3.1. From freezing to freeze-casting pectin foams

Self-supporting, low density macroporous biopolymer materials were obtained by ice-templating pectin solutions. Ice templating is particularly adapted to the processing of biopolymers that are prone to thermal degradation such as pectin since the processing steps are carried out below ambient temperature. In addition, the technique does not require leaching with possible denaturing solvents to unveil the porosity as required for other porogens such as latex beads. Since most chemical species are largely insoluble in ice, an increase in concentration of the solutes occurs in the interstices formed between the growing ice crystals. When ice crystallization stops due to the lack of available water to freeze, the biopolymer located in between the ice crystals is structured into a solid macroporous network. The biopolymer foam obtained after ice sublimation therefore corresponds to the negative imprint of the formed ice crystals.

Different freezing conditions were explored to highlight the relationship between the conditions of ice formation and the final morphology of the porous monolith. [Fig. 1](#) displays the temperature profile at the core of the samples during freezing. The first three conditions (freezers at –20 °C, –80 °C and LN bath) differ in the target temperature (–20 °C, –80 °C or –196 °C respectively) but the orientation of the temperature gradient within the samples is similar. In the case of freeze-casting however, multiple parameters differ. This setup allows controlling the freezing conditions both spatially (a specific temperature gradient is applied thanks to the marked difference in thermal

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