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Cellulose Nanofibers from Recycled Cellulose Pulp

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In recent years, cellulose nanofibers have been extensively studied in several research fields due to their renewability, availability and other remarkable properties. Several methods of cellulose nanofibers obtaining from different feedstock have been reported in the bibliography. The most common obtaining systems are based on the use of mechanical treatment such as grinding and homogenization. In this work, the production of cellulose nanofibers from recycled cellulose pulp using ultrasound technology was studied. The effect of different sonication times on nanofiber size was evaluated. The properties of the paper sheet formed with different percentages of cellulose fibers and nanofibers were determined. The obtained results showed that the paper sheet properties were improved by the nanofibers addition.

1. Introduction

Cellulose is the most abundant polysaccharide in nature, comprising about 30 – 50 % of the lignocellulosic material. The worldwide production of this biopolymer is estimated to be over 7.5×10^{10} t/y (Habibi et al., 2010). Cellulose, composed exclusively by glucose molecules, is rigid, insoluble in water and contains from several hundred to several thousand units of β-glucose. The cellulose backbones consist of crystalline and amorphous regions forming elementary fibrils which pack into larger units called microfibrils which are finally assembled in fibers (Habibi et al., 2010). The degree of polymerization (DP) of cellulose is about 1,000-10,000, and it is intimately associated with other polysaccharides, like hemicellulose and lignin in the cell wall of the plant.

For centuries, cellulose has been used in the form of wood and plant fibers as energy source, for building materials, paper, textiles and clothing. These applications have been considered by some authors (Moon et al., 2011) as first generation uses of cellulose, which take advantage of this hierarchical structure. The use of natural cellulose based materials continues today (Mariano et al., 2014), as can be verified by the huge number of industries based on this source (Schmidt et al., 2013).

Among the industrial applications of cellulose, one of the most remarkable ones is the production of pulp and paper using different types of raw materials and processes. Today recycled papers are a major source of sustainable fibers for the papermaking industry. In 2013, in Europe, 91.1 Mt of papers were produced with 41.2 Mt of wood pulp and 47.5 Mt of recovered papers. Paper recycling rate reaches today 71.7 %.

Cellulose nanofibrils (CNF) are long and flexible nanoscaled fibrils, composed of more or less individualized cellulose microfibrils and consisting themselves of alternating crystalline and amorphous strings. The number of published scientific articles involving keywords like “nanocellulose” (including mechanically extracted cellulose nanoparticles or nanofibrillated cellulose-NFC) or “nanocrystals” or “cellulose (nano)whiskers” has experienced a considerable grow in the last years indicating the interest of the topic.

The main advantage of CNF preparation lies in the fact that no additives are required, surface charge stays as raw material and very high yield (> 90 – 95 %) are achieved. CNF were discovered in the 80’s, obtained from cellulose where wood pulp fibers had been rapidly expanded in a surface area and opened into their sub-structural microfibrils by mechanical action and heat (homogenization at 70 - 80 °C). After repeated homogenization, a diluted dispersion of CNF with a gel-like appearance is obtained. Several physical treatment have been developed to limit energy consumption during their preparation and to obtain homogeneous nano-scaled material.

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Mechanical approaches to diminish cellulosic fibers into nano size scale can be divided into refining and homogenizing, microfluidization, grinding, cryocrushing and high intensity sonication. Ultrasound energy is transferred to cellulose chains through a process called cavitation, which refers to the formation, growth, and violent collapse of cavities in water. The energy provided by cavitation in this so-called sonochemistry is approximately 10 – 100 kJ/mol, which is within the hydrogen bond energy scale. Thus, the ultrasonic impact can gradually disintegrate the micron-sized cellulose fibres.

Recently, the ultrasonic technique has emerged as an interesting method to reduce the cellulose fibres size. Some publications on the topic can be found. Cheng et al. 2009) and further developed in (Cheng et al., 2010 have presented the results of using high-intensity ultrasonication to obtain cellulose fibrils. Chen et al. (2011) combined high-intensity ultrasonication with chemical pretreatments and Renouard el al. (2014) studied the ultrasonic impact on coir, flax and hemp fibers. However, no studies have been published regarding the application of sonication to produce CNF from recycled paper.

