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All-cellulose composite aerogels and cryogels

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Abstract

Porous all-cellulose composites were prepared from pulps dissolved in 8 wt-% NaOH-water and dispersed softwood kraft fibers. Freeze-drying and drying with supercritical CO₂ were used to vary the morphology of the composites. As cellulose dissolution in NaOH-water is known to be limited by pulp degree of polymerization, the latter was varied to obtain different amounts of non-dissolved fractions in solution. The goal of the work was to understand the influence of fibers originating from the incomplete dissolution and/or from added kraft fibers on the morphology and properties of porous all-cellulose composites. Density, porosity, pore volume, specific surface area and mechanical properties under compression were determined and correlated with the composite formulations and morphology.

Key-words: A. Biocomposite; A. Wood fibers; B. Mechanical properties; B. Porosity

1. Introduction

Modern society requires materials' higher sustainability, and one way to decrease the environmental load is to use natural polymers. A well-known example is cellulose which is globally available, biodegradable and renewable. The most known cellulose-based products are paper, cardboard and textile fibers, but natural cellulose fibers can also be used as reinforcement in composites, where they provide light weight and reduce the use of petroleum-based compounds.

Conventional natural fiber reinforced polymer composites often require a compatibilizer to improve the adhesion between hydrophilic fibers and hydrophobic polyolefin matrix. Poor adhesion leads to problems in stress transfer, which results in a weak mechanical performance of the composite. However, the addition of compatibilizers requires the synthesis of new compounds and decreases the recyclability of the composites. An alternative approach for increasing the adhesion between the fibers and the matrix was introduced in the 70's, when Capiati and Porter [1] reported a concept of "single polymer" (or "all-polymer") composites, in which both the matrix and the reinforcement originate from the same material, thus minimizing the chemical incompatibility between the components.

The "single polymer" approach was extended to cellulose by Nishino et al [2]. As cellulose cannot melt, the matrix is prepared either by partially dissolving the fibers themselves or by using a separate cellulose solution. The dissolved cellulose is then coagulated, and the solvent is removed by washing it out, often with water. Drying is commonly performed in ambient conditions or at a slightly elevated temperatures, often under compression. The reinforcement can originate from various types of either long or short cellulose fibers. Nanocellulose can also be used, but it is not in the scope of our work and thus will not be considered here. Multiple processing parameters, such as cellulose concentration, solvent, dissolution conditions, non-

solvent and drying method, can be varied resulting in materials with different properties (see, for example, the review from Huber et al [3]).

A special class of cellulose-based materials is porous cellulose, which can be used in a wide range of applications, from packaging to membranes, as well as in life sciences (pharmacology, cosmetics, bio-medical). Here again we do not consider porous materials based on nanocellulose; we focus on the cases when porous cellulose materials are produced by replacing the non-solvent in coagulated cellulose by air while preventing pores to collapse. This requires special drying methods since evaporative drying often leads to non-porous materials due to high capillary stresses. In order to maintain pores opened, either freeze-drying or drying with supercritical CO₂ is performed. During freeze-drying, the frozen liquid, often water, is sublimated from the pores. Freezing results in the growth of ice crystals, which push apart pore walls in the cellulose network leading to a material with very low density, rather thick pore walls and large macropores [4]. For simplicity, this type of porous cellulose material will be called “cryogel”. To perform drying in supercritical conditions, the liquid in the pores must be miscible with CO₂, and thus solvent exchange step is performed [5]. The material obtained with this drying method has low density and very high specific surface area (several hundreds of m²/g); it will be called “aerogel” [5]. IUPAC Gold Book defines “aerogels” as a microporous material [6], however, modern literature agrees that aerogels are open pores materials with high porosity (at least 90%) and meso- and small macropores resulting in high specific surface area (“although no official convention really exists” according to Pierre [7]).

Contrary to silica aerogels, the literature on the reinforcement of cellulose aerogels, and, in general, on composite cellulose aerogels is scarce. Composite cellulose aerogels were usually made by the impregnation of aerogel precursor (before drying) by a second non-cellulose component which is polymerized inside cellulose network, the whole was then dried with

supercritical CO₂. For example, Pircher et al. [8] reported a strong increase in the mechanical properties of cellulose/polymethylmethacrylate interpenetrated aerogel network as compared to the neat cellulose aerogel. When cellulose/silica aerogel composites were made, a “softening effect” (decrease of the modulus) due to the presence of silica was obtained [9] while other authors demonstrated a strong increase in the compressive modulus of cellulose/silica aerogel composites [10, 11].

Except the case when nanocellulose is used to produce porous cellulose materials, complete dissolution of cellulose is seen as a requirement for making aerogels and cryogels; no publication reveals the influence, if any, of non-dissolved fibers or their parts on aerogel properties. Thus, the first question we are asking is if indeed a complete dissolution of cellulose is needed to obtain low density and high specific surface area porous cellulose? As a consequence, the second question is as follows: can all-cellulose composite approach be used for making aerogel-like materials? To the best of our knowledge, only one publication reported on porous all-cellulose composites; they were prepared by using partial dissolution of microcrystalline cellulose (MCC) in LiCl/dimethylacetamide [12]. Non-dissolved MCC fragments were acting as reinforcement of the freeze-dried composites. The flexural modulus and strength had a convex shape as a function of cellulose concentration, while crystallinity of these cryogels increased with cellulose concentration due to the presence of higher content of non-dissolved cellulose [12].

