

# FABRICATION AND CHARACTERIZATION OF CELLULOSE NANOFIBERS FROM RECYCLED AND NATIVE CELLULOSE RESOURCES USING TEMPO OXIDATION

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Cellulose nanofibers (CNFs) were fabricated from different cellulose resources, namely, native hardwood (HW), cotton linter (CO) and recycled deinked paper (DIP), using the TEMPO oxidation method. The CNF properties were investigated by thermogravimetric analysis, X-ray diffraction, atomic force microscopy, Fourier transform infrared spectroscopy and CNF yield. The width of CNFs was in the range of 20-30 nm. The CNFs showed lower thermal degradation than the initial cellulose resources. The CNFs isolated from DIP showed the highest thermal degradation among the prepared CNFs. Recycled deinked paper could be a potential source for CNFs, offering the advantages of comparatively good thermal stability, environmental friendliness and resource recycling. XRD and FT-IR investigations confirmed that the filler content in the recycled DIP was calcium carbonate. The ash contents of DIP, CO and HW were of 19.24%, 0.06% and 0.10%, respectively. The high ash content contributed to the high thermal stability of DIP. Additionally, HW exhibited the highest CNF yield, compared with DIP and CO.

**Keywords:** cellulose nanofibers, TEMPO oxidation, recycled deinked paper, cotton linter, ash content

## INTRODUCTION

Cellulose, one of the most abundant natural resources in the world, is a carbon neutral, biodegradable, renewable, non-toxic, biocompatible, high performance material with unique functionalities. The width of cellulose fiber influences its properties: as the width decreases, more cellulose chains appear on the surface, resulting in huge property changes. For example, once 60  $\mu\text{m}$  wood fiber is separated into 6 nm cellulose nanofiber, its surface area is increased by 10,000 times. Recently, a new observation of cellulose nanopaper reported that both the strength and toughness of cellulose nanopaper increase simultaneously as the size of the constituent cellulose fibers decreases from a mean width of 27  $\mu\text{m}$  to 11 nm.<sup>1</sup>

Nanocellulose has gained a lot of interest due to its light weight, high strength, renewability and environmental friendliness. Many reports have already been published concerning the isolation of nanocellulose from various wood and non-wood resources.<sup>2-8</sup> Nanocellulose isolated from different resources was investigated for various applications, such as coatings, lubricants, dyes, medicines, reinforcing composites and so on. There are different ways to isolate nanocellulose, such as TEMPO oxidation,<sup>3,6,9-14</sup> acid hydrolysis,<sup>5,8,15</sup> mechanical methods<sup>16-18</sup> and the high pressure method.<sup>16</sup> However, after a literature review, to the best of our knowledge, no study on TEMPO oxidized CNF from recycled deinked paper has been reported so far. This study investigates the properties of TEMPO oxidized cellulose nanofibers isolated from recycled paper. If the properties of CNFs isolated from recycled paper are similar to those of CNFs from native cellulose resources, then the use of deinked paper will be promising. In this research, cotton linter, hardwood and recycled deinked paper were selected as resources of CNFs and their properties were investigated.

Generally, nanocellulose can be divided into cellulose nanofiber (CNF), cellulose nanocrystal (CNC), cellulose microfibril (CMF) and cellulose microcrystal (CMC). Nanocellulose produced by acid hydrolysis is called CNC or cellulose nanowhisker (CNW). The width of CNFs usually varies from 3 to 100 nm. In mechanical extraction methods, the isolation of CNFs is performed using a super-mass collider or a high-pressure homogenizer achieving dimensions of less than 100 nm in

width and up to a micrometer in length. Recently, TEMPO oxidation has been also successfully applied in the isolation of CNFs. According to previous works,<sup>6,9-11,20</sup> CNFs isolated by TEMPO oxidation are 3-4 nm in width and a few microns in length. The TEMPO oxidation method produces CNFs with high aspect ratio. Furthermore, this approach can produce individual CNFs, meanwhile most mechanical extraction methods produce fibrillated ones. This kind of CNFs with individual fibers is easy to characterize and useful for many applications.

To evaluate the properties of cellulose and cellulose nanofibers, researchers have used various techniques, such as thermogravimetric analysis (TGA), X-ray diffraction (XRD) and atomic force microscopy (AFM). Thermal degradation and thermal stability are important and preferred for many applications. Several research groups have reported that the thermal stability of CNFs is lower than that of the cellulose resources.<sup>6,8,21,22</sup> A research group<sup>23</sup> analyzed the thermal properties of CNC isolated from recycled cellulose resources. It is known that the crystallinity indices of nanocellulose and the initial cellulose resources are different depending on the isolation methods and the measurement methods, including the crystallinity index (CrI) calculation. According to some previous works,<sup>6,21</sup> TEMPO oxidized CNF keeps its CrI constant, in comparison with that of the initial cellulose resource, while another research group<sup>3</sup> reported that the mechanical treatment decreases its CrI. Nevertheless, CrI is still one of the most important properties, which need more investigation for further understanding nanocellulose.

The thermal degradation, CrI and morphology of isolated CNFs from recycled paper have not been discussed thoroughly so far. Thus, this study aims at isolating CNFs from three different cellulose resources (HW, CO, DIP) using the TEMPO oxidation method and investigating the CNFs isolated from DIP in comparison with those from HW and CO. AFM, TGA, XRD and FT-IR techniques have been used to characterize the CNFs and