In the present work, the effect that the addition of CNF obtained from recycled pulp by sonication had on the mechanical properties of the paper sheet formed was analyzed. Different concentration of CNF were used.

2. Materials and methods

2.1 Preparation of NF

The used recycled pulp (gently supplied by Papresa company, Spain) for the production of NF presented an average ash content of 11.26 % (TAPPI T211 om-93). 0.066 g of pulp were diluted in 30 mL of water.

The ultrasounds were applied to the mixture using a VC 505 – VC 750 equipment. To avoid direct contact of the mixture with the tip a cup horn was used. The mixture was placed in a flask inside the cup horn and the temperature of the mixture was kept constant by tap water recirculation inside the cup horn jacket.

To obtain the NF, the pulp was treated 5 h using an energy supply of 1 kJ with wave amplitude of 20 %. 0.055 W were used to convert the 0.066 g of pulp to NF. Optical microscopy was employed for monitoring the size of the cellulose fiber and to determine the sonication time required to reach the nano-scale.

2.2 Fabrication of nanopapers

The amount of required pulp and nanofibers to obtain a nanopaper sheet with a grammage of 100 g/m^2 (shown in Table 1) was vacuum filtered through a 0.45 µm nylon filter to obtain a homogeneous gel. This gel was then dried in an oven for 25 min at 50 °C to remove excess humidity and then submitted to a series of pressing cycles and press curing. For this purpose, the previously dried gel was placed between two copper plates in a Santec hydro-pneumatic molding press (30 tons) and four cycles of increasing pressure were performed at a constant temperature to avoid shape malformations in the paper due to high pressure. The cycles were performed at 10 bar at 100 °C. Finally, a curing pressure of 20 bar at 100 °C was carried out for 10 min.

Table 1: Required mass of recycled pulp and CNF.

Recycled pulp (g)	CNF (g)	% of CNF
1.296	0	0
1.167	0.129	10
0.972	0.324	25
0	1.296	100

2.3 Atomic Force Microscopy (AFM)

AFM images were obtained operating in tapping mode with a scanning probe microscope (NanoscopeIIIa, Multimode^{TM} from Digital Instruments, Veeco) equipped with an integrated silicon tip cantilever with a resonance frequency of 300 kHz. To obtain representative results, different regions of the samples were scanned. Similar images were obtained, thus demonstrating the reproducibility of the results.

2.4 Mechanical properties

Tensile tests of the nanopapers were performed using MTS Insight 10 equipment provided with pneumatic clamps (Advantage Pneumatic Grips) and with a 250 N loading cell and a speed of 5 mm/min. Samples were prepared, dog bone-shaped, 38 mm long, with a width of 5 mm and at a thickness of 0.035 - 0.138 mm. The starting distance between the clamps was 20 mm. The values quoted are the average of eight measurements.

3. Results and discussion

3.1 Atomic Force Microscopy (AFM)

Five samples of NF were analyzed by AFM (Figure 1). The nanofibers had an average length of 1.925 µm. Regarding the diameter, the fibers had a width of 40 - 60 nm. This type of nanofiber, which is long and thin, has these dimensions due to the mechanical treatment used in the pulping stage.