In our work we prepared all-cellulose composite aerogels and cryogels by dissolving pulps of various degrees of polymerization (DP) in 8 wt% NaOH-water, and adding softwood kraft fibers to these solutions. It is known that in this solvent cellulose solubility decreases with the increase of polymer molecular weight [13] resulting in the presence of non-dissolved fiber fragments in the solutions of higher DP [14]. In all-cellulose composites prepared from such systems, the “fibers” can thus originate from *i*) incomplete dissolution of high molecular

weight cellulose in NaOH-water and/or *ii*) added cellulose fibers [14]. The density of all-cellulose composites produced via pulp dissolution in 8 wt% NaOH-water, followed by coagulation, washing solvent out and drying under hot press varied from 0.9 to 1.2 g/cm³ [14]. The scientific goal of this work was to understand the influence of each fiber type (non-dissolved, added and their sum) on the morphology and properties of porous all-cellulose composites made from the same starting materials as in ref.14, but dried either with supercritical CO₂ (aerogels) or lyophilized (cryogels). The practical goal was to produce porous cellulose materials from cellulose pulps and recyclable low-cost solvent, NaOH-water, and reveal if complete dissolution is needed or not for obtaining low density and high specific surface. We used dissolving pulps of three degrees of polymerization, which resulted in different amounts of fibers originating from the incomplete dissolution. The concentration of added kraft fibers was also varied. The density, morphology, specific surface area and mechanical properties under compression of all-cellulose composite aerogels and cryogels were investigated, and the best formulation in terms of the highest surface area combined with the highest compressive modulus was suggested.

2. Materials and Methods

2.1. Materials

Birch dissolving pulp (DP 1100 [14]) and softwood kraft fibers (DP 2550 [14]) were kindly provided by Stora Enso Oyj as air-dried sheets and were disintegrated by a laboratory mill. NaOH flakes (analytical grade, purchased from Fischer Scientific) were dissolved in distilled water. Sulphuric acid (95–97 %, EMSURE® ISO) was purchased from Merck and it was diluted with deionized water. Ethanol (purity > 99%) was purchased from Fisher Chemicals.

2.2. Methods

2.2.1. Characteristics of the pulps

The DP of pulps was determined via intrinsic viscosity and Mark–Houwink equation according to the standard SCAN-CM 15:88.

The DP of the dissolving pulp was adjusted via acid hydrolysis as described in detail elsewhere [14]. Pulp with the initial DP of 1100 was hydrolysed to 640 using 0.1 M H₂SO₄ and 3 wt-% consistency at 82° C for 60 minutes under overhead mixing of 125 rpm. Similarly, DP was adjusted to 320 using 0.6 M H₂SO₄ at 88 °C for 60 minutes in the identical conditions. Subsequently, pulps were washed with deionised water to neutral pH and dried in a fume hood overnight. The molecular weight distributions of all pulps were determined via gel permeation chromatography, see ref.14. After drying, pulp aggregates were disintegrated using a laboratory mill.

All dissolving pulps had 92 wt-% of cellulose, 7 wt-% of hemicelluloses and less than 1 wt-% of lignin [14]. Kraft fibers contained 80 wt-% of cellulose, 19 wt-% hemicelluloses and less than 1 wt-% of lignin [14]. All lignin contents were originating from acid-soluble lignin fraction, no Klason lignin was detected.

Moisture content in the pulps was 5 wt-% as determined by vacuum oven drying. It was taken into account when calculating pulp concentrations, the latter calculated on the dry basis.

2.2.2. Determination of non-dissolved cellulose in cellulose-NaOH solutions

Cellulose solubility in aqueous NaOH is known to strongly depend on DP [13], resulting in incomplete dissolution [15]. Solubility of cellulose with DP 320, 640 and 1100 in 8 wt-% NaOH-water was studied according to the method described by Korhonen et al. [14]. 5 wt-% of each dissolving pulp was dissolved in 8 wt-% NaOH at -7 °C for 2 h under overhead mixing of 300 rpm. After dissolution, the solid (or non-dissolved) cellulose was separated

from the dissolved fraction via centrifugation (11000 rpm, 15 min, Eppendorf Centrifuge 5804R) followed by washing first twice with 8 wt-% NaOH and then with deionised water until neutral pH and filtered using filter paper (Whatman, 589³, ashless). Filtered residue was dried at 105 °C overnight and weighted, $m(\text{solid fraction})$. The weight-based concentration of non-dissolved cellulose in the solution, $C(\text{non-dissolved})$, wt-%, was determined according to the equation 1:

$$C(\text{non-dissolved}), \text{wt}\% = \frac{m(\text{solid fraction}, g)}{m(\text{dissolving pulp}, g) + m(\text{solvent}, g)} \times 100\% \quad (1)$$

where $m(\text{dissolving pulp})$ and $m(\text{solvent})$ are the weights of the dissolving pulp and of the solvent, respectively. The presence of non-dissolved cellulose fraction in solution leads to the decrease of the concentration of dissolved cellulose, initially targeted to $C_0 = 5$ wt-%. Thus, the weight-based concentration of dissolved cellulose in the solution, $C(\text{dissolved})$, wt-%, was determined according to the equation 2:

$$C(\text{dissolved}), \text{wt}\% = C_0 - C(\text{non-dissolved}) \quad (2)$$

2.2.3. Composite preparation

5 wt-% of dissolving pulp with DP of 320, 640 or 1100 was dissolved in 8 wt-% NaOH-water at -7 °C for 2 hours under overhead mixing at 300 rpm. Softwood kraft fibers were wetted with 8 wt-% NaOH-water to ease the dispersion (dry pulp:NaOH solution = 1:4) and mixed with cellulose-NaOH solution immediately after removing the latter from the cooling bath. The volume of NaOH-water was absorbed by the fibers during the wetting. The samples were placed in glass tubes with internal diameter of 1.6 cm and gelled for 1 hour at 50 °C to stabilize the shape. Finally, samples were coagulated and washed in water for several days (water changed 3 times per day) until the effluent was neutral.

