Nanofibrillated Cellulose-Based Aerogels: A New Chemical Approach for Tuning their Micro-Architectures

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Abstract
Freeze-dried nanofibrillated cellulose based-aerogels were produced using Eucalyptus urograndis as a raw material. Nanofibers were isolated under high pressure and modified with TEMPO-mediated oxidation and/or hydroxyapatite (HPa). Different degrees of oxidation (DO) were reached and measured by conductimetric titration (~ 0.1 and 0.2). Oxidized and non-oxidized samples were modified with hydroxyapatite (HPa) in a level of HPa:cellulose ratio of 0.2:1. Morphology (FE-SEM), rheological and physical properties were used to characterize produced aerogels. The results shown a well-organized morphology and a greater mechanical strength for aerogels fabricated with oxidized nanofibers.

Keywords:aerogels; nanofibrillated cellulose; TEMPO; hydroxyapatite.

Introduction
Aerogels are highly porous materials possessing low solids content, considerably lightweight, high strength and good dimensional stability. In a “nano” perspective, the extensive interconnected chains confers stable three-dimensional network due to the linkage of the nanoparticles to each other with inter-chain distances typically being in order of 10-100 nm. For being promptly accessible, these structures have attractively led to the development of variety of applications such as storage media for gases, filter materials, carrier for catalysis, scavengers for dust particles, shock absorbers and heat and sound insulators.[1, 2].

Although aerogels can be prepared from an extensive range of materials, a particular promising candidate for addressing novel applications is cellulose. Cellulose is the most abundant sustainable material in the biosphere, but it has not been as exploited for novel materials as may be surmised; yet, with the pressing concerns surrounding petroleum supplies and increasing environmental consciousness, it has been slowly gaining ascendancy as a raw material for various market applications.

Tuning the properties of any chemical assembly such as an aerogel to obtain specific applications may require chemical tweaking of the existing structure(s). Such modifications of cellulose are interesting approaches for value-added products. One common modification is its catalytic oxidation using 2,2,6,6-tetramethylpyperidine-1-oxy radical (TEMPO) to introduce functionalities such as aldehyde and carboxyl groups and thus derive new industrial use.[3, 4] Another alternative for cellulose modification, relatively unexplored until the present, is the use of HPa. HPa has a wide variety of uses and its effects on the mechanical properties of cellulose fiber have been also investigated.[5]

The aim of this work is 1) to produce aerogels from nanofibrillated cellulose (NFC) by direct water removal by freeze-drying; 2) modify NFCs using TEMPO and/or HPa and 3) characterize the novel aerogels according to their morphology (FE-SEM) and rheological properties.

Experimental
Cellulose was extracted from hardwood Eucalyptus urograndis specimens. Extractives-free sawdust of wood samples was subjected to delignification with peracetic acid at 15% and to yield holocellulose. The hemicelluloses were removed from holocellulose by using KOH 24% at room temperature. Cellulose fibers left were washed several times. Cellulose fibers were swollen for 1 day in deionized water. Next, the sample was dispersed using a blender for 3 minutes. Finally, the nanofibrillated cellulose (NFCs) aqueous gel was formed under high pressure homogenizer.

Once NFCs suspensions were produced, TEMPO-mediated oxidation of NFCs was carried out [6] to
obtain 2 different degrees of oxidation. The oxidized and non-oxidized NFCs were dialyzed against deionized water and centrifuged to remove the excess of water. The carboxyl content of oxidized cellulose samples was determined by conductimetric titration, from which the degree of oxidation (DO) was calculated [7]. FT-IR spectroscopy was performed to confirm the different degrees of oxidation. HPa was also used to modify the NFCs. The final molar ratio of HPa:cellulose on the NFCs was 0.2:1. Afterwards, all 6 samples were placed on the mold and freeze-dried. Mechanical properties were measured. Also, the morphology of the aerogels was interrogated by field emission scanning electron microscopy (FE-SEM).

**Results and Discussion**

The conductimetric titration indicated a DO of 0.1 and 0.2 for the 2 samples oxidized by TEMPO. The non-oxidized sample showed little DO (~ 0.03%), probably due the use of peracetic acid during the delignification of wood. The band at 1720-1740 cm\(^{-1}\) on the FT-IR spectra (Figure 1) confirms the presence of carboxylic groups, and the higher the carboxylic content, the higher the degree of oxidation.

![Figure 2. FTIR of the NFCs. (A) Non-oxidized, (B) Oxidized with DO= 0.1, (C) Oxidized with DO= 0.2.](image)

The mechanical properties of the aerocellulose samples were obtained by measuring the force applied to compress the samples at 50% of their original length (Figure 2). Once again, the effect of the oxidation leads to a more highly compression-resistant sample. Similarly, the addition of HPa to the samples increased the resistance of the NFC aerogel as well.

![Figure 3. Rheological behavior of NFC based aerogel. Bold lines represent aerogel without addition of HPa. Solid lines: non-oxidized aerogels, long-dashed line: oxidized aerogels with DO=0.1, short-dashed line: oxidized aerogels with DO=0.2.](image)

The aerogels presented diverse macroscopic morphologies, especially when contrasting samples with different DOs. It became clear that the samples with higher DOs displayed a more organized distribution of pores. With respect to the effect of HPa, the aerogels showed similar morphologies (Figure 3) with the structures presenting closer porous, but also well-organized.
Conclusions
Nanofibrillated cellulose seem to be an alternative for aerogels production. Oxidation of NFCs plays an important role on the homogeneity of the aerogels. NFC priori modified by TEMPO improves the strenght of the aerogels and the use of HPaas modifying agent for the aerogels is offered as a viable pathway for the production of high value cellulose aerogels.

References

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