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EXTRACTION OF CELLULOSE NANOCRYSTALS FROM SECONDARY PAPER WASTE AND THEIR USE IN PAPER PRODUCTION

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Abstract. Cellulose nanocrystals were obtained by hydrolysis process from waste paper industry. The result of Fourier transform infrared spectroscopy (FTIR) for nanocellulose showed that no new chemical bonds were formed during the preparation of nanocellulose. The results of X-ray diffraction showed that the crystallinity of the macules produced in the treated and untreated paper industry was 66% and 73.8%, respectively. The results of nanocellulose revealed a natural needle-like fiber with a length of 300 nm to 600 nm, a diameter of 10 nm to 30 nm, and an aspect ratio in the range of 10 to 60. It was found that the obtained nanocellulose particles improve the physical properties of paper sheets, in particular, tear resistance strength, traction and burst indices. The maximum increase in mechanical properties was achieved with the addition of 6.0% nanocellulose.

Keywords: Paper, waste paper, composite material, cellulose, degree of polymerization, color intensity, tear strength, breaking length, rupture index, nanocellulose, nanocrystal.

INTRODUCTION. One of the challenges in the paper industry today is the source of raw materials. From this point of view, the depletion of non-renewable resources has led to the tendency to increase the efficiency of the use of waste paper generated in the paper industry as raw material for various products. As a waste biomass material, waste paper generated in the paper industry typically accounts for about 7% of municipal solid waste and contains low-cost cellulosic material. In industrialized countries, millions of tons of paper boxes are produced and used, resulting in a huge amount of waste paper. Due to the cellulosic content of paper boxes, the production of high-value cellulose-based materials from them may provide an alternative recycling method. Cellulose is one of the most renewable natural resources and consists of linear bonds of glucose as a monosaccharide $(C_6H_{10}O_5)_n$; cellulose polymer contains both crystalline and amorphous regions. In addition, cellulose has been widely used in various industries such as paper, clothing, adhesives, textiles, food, cosmetics, and pharmaceuticals. With the advent of nanotechnology, there has been an increased focus on the extraction of nanocellulose from various renewable sources and its application in technical fields. The production of nanocellulose from waste paper has aroused the interest of researchers today. For example, we have successfully extracted nanocellulose from waste paper by treating waste paper with alkali and acid. Nanocellulose exhibited the following characteristics: diameter from 3 nm to 10 nm, length from 100 nm to 300 nm, and crystallinity index of 75.9%. Literature review showed that foreign scientists have produced high-quality nanocellulose directly from old newspapers and recycled newsprint. In recent years, several studies using nanocellulose as a reinforcement within biocomposite materials have been published; however, little information is provided on its use in pulp and paper. There are several studies where nanocellulose was produced from old newspapers or newsprint; therefore, a deeper knowledge in this area is of interest. Nanocellulose has received considerable attention for its use as an additive in papermaking, for example, in improving mechanical properties such as burst, tear, and tensile strengths. In addition, nanocellulose has several advantages: large

surface area, biodegradability, high tensile strength and high. Therefore, the addition of nanocellulose to the paper pulp shows a high potential in increasing the hydrogen bonding between the pulp fibers, resulting in a strongly formed paper.

Hydrolysis of strong sulfuric acid is one of the promising preparation processes widely studied in the literature. During acid hydrolysis, disordered cellulose is preferentially attacked and crystalline cellulose remains as the final nanocellulose product. The unique properties associated with nanocellulose, such as high elastic modulus, abundant hydroxyl (-OH) groups, and chemical activity, make it highly desirable for its value. Cellulose Nano-Crystals Nanocelluloses have emerged as a new material in many potential fields, such as food, medicine, cosmetics, paper pulp and paper, reinforcement and other special functional additives.

In this study, chemical pretreatment with hydrogen peroxide and sodium hydroxide was used to treat waste paper generated in the paper industry. The chemical composition, fiber morphology and brightness of waste paper produced in the paper industry were analyzed to optimize the technological conditions for ink removal. To prepare nanocellulose, the hydrolysis process is carried out using sulfuric acid. Chemical characterization was performed using atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Nanocellulose and carboxymethylcellulose have also been used as dry strength additives in papermaking. In this study, the effect of different additives on tensile strength, burst strength, tear strength and elongation of paper sheets was also analyzed.