Samples were dried using two approaches, supercritical carbon dioxide drying (scCO₂) and freeze-drying. In the former case, water was exchanged to ethanol since water is not miscible

with carbon dioxide. Samples soaked in ethanol were placed inside the autoclave and pressurised to 5 MPa at 37 °C using CO₂. After draining of ethanol, the pressure was increased to 8 MPa to exceed the critical point of carbon dioxide in order to solubilize the remaining ethanol inside the sample pores. Washing was performed in three steps. First, dynamic wash was performed for one hour at 8 MPa and 37 °C and carbon dioxide output of 5 kg/h. Then, a 1-2 h static washing mode was conducted at the same conditions without CO₂ output. The final step was 2 hours of dynamic washing as in the first step. The drying was finished by decreasing the pressure in the autoclave by 0.4 MPa per hour at 37 °C and cooling down the system to room temperature before opening.

For freeze-drying, the cellulose coagulated in water was first frozen in liquid nitrogen (-196°C). Lyophilisation was performed overnight in the shelf freeze dryer (Cryotec COSMOS 80) with the temperature of condenser -80 °C in vacuum (pressure 40 mTorr) in the automatic mode. Figure 1 presents the process scheme for both all-cellulose composite aerogels and cryogels.

As mentioned in the Introduction, two types of fibers are present in all-cellulose composites when using NaOH-water solvent: the non-dissolved fraction originating from incomplete cellulose dissolution and the added kraft fibers [14]. The weight-based concentrations of added kraft fibers in the solution ($C(kraft, wet)$) and in the dry composite ($C(kraft, dry)$) were determined according to the equation 3 and 4, respectively:

$$C(kraft, wet), wt\% = \frac{m(kraft, g)}{m(dissolving\ pulp, g) + m(kraft, g) + m(solvent, g)} * 100\% \quad (3)$$

$$C(kraft, dry), wt\% = \frac{m(kraft, g)}{m(dissolving\ pulp, g) + m(kraft, g)} * 100\% \quad (4)$$

where $m(kraft)$ is the weight of added kraft fibers.

The weight-based total fiber concentration in the solution ($C(fibers\ total, wet)$) was determined as a sum of the concentrations of non-dissolved fibers in the solution (equation 1) and the concentration of kraft fibers in the solution (equation 5):

$$C(\text{fibers total, wet}), \text{wt}\% = C(\text{non - dissolved}) + C(\text{kraft, wet}) \quad (5)$$

Finally, the weight-based concentration of the total fibers in the dry composite ($C(\text{fibers total, dry})$) was determined according to the equation 6:

$$C(\text{fibers total, dry}), \text{wt}\% = \frac{m(\text{solid fraction, g}) + m(\text{kraft, g})}{m(\text{dissolving pulp, g}) + m(\text{kraft, g})} * 100\% \quad (6)$$

2.2.4. Characterization

Morphology was studied using a scanning electron microscope (Supra40 Zeiss SEM FEG, Field Emission Gun) with an acceleration voltage of 3 kV. Before imaging, a 7 nm platinum layer was sputter-coated on the surface of the sample (Q150T Quorum metallizer).

The bulk density of the composites was determined by measuring sample's mass and volume. The standard deviations were around $\pm 0.01 \text{ g/cm}^3$.

Specific surface area was determined with Tristar II Surface area & porosity analyzer (Micromeritics) using BET-approach [16]. Samples were degassed by flushing the system with nitrogen gas in two steps; first at room temperature for 15 minutes and then for 60 minutes at 70 °C. Finally, the samples were cooled back to room temperature before starting the BET analysis.

Mechanical performance of the composites was studied using a compression testing device (Zwick 2.5 kN) according the method described in Buchtová et al. [17]. **The samples were cylinders with about 1.5 cm height and the same diameter. These equal dimensions were selected to minimize shear that may appear when height is larger than diameter. The surfaces of all samples were polished with P320 sandpaper (grain size of about 50 μm) to obtain regular cylinders with smooth walls and parallel and planar upper and lower planes.** The device was equipped with 1 kN load cell and teflon tools were used to minimize friction between the sample and the compressing surfaces. The rate of compression was 1 mm/min. Samples were polished using sandpaper (P240 with particle size 60 μm) in order to obtain

smooth cylinders with parallel top and bottom planes. Minimum of 3 samples were tested, and the properties calculated from stress-strain curves are given as arithmetic averages.

Compression modulus was determined as the slope of the linear part, and absorbed energy as the area under the stress-strain curve up to 40 % strain.

3. Results

3.1. Dissolution of pulps in 8% NaOH-water

Cellulose is known to be moderately well dissolved in 6-9 wt-% NaOH-water having two main limiting factors: DP and concentration. High DP decreases the solubility [13] and even for low DP cellulose, the maximum concentration of dissolved polymer is 7-8 wt-% [18]. A detailed study of the content of dissolved and non-dissolved cellulose in the solutions of pulps with DP 320, 640 and 1100 in 8 wt-% NaOH (aq) was performed by Korhonen et al. [14]. Here the main results are revised since they are important for the further understanding of the findings obtained on all-cellulose composite aerogels and cryogels.

The non-dissolved fraction in solutions of DP 640 contains swollen particle-like fibers and their fragments (Figure S1a) with the average length of $185 \mu\text{m} \pm 105 \mu\text{m}$ and width of $52 \mu\text{m} \pm 15 \mu\text{m}$, resulting in fibers of low aspect ratio around 4 (see details in ref.14). The non-dissolved fraction in the solution of pulp of DP 1100 is a combination of swollen fibers and almost intact ones (Figure S1b). The swelling is heterogeneous via ballooning [19]; the average fiber length is $416 \mu\text{m} \pm 189 \mu\text{m}$ and width is $24 \mu\text{m} \pm 10 \mu\text{m}$ similar to the width of non-dissolved pulp fibers which is around 10 – 20 μm . The average aspect ratio is 19 ± 9 [14].