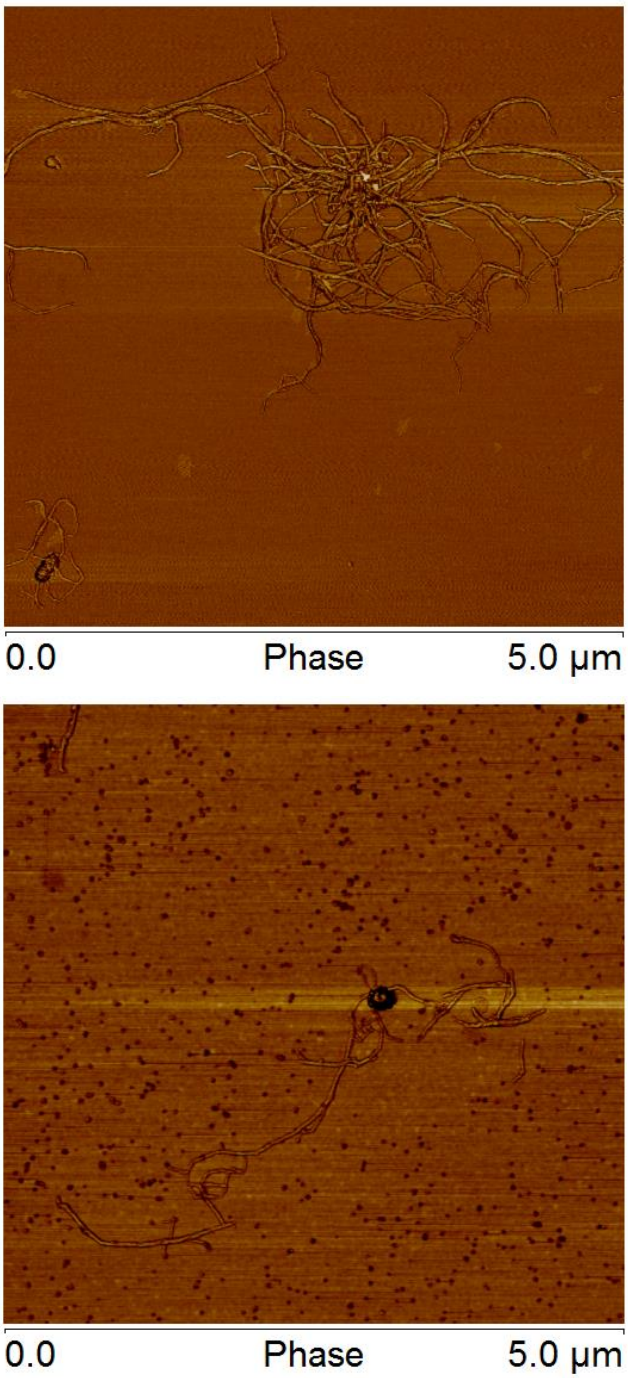

Figure 1: AFM pictures of samples of 3 and 4 de microfibrils

3.2 Mechanical properties

The stress−strain curves and mechanical properties obtained from uniaxial tensile tests are presented in Figure 2.

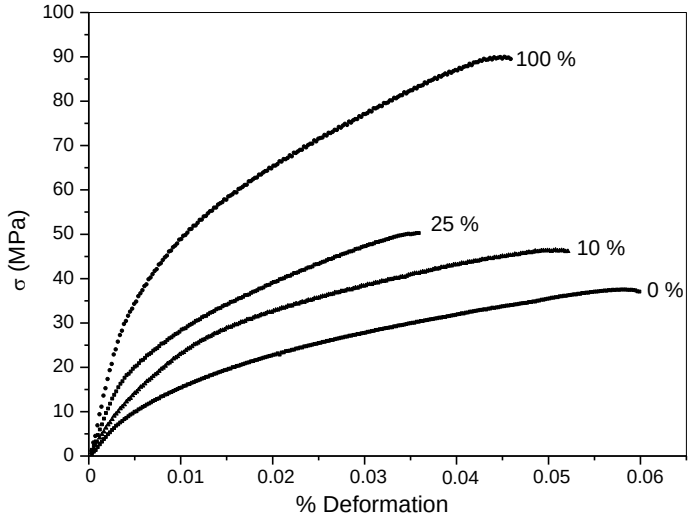

Figure 2: Tensile strenght as function of thenanofibre content.

As can be observed in Figure 2, the paper sheet that had 100 % of CNF was found to be tougher than the initial sheet (no CNF) as the area under the curve was greater, i.e., it absorbed more energy before breaking. Higher amount of CNF produced less ductile sheet. Regarding the experiment with 25 % of CNF, it seemed that the bad orientation fibers may have affected their mechanical properties. It was expected that the percentage of deformation presented by this sample was smaller than the one presented by the sheet with10 % but greater than the one made with 100 % of CNF.

Table 2 summarize the results of mechanical properties of the tested paper sheets.

Table 2: Measured mechanical properties of the paper sheets.

Systems (%)NF	Modulus (GPa)	Tensile strength (MPa)	Deformation (%)
0	4.57±1.67	25.48±9.47	0.060
10	6.77±2.77	37.48±9.87	0.052
25	8.70±1.19	41.73±11.83	0.035
100	15.32±2.15	74.64±10.49	0.045

In Figure 3, the value of the elastic modulus obtained for the different paper samples as function of their content in CNF is presented.