MATERIAL AND METHODS. Waste paper produced in the paper industry was used as a raw material in this study. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2), microcrystalline cellulose, carboxymethylcellulose, $NaClO_2$ and sodium silicate (Na_2SiO_3) were used as chemicals. All reagents used were of analytical grade.

Preparation of raw materials. Waste paper from the paper industry was cut into small pieces (2×2 cm) and then treated with 5% NaOH, 10% H_2O_2 and 10% sodium silicate at 60°C for 1.5 h. It was mixed at 1000 stirring speed for 30 minutes and allowed to stand for 1 hour. The purified mass is then filtered and washed with distilled water until a neutral pH medium is reached. The cleaned sample is dried at 105°C for one day.

Nanocellulose and papermaking processes. Nanocellulose obtained by acid hydrolysis with high precision and purified waste paper (5g) were mixed by adding 60 wt% H_2SO_4 at 45°C. The optimal reaction time was set at 1 h and the fiber-to-liquid ratio was maintained at 1:20. Deionized water was then added to the mixture to terminate the reaction of H_2SO_4 with the paper pulp. The mass was centrifuged to remove H_2SO_4 from the mixture. Next, the nanocellulose is filtered and washed several times with distilled water, placed in a dialysis bag with a molecular weight of 12,000-14,000, and dialyzed until reaching a neutral medium. The resulting nanocellulose was molded for 20 minutes and stored in a refrigerator at 4°C.

As the main raw material, cellulose of the flax plant crushed to the level of 46.2 ShR was used. The concentration of the prepared mass is 1%. Then, different compositions of nanocellulose were added to the mass during the mixing process. After that, the mixture of pulp and nanocellulose was sent to the mesh table and the paper was dried under vacuum at 105°C for 15 minutes. The resulting paper was then placed in a controlled temperature and humidity chamber with a constant temperature of 25°C and 60% relative humidity to equilibrate the moisture before mechanical testing. For comparison, different percentages of carboxymethylcellulose (5-10%) were added to the mass in the same way as nanocellulose during the mixing process. Then, after the above process with the addition of nanocellulose, paper reinforced with carboxymethylcellulose was obtained.

Fiber length and diameter. A mass of 0.5 g of waste paper was diluted in 500 ml of distilled water with constant stirring until the fibers were separated. The fibers were then

placed under an optical microscope to measure their length and width. About 200 fibers were measured with length and width values of the pulp mass and calculated.

RESULTS AND DISCUSSION. Optimum conditions were achieved using H_2O_2 , NaOH and Na_2SiO_3 dosages, and the three optimal parameters were determined by the final brightness of the mass. In this experiment, single factor analysis was used to explore the optimal conditions. To study the effect of NaOH content on varnish removal, the remaining two factors were at optimal conditions (10% Na_2SiO_3 and H_2O_2). The effect of H_2O_2 , Na_2SiO_3 and NaOH doses on the brightness of the pulp cleaning mass is presented in Figure 1.

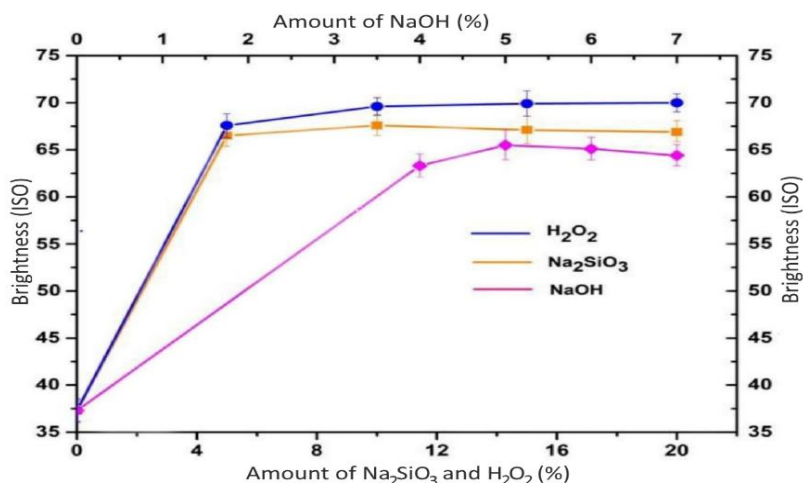


Fig 1. The effect of the amount of H_2O_2 , NaOH and Na_2SiO_3 on the brightness of the waste paper pulp