Table 1 shows the concentrations of non-dissolved cellulose in 8 wt-% NaOH-water, of added kraft fibers in 8 wt-% cellulose-NaOH-water solution (eq. 3) and in dry composite (eq.4), and of total fiber concentration in solution (eq. 5) and in dry composite (eq.6). A strong decrease in cellulose solubility was observed with the increase of pulp DP, from almost

5 wt-% for DP 320 to 1.2 wt-% for DP 1100. As a consequence, the non-dissolved fraction starts to play a noticeable role in the concentration of total fibers in the system. For example, for the concentration of 77 wt-% of total fibers in the dry matter, only 1 wt-% is from non-dissolved fraction for DP 320, 12 wt-% for DP 640 and all 77 wt-% are from non-dissolved fraction for DP 1100.

3.2. Morphology, density and specific surface area of porous all-cellulose composites

The examples of the morphology of all-cellulose composite aerogels and cryogels are shown in Figure 2a and b, respectively, for the samples made from the pulp of DP 320, where the content of non-dissolved fragments is negligible (see Table 1). Composite aerogel and cryogel based on the same matrix but with added 0.3 wt-% and 2.1 wt-% kraft fibers in solution (10 wt-% and 34 wt-% in dry matter, respectively) are shown in Figure 2c and d, respectively. All samples have open porosity, but the morphology of aerogels and cryogels is very different. Aerogels are a fine network of pores of sub-micron size and thin pore walls, while cryogel counterparts have pores of the size of few microns and thick, flat and sheet-like pore walls. The latter can be explained by the growth of ice crystals pushing and “compacting” pore walls within coagulated cellulose during freezing. Similar result was reported by Buchtová and Budtova [4] for cryogels made from microcrystalline cellulose dissolved in ionic liquid without any non-dissolved fibers.

No orientation of pores in cryogel composites was observed, contrary to what is known for cryogels or foams based on nanocellulose. Nanocellulose is a suspension of “particles” that can align in the direction of the growth of ice crystals leading to anisotropic morphology [20-22]. On the opposite, upon coagulation cellulose network the morphology is fixed. For cellulose cryogels made from cellulose dissolved in ionic liquid/DMSO no anisotropy was

recorded even in the case of unidirectional freezing [4]. In our case freezing was performed with no preferential orientation of ice crystals growth.

The adhesion between the fibers and the matrix is excellent for both composite aerogels and cryogels, as shown in Figure 2c and d, respectively, and Figure S2. However, successful adhesion is not the only factor to consider when analysing the properties of porous composites. Figure 3 shows the morphology of all-cellulose composite aerogels with total fiber concentration 77 wt-% (in dry matter) for the case of matrix DP 320 (a) and 640 (b). As mentioned in the Section 3.1, the incomplete dissolution of cellulose of higher DP in aqueous NaOH decreases the content of dissolved cellulose in the solution, consequently affecting the content of dissolved cellulose in the matrix. The composite aerogel with DP 320 (Figure 3a) contains 4.8 wt-% of dissolved cellulose in the solution and 77 wt-% of added kraft fibers in the dry composite. Fibers are well embedded in the matrix indicating that 4.8 wt-% of dissolved cellulose is sufficient to provide matrix even with high reinforcement content. However, as shown in Figure 3b, when decreasing the content of dissolved cellulose in the solution to 3.3 wt-% as in the case of DP 640 matrix, the amount of cellulose in the matrix is insufficient for the same total fiber content of 77 wt-%. This leads to the appearance of voids in a similar manner as reported for all-cellulose composites dried under compression [14]. The porosity of the all-cellulose composite aerogels made from pulps dissolved in 8 wt% NaOH-water thus originated from two sources: from the aerogel matrix itself and from the voids created due to the insufficient cellulose in the matrix.

The bulk density of all cellulose composite aerogels and cryogels is shown in Figure 4a as a function of total fiber concentration in the dry composites, and in Figure S3a, b as a function of added kraft fiber concentration and of total fiber concentration in the system before coagulation, respectively. Density increases with the increase of the total fiber concentration (Figure 4a) and of the concentration of added kraft fibers (Figure S3a). This is the expected

result as *i*) total concentration of the matter in the system increased and *ii*) fibers have much higher density than porous matrices. Composite aerogels have slightly higher density, from 0.11 g/cm³ to 0.23 g/cm³, compared to the composite cryogels with density from 0.08 g/cm³ to 0.17 g/cm³. A similar trend was reported previously for aerogels and cryogels from microcrystalline cellulose without any fibers [4]. If no large voids were added due to the insufficient cellulose in the matrix, the dependence of the density on reinforcement content would be much steeper because of added kraft fibers.

Porosity and pore volume of all-cellulose composite aerogels and cryogels were calculated using bulk ρ_{bulk} and cellulose skeletal density $\rho_{skeletal}$ (1.5 g/cm³) as follows:

$$Porosity = \left(1 - \frac{\rho_{bulk}}{\rho_{skeletal}}\right) \times 100\% \quad (7)$$

$$Pore\ volume = \frac{1}{\rho_{bulk}} - \frac{1}{\rho_{skeletal}} \quad (8)$$

Porosity of composite aerogels and cryogels is decreasing with the increase of total fiber concentration (Figure 4b) or added kraft fibers (Figure S4), as expected. Specific pore volume is presented in Figure 5a as a function of total fiber concentration and as function of kraft concentration in Figure S5. Pore volume decreases with the increasing total fiber content, and it is higher for cryogels than for aerogels. It should be noted that nitrogen adsorption-desorption (BJH approach) is not applicable for the determination of pore volume and pore size distribution in bio-aerogels. The reason is that this approach distinguishes only 10–20% of the total pore volume as it considers only mesopores and small macropores while most bio-aerogels possess many large macropores [23, 24].