It was observed that the higher the percentage of CNF, the higher the associated elastic modulus. Starting from an elastic modulus of 4.57GPa for paper without CNF, 15.32 GPa were reached for the paper sheet made entirely with a 100% of CNF.

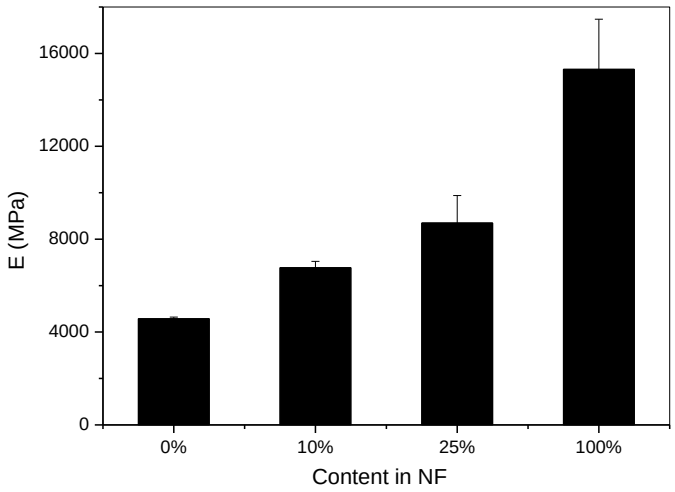

Figure 3: Variation of the module as a function of the content in nanofibers.

In Figure 4, the variation of the tensile strength as a function of the nanofibers content is presented.
It can be observed that the increase of CNF content produced a significant increase in paper strength, from 25 MPa, for the paper without CNF, up to 74.6 MPa, for the paper made with 100% of CNF.
Furthermore, it was also interesting to remark that adding 10 % of CNF increased the resistance of the modified paper by 47 % but the deformability was increased only by 15 %. From this fact, it could be concluded that, with the addition of small amounts of CNF, the resistance was substantially improved, observing a reduction of the deformability which could make this kind of paper interesting for certain applications.
A recent study reports a benchmarking of cellulose nanocrystals from different sources, showing elastic modulus comprised between 0.5 GPa and 17 GPa for CNF obtained respectively from Ramie and Tunicin (Bras et al., 2011). The results obtained in this work for the 100 % CNF are similar to those reported in the bibliography.

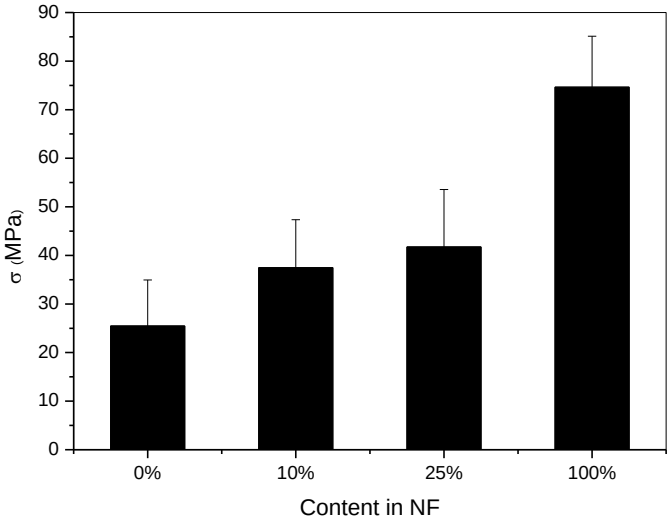

Figure 4:.Variation of the tensile strength as a function of the nanofibers content

4. Conclusions

The obtained results showed that it is possible to obtain CNF from recycled pulp using the sonication process. The use of recycled pulp as source of nano fibrils is interesting as it allows to use a sustainable

raw material. Furthermore, the application of sonication to reduce the cellulose fibres size has been found to be a rapid and efficient process with a low energy consumption.
The obtained results showed that the addition of CNF to the recycled pulp improved the elastic modulus of the paper sheets due to the creation of stronger hydrogen bonds between the fibers and the CNF. Furthermore, the measured elastic modulus increased with the proportion of CNF added to the sheets. However, the deformation of the paper sheet decreased with the amount of CNF.

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