The brightness of the extinguished waste paper increased gradually at first and then stabilized with the increase in the dose of H_2O_2 , Na_2SiO_3 , NaOH. The results showed that the highest brightness of the treated waste paper was obtained when the content of H_2O_2 , NaOH and Na_2SiO_3 was 10%, 5% and 10%, respectively. Brightness was increased to 32.35% ISO, 30.3% ISO, and 28.2% ISO with 10% H_2O_2 , 10% Na_2SiO_3 , and 5% NaOH, respectively.

Chemical composition analysis. The chemical composition of purified and untreated flax plant celluloses was studied. Compared to untreated celluloses, extractive, lignin and pentosan content of purified celluloses decreased by 0.34%, 2.83% and 1.47%, respectively. The initial extractive content of untreated celluloses was about 0.85% and decreased to 0.55% after chemical pretreatment. This decrease was probably caused by the removal of ink during ink cleaning. The lignin content decreased from 19.45% to 16.10% due to lignin degradation during the bleaching step. The chemical composition of cellulose was completely changed after de-inking, indicating the highly efficient removal of components such as lignin, extractives and hemicellulose during the alkali and bleach treatment steps. The filled celluloses were enriched with 60.15% α -cellulose, resulting in highly purified cellulose suitable for nanocellulose production. Figure 1. Effect of dosages of H_2O_2 , NaOH and Na_2SiO_3 on the brightness of bleached cellulose.

X-ray diffraction analysis. The XRD spectra of untreated and purified celluloses are depicted in Figure 2. Figure 2 shows the diffraction peaks of the dyed celluloses at $2\theta = 16.10^\circ$ and 22.95° , which largely correspond to untreated celluloses. In addition to the main diffraction peaks at $2\theta = 16.10^\circ$ and 22.95° , untreated celluloses showed two minor peaks at 12.55° and 29.85° , which may be attributed to the presence of kaolin and calcium carbonate. The peak for kaolin is typically found at 12.35° and for $CaCO_3$ the most intense peak is typically found at $2\theta = 29.85^\circ$.

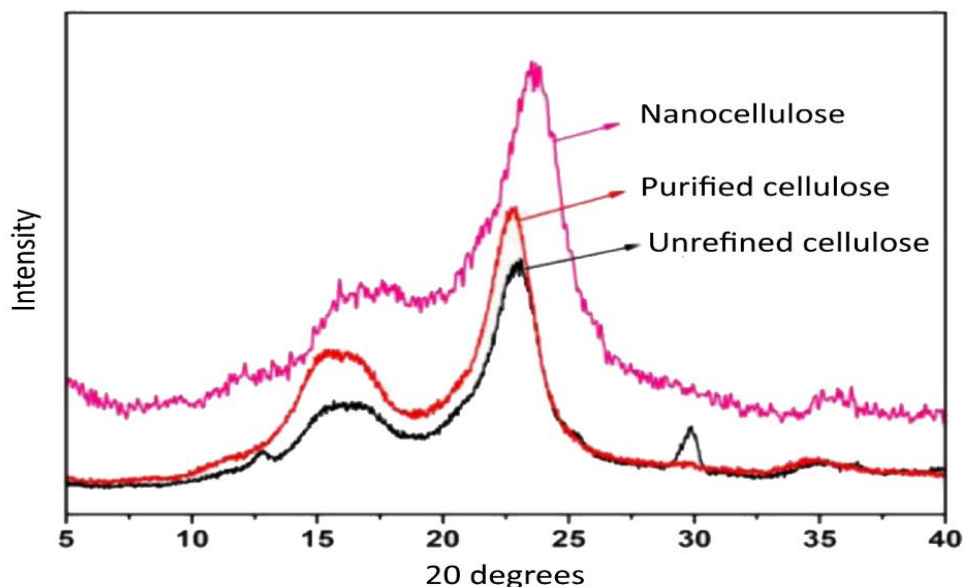


Fig 2. X-ray diffraction patterns of untreated (a) and purified (b) celluloses.