Specific surface area is one of the most important characteristics of porous materials since high surface area is often targeted when functionalization of pores is required, for example, for adsorption and/or release applications. The increase in total fiber concentration in aerogels and cryogels results in a decrease of the specific surface area of both types of composites, as

presented in Figure 5b. Composite cryogels have specific surface area from 5 m²/g to 50 m²/g, which is significantly lower compared to the composite aerogels, the latter having specific surface area from 140 m²/g to 340 m²/g. This difference is due to much larger size of the pores in cryogels as compared to those of aerogels. The specific surface area of composite aerogels is decreasing with the increase of the total fiber concentration almost according to the mixing rule, which indicates that the decrease is due to the added non-porous fibers as the matrix remains the same for a fixed pulp DP. Similar behaviour was previously reported for silica aerogels reinforced with short cellulose fibers [25]. At high fiber concentrations, the specific surface area deviates from the mixing rule. Several reasons can be speculated: the deviation can be due to the additional input of the voids created due to the insufficient matrix content and/or some porosity created in non-dissolved fibers due to supercritical drying. Higher DP of the matrix provided slightly higher specific surface area for both types of composite.

3.3. Compression properties of all-cellulose composite cryogels and aerogels

The mechanical properties of composite aerogels and cryogels under the uniaxial compression are presented in Figure 6 (the representative examples of stress-strain curves are shown in Figure S6 of the Supporting information). All composite aerogels were compressed without breaking within 70 – 80 % strain, as reported for other cellulose aerogels without fibres [5]. The same was observed for cryogel samples with added kraft fibers, however, cryogels of DP 320 without kraft broke at 10-20% strain.

The compressive modulus and absorbed energy up to 40% strain increase as a function of density, as expected. Modulus was found not to depend on kraft fiber content (Figure S7 of the Supporting information). Generally, composite cryogels have higher modulus, from 4 MPa to 20 MPa, compared to the aerogel counterparts with modulus ranging from 3 MPa to 8

MPa. Cryogels are stronger than aerogels, both with and without the fibers, the latter being reported also by Buchtová et al. for microcrystalline cellulose dissolved in ionic liquid/DMSO (without any non-dissolved fibers) [17]. The higher modulus and absorbed energy of cryogels can be explained by the morphology of the pores (Figure 2b). Cryogels have thicker and wider pore walls, which can withstand higher pressure compared to the fine pore structure of aerogels.

4. Discussion

The results presented above demonstrate that several factors must be considered when analysing the properties of porous all-cellulose composites. The incomplete dissolution of the pulp of higher DP in NaOH-water is an important feature as it may lead to voids in addition to pores formed in the matrix due to the specific drying, either with supercritical CO₂ or freeze-drying. The drying method is also of significant importance as it determines the morphology of pores. The concentration of added kraft fibers does not lead to the variation in compressive modulus, however, total fiber concentration does influence material density, mechanical properties and specific surface area.

We deduce that crystallinity should not play a role when considering the results shown here. On the one hand, it was previously demonstrated for all-cellulose composites produced from the same starting materials, but dried by evaporation under compression, that their crystallinity was between 36% and 50% and did not depend either on the total fiber concentration or on matrix DP [14]. Kraft fibers have rather low crystallinity, around 42%. On the other hand, drying method (supercritical CO₂ or freeze-drying) was shown to have no influence on the crystallinity provided that all other processing conditions are the same, in particular, the type of coagulation bath [17]. Because in the compressed (ref. 14) and in the porous composites (this work) cellulose was coagulated in water, we suppose that the

crystallinity is the same, not varying much, and thus not influencing the mechanical properties within the experimental errors. It was previously reported that cellulose coagulated in aqueous non-solvents possess higher crystallinity as compared to cellulose coagulated in non-aqueous non-solvents, the latter resulting in practically amorphous cellulose [26-30].

Figure 7 shows specific surface area and compressive modulus for all prepared composite aerogels and cryogels. When aiming for strong porous cellulose materials with high specific surface area, several conditions should be fulfilled. The material combining the highest compressive modulus (8.2 MPa) with the highest specific surface area (around 340 m²/g) is an aerogel composed of the matrix from dissolving pulp of DP 640 with 34 wt-% of total fiber concentration. For this DP, the fibers are non-dissolved fragments originating from cellulose incomplete dissolution, no kraft fibers are added. Similar specific surface area (340 m²/g) with weaker modulus (5.9 MPa) were obtained for aerogel sample based on DP 320 with no added kraft fibers. These properties are achieved as a compromise between several factors. First, in order to have a material with high specific surface area, drying with supercritical CO₂ must be performed, and a sufficient matrix content is required; an extensive concentration of fibers, whatever the origin, should be avoided. Second, a sufficient content of matrix is also needed in order to avoid large voids created due to the “lack” of the matter, which increases material heterogeneity thus being detrimental for the mechanical properties. Finally, to obtain the improved compression properties, higher cellulose DP and certain content of fibers are needed to reinforce the matrix. Therefore, when higher dissolving pulp DP is used, the non-dissolved fibers play the role of the reinforcement and the addition of “other” fibers is not necessary.

The properties of the obtained all-cellulose composite aerogels are similar to those reported in literature for cellulose II aerogels of comparable density, but prepared via complete cellulose dissolution, for example, in ionic liquid [5]. The main outcome of this work is that complete dissolution of a pulp is not required in order to obtain strong aerogels with high

specific surface area. This is an important result as it removes the restriction on using only low DP cellulose for the production of porous cellulose materials when using aqueous NaOH-water as a solvent. Mild mixing conditions and absence of additives, such as urea, thiourea or ZnO, also enlarge the scope of using NaOH-water for making cellulose materials with high added value and easily recyclable solvent.