Refined celluloses accounted for 66%, which is 7.8% lower than untreated celluloses; It was found that the crystallization area of cellulose was destroyed by NaOH during the reaction. The crystallinity index of nanocellulose was 70.25%. The crystallinity index of nanocellulose was higher than that of purified celluloses, but lower than that of untreated celluloses, which was attributed to the higher proportion of cellulose crystallites present in untreated celluloses. During hydrolysis, the amorphous region of cellulose was removed, which contributed to the low yield (35.55%) and high crystallinity of nanocellulose. Thus, nanocellulose had high crystallinity, and this property could be important for paper production

Fourier transform infrared spectroscopy (FTIR) analysis. The infrared spectra of untreated cellulose (a), purified cellulose (b), nanocellulose (c) and microcrystalline cellulose (d) are presented in Figure 3. The absorption peak at 1165 cm^{-1} was consistent with the stretching of the glycosidic bond (C-O-C) of cellulose.

The FTIR spectra in Figure 3 showed an extended vibrational absorption peak of -OH from about 3200 cm^{-1} to 3600 cm^{-1} , which was significantly stronger than that of the untreated celluloses (Figure 3 a). reported that the ink had an absorption band at 3380 cm^{-1} , which reduced the concentration of hydroxyl groups from untreated cellulose. In the spectrum of untreated (a) cellulose, the characteristic peak at 1733 cm^{-1} corresponds to the C=O stretching frequency of carboxyl groups in their acidic forms. In addition, the absorption peak at 1733 cm^{-1} can be attributed to the C=O stretching of hemicelluloses.

The peak intensity at 1733 cm^{-1} of purified cellulose (spectrum b) was lower than that of untreated cellulose C (spectrum a), which may be caused by the degradation of hemicelluloses by NaOH pretreatment. Figure 3 a (unrefined cellulose) showed the presence of lignin in areas at 1505 cm^{-1} due to aromatic vibrations in the C plane. The peak of cellulose at 1505 cm^{-1} (Figure 3 a) was significantly weaker than that of untreated celluloses (Figure 3 b), indicating the effectiveness of using chemical treatment to remove lignin.

The 1263 cm^{-1} peak presented in the cellulose spectra was also a weak intensity attributed to lignin. Compared to the starting material, changes in the peaks at 1733 , 1505 and 1263 cm^{-1} indicated that the chemical treatment removed hemicellulose and lignin from the surface of the fibers. These results were consistent with the results of the chemical composition analysis.

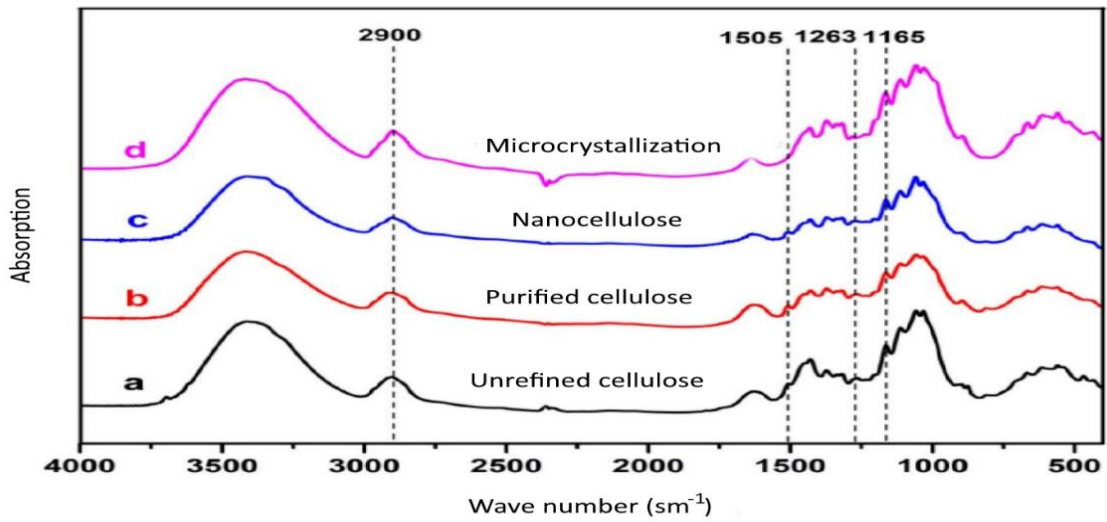


Fig 3. FTIR spectra of untreated cellulose (a), purified cellulose (b), nanocellulose (c), and microcrystalline cellulose (d)

The spectrum of nanocellulose includes areas similar to microcrystalline cellulose. The peak near 1635 cm^{-1} was due to adsorbed water. The characteristic bands of β -(1-4) glycosidic bonds at 896 cm^{-1} as well as the C-O-C stretching vibration of pyranose at 1165 cm^{-1} were also clearly shown in the spectra, which were the main features.