5. Conclusions

Cellulose pulps of various degrees of polymerisation were dissolved in 8 wt-% NaOH-water and two drying routes, freeze-drying and with supercritical CO₂, were used to make porous materials, cryogels and aerogels, respectively. Kraft fibers were added to probe all-cellulose composite approach. Both types of materials had low density and open pores' structure. Cryogels were with micron-size pores and flat and sheet-like pore walls, while aerogels were with sub-micron-size pores and fine web-like pore network. The density varied from 0.08 g/cm³ to 0.17 g/cm³ for cryogels and from 0.11 g/cm³ to 0.23 g/cm³ for aerogels. Due to the difference in material morphology, the specific surface area for cryogels was much lower than that of aerogels, 5 - 50 m²/g vs. 140 - 340 m²/g, respectively. The compressive modulus of cryogels was higher than that of aerogels at the same material density.

Several factors have to be taken into account to understand and control the properties of all-cellulose composite porous materials. The increase in pulp DP was shown to increase the content of non-dissolved fraction in solution, which decreased the content of dissolved cellulose in the matrix solution resulting in voids in the dry matter. Despite the excellent adhesion between the kraft fibers and the matrix, the incomplete dissolution of high DP pulps and increasing material heterogeneity at high kraft concentrations compromised composites' mechanical properties under the uniaxial compression. The presence of non-porous fibers decreased the specific surface area of aerogels. The highest specific surface area with the

highest compressive modulus was found for aerogel with matrix based on pulp with DP 640 containing 34 wt-% of fibers originating only from the non-dissolved fraction in cellulose-NaOH-water solution. The results show that complete dissolution of cellulose is not required in order to produce strong porous materials with high specific surface area. Non-toxic low-cost solvent, 8 wt-% NaOH-water, can be used for making versatile porous cellulose materials.

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Figure captions

Figure 1. Process scheme for all-cellulose composite aerogel and cryogel production

Figure 2. Morphology of aerogels (a, c) and cryogels (b, d) based on cellulose of DP 320 without added fibers (a, b) and of composite samples with 0.5 wt-% (c) and 2.1 wt-% (d) of added kraft fibers in solution (10 wt-% and 34 wt-% in dry matter, respectively).

Figure 3. Morphology of all-cellulose composite aerogel with total fiber content of 77 wt-% and matrices of cellulose of DP 320 (a) and 640 (b)

Figure 4. Bulk density (a) and porosity (b) of all-cellulose composite aerogels and cryogels from different matrix DP as a function of total fiber concentration in dry composite (eq.6).

Circles visually separate data on aerogels from cryogels

Figure 5. Pore volume (a) and specific surface area (b) of all-cellulose composite aerogels and cryogels as a function of the total fiber concentration (eq. 6). The line corresponds to the mixing rule

Figure 6. Compressive modulus (a) and absorbed energy at 40 % strain (b) for all-cellulose composite aerogels and cryogels as a function of density

Figure 7. Specific surface area and compressive modulus for all aerogel- and cryogel-composites. The best samples are highlighted with larger markers

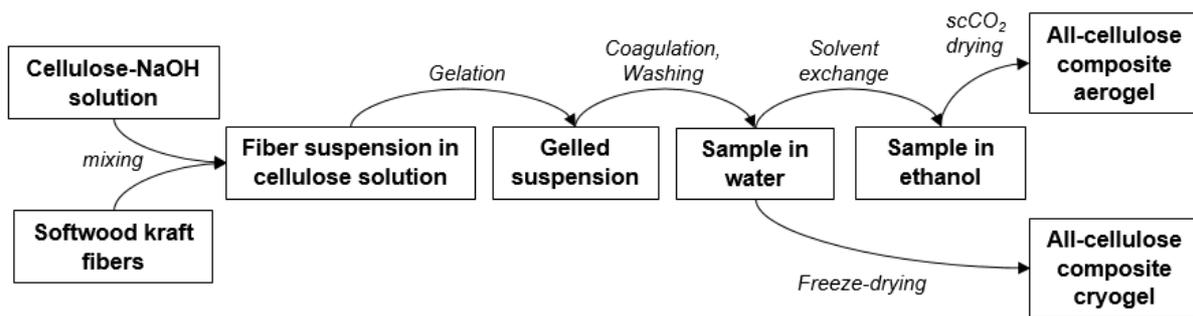


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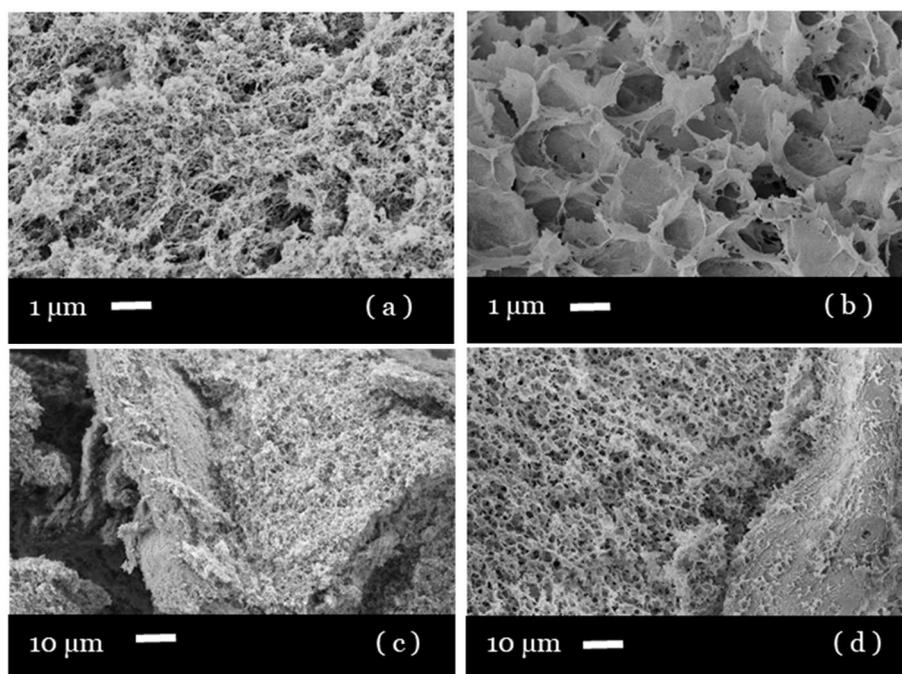


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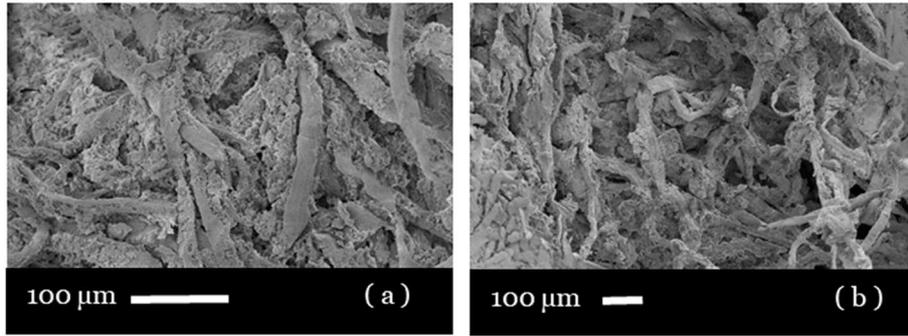


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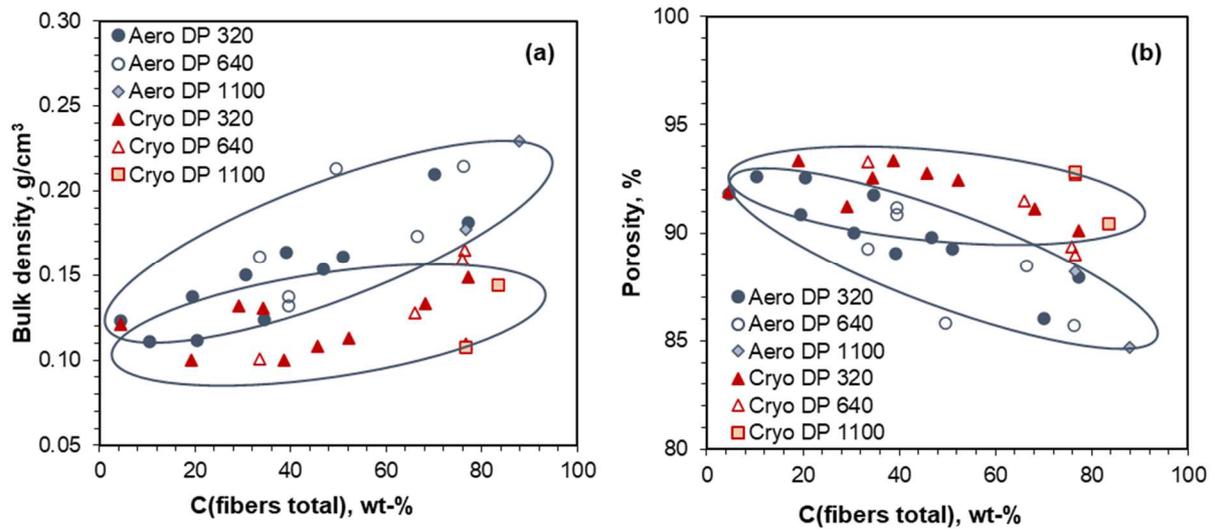


Figure 4.

Bulk density (a) and porosity (b) of all-cellulose composite aerogels and cryogels from different matrix DP as a function of total fiber concentration in dry composite (eq.6). Circles visually separate data on aerogels from cryogels