Accordingly, the intensity of the C-H stretching at 2900 cm^{-1} was lower for the treated celluloses than for the untreated celluloses, indicating that the distortion of the hydrogen-bonding structure and crystal shape occurred during the ink purification process.

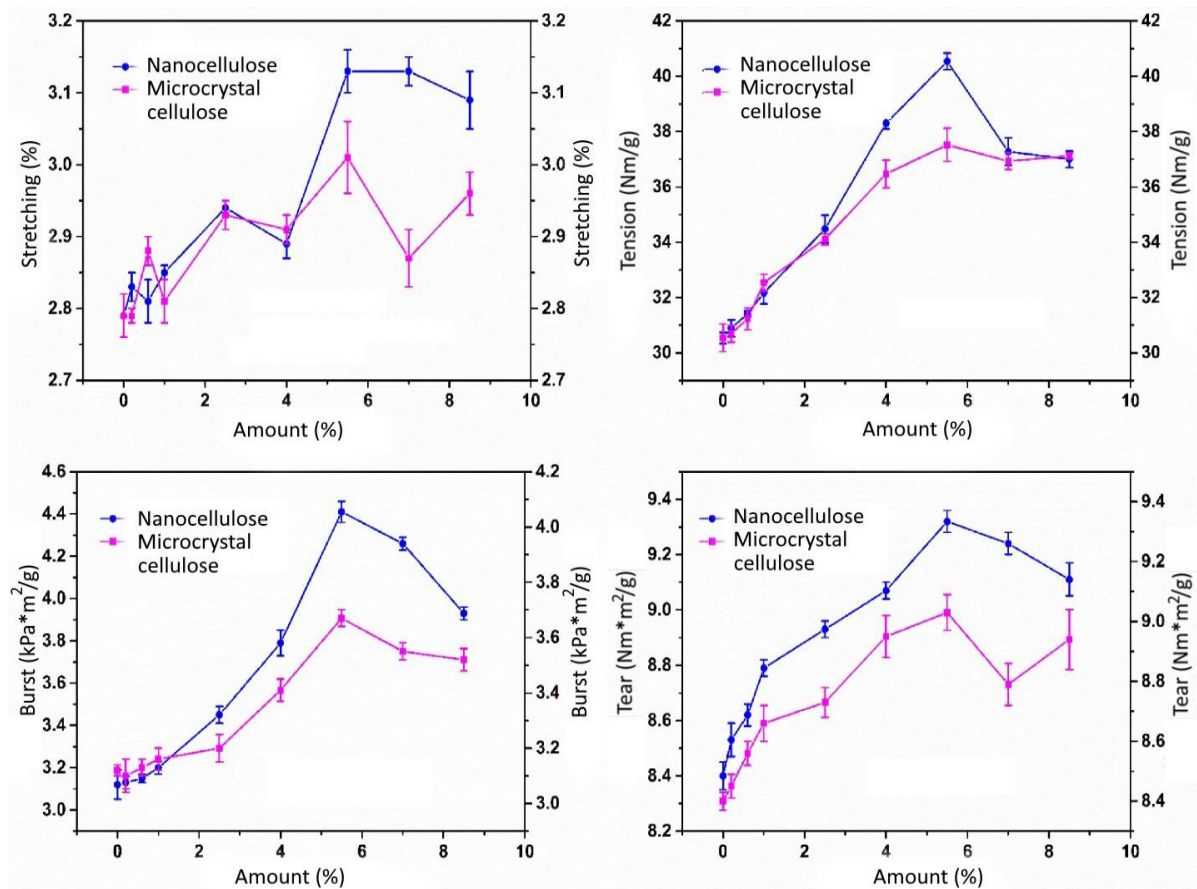


Fig 4. Effect of nanocellulose and carboxymethylcellulose content on elongation, burst and tear indices of paper sheets

This result was consistent with the (XRD) result. Overall, these results showed that the molecular structure of cellulose was not destroyed after pretreatment with H_2SO_4 , and the nanocellulose still showed the basic chemical structure of cellulose.