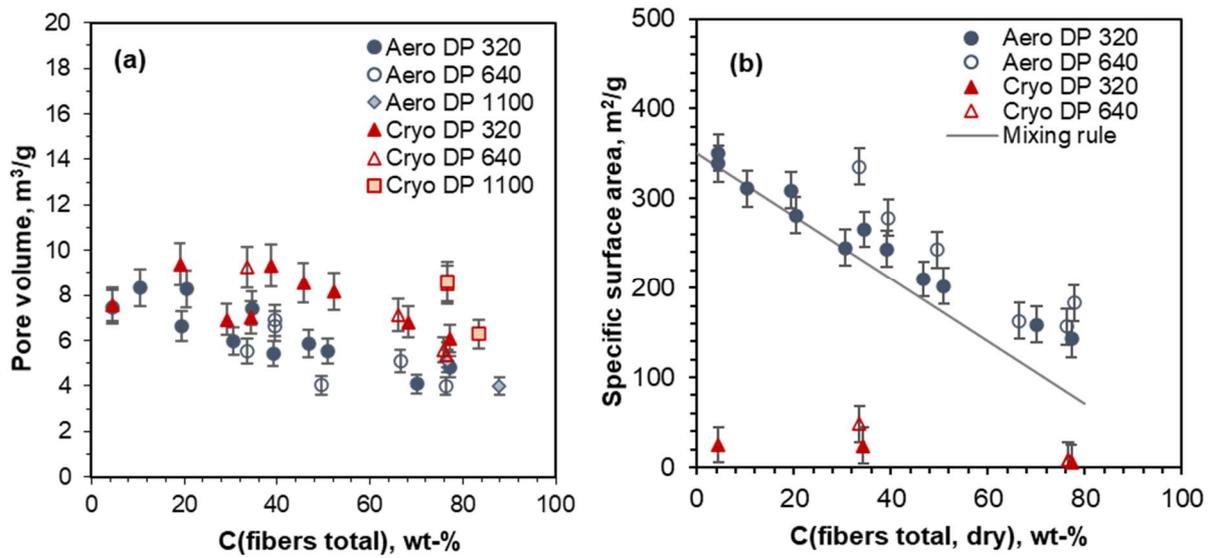


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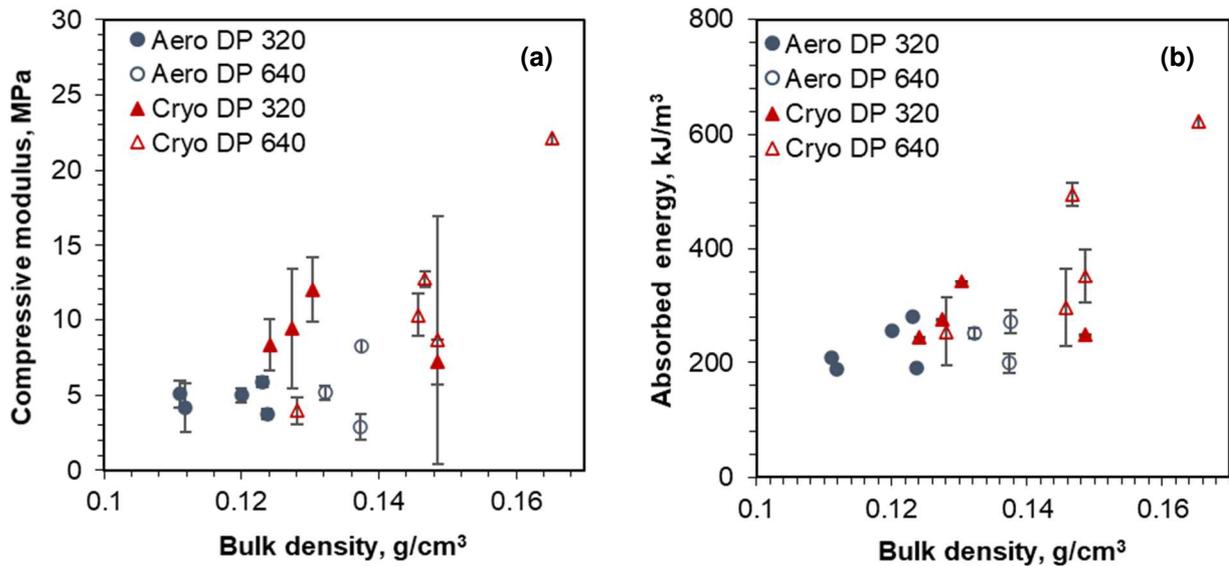


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Compressive modulus (a) and absorbed energy at 40 % strain (b) for all-cellulose composite aerogels and cryogels as a function of density

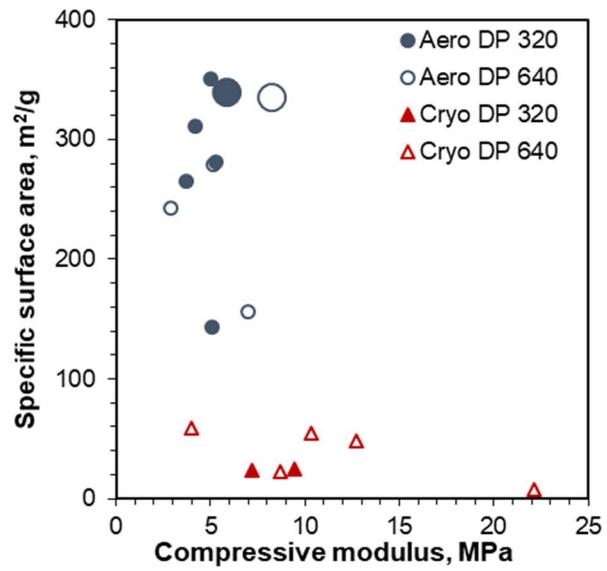


Figure 7.

Specific surface area and compressive modulus for all aerogel- and cryogel-composites. The best samples are highlighted with larger markers

Table 1. Composition and concentrations of cellulose and of fibers in solutions and in dry composite: concentration of added kraft fibers in the solution $C(kraft, wet)$ (eq.3); concentration of added kraft fibers in the dry composite $C(kraft, dry)$ (eq.4); total fiber concentration in the solution $C(fibers total, wet)$ (eq.5) and total fiber concentration in the dry composite $C(fibers total, dry)$ (eq.6)

	$C(kraft, wet)$, wt-%, in solution	$C(kraft, dry)$, wt-%, in dry matter	$C(fibers total,$ $wet)$, wt-%, in solution	$C(fibers total,$ $dry)$, wt-%, in dry matter
DP 320: 4.8 wt-% of dissolved and 0.2 wt-% of non- dissolved cellulose in the solution	0	0	0.2	4
	0.3	6	0.5	10
	0.9	17	1.2	20
	1.6	27	1.8	30
	2.1	31	2.3	34
	2.4	36	2.6	39
	3.3	44	3.5	47
	3.9	49	4.1	51
	8.4	69	8.6	70
	8.8	76	8.9	77
Matrix DP 640: 3.3 wt-% of dissolved and 1.7 wt-% of non- dissolved cellulose in the solution	0	0	1.7	34
	0.5	9	2.1	39
	1.5	24	3.0	50
	4.4	50	5.8	67
	6.3	64	7.5	76
	7.8	66	9.1	78
Matrix DP 1100: 1.2 wt-% of dissolved and 3.8 wt-% of non- dissolved cellulose in the solution	0	0	3.9	77
	3.9	48	7.1	88