Effect of nanocellulose on physical properties of paper. With an abundance of surface hydroxyl groups, large specific surface area, high aspect ratio, excellent mechanical properties, and high heat resistance, nanocellulose has demonstrated its potential as a reinforcement in papermaking and to increase the strength of paper sheets. Nanocellulose and carboxymethylcellulose have been used in papermaking to improve the physical performance of paper sheets without structural damage to the fibers

In the current study, flax plant cellulose nanocellulose and carboxymethylcellulose were added to the pulp to make paper. In addition, the effects of additives with different dimensions were evaluated on the tensile strength, tear index, burst index and elongation of the paper sheets with the results shown in Figure 4.

The tensile strength of the paper sheets was increased by the addition of nanocellulose, which caused the creation of bonds between the fibers. More specifically, the tensile index was increased to a maximum value at the level of 5.5-6% nanocellulose, which was 32.75% higher than that of non-nanocellulose paper sheets. The maximum values of burst index, tear index and elongation of paper sheets were obtained at 5.5-6 wt% nanocellulose content. These measures were increased by 41.45%, 11.01% and 12.25% respectively. An increase in various physical properties was obtained with the addition of nanocellulose, which depended on the adhesion between the fibers. In addition, the physical properties of paper sheets were improved by the combination of hydrogen bonds. In addition, the relative binding area can be increased by the high specific surface area of nanocellulose to improve its physical properties. The maximum increase in physical properties was achieved with the addition of 5.5-6% nanocellulose. Regardless, when the addition of nanocellulose exceeded 5.5–6%, the physical properties showed a tendency to decrease due to the aggregation of nanofiber particles. The results lead to the conclusion that nanocellulose has demonstrated the ability to improve the physical properties of paper sheets.

The effect of carboxymethylcellulose as an additive in papermaking was also measured in this study. Figure 4 shows a comparison of the effects of different amounts of additives on physical properties. With the addition of 5.5-6% nanocellulose and 5.5-6% carboxymethylcellulose, the tensile index reached maximum values of 40.55% and 37.55%, respectively. The burst index initially increased and then decreased with increasing carboxymethylcellulose content. This behavior can be attributed to the increase in peak pressure caused by the addition of appropriate carboxymethylcellulose before the paper breaks. However, adding more creates more negative charges in the system, which increases the electrostatic repulsion between the carboxymethylcellulose and the fibers. Therefore, the explosion index of the paper sheet has decreased. The explosion index was gradually increased to 17.65% with the addition of 5.5-6% carboxymethylcellulose. The tear index and elongation increased by 12.85% and 7.95% with the addition of 5.5-6% carboxymethylcellulose, respectively.

This study clearly showed that the physical properties were related to nanocellulose and carboxymethylcellulose additives. The most obvious finding of this study is that the greatest reinforcement strength of paper sheets was obtained with the addition of nanocellulose rather than the addition of carboxymethylcellulose. For example, compared to carboxymethylcellulose, nanocellulose as an additive improved the physical properties of paper sheets. Therefore, nanocellulose is a good candidate as an industrial-scale reinforcement to improve the physical properties of paper sheets.

CONCLUSION. The best ink removal conditions for waste paper were determined as follows: H₂O₂ 10%, NaOH 5% and Na₂SiO₃ 10%. In optimal conditions, the brightness level has improved to ISO 32.55%. Compared to the extractive, lignin and pentosan contents of untreated celluloses, the purified celluloses decreased by 0.35%, 2.85% and 1.48%, respectively. XRD patterns showed that the crystallinity index of nanocellulose was higher than that of purified celluloses but lower than that of untreated celluloses. FTIR spectra showed that hemicellulose and lignin were removed after chemical treatment. And the thermal stability index of nanocellulose was lower than that of untreated cellulose. TEM showed that nanocellulose was 300 nm to 600 nm in length and 10 nm to 30 nm in width. Nanocellulose improved the physical properties of paper sheets. These physical properties reached maximum values with the addition of 5.56% nanocellulose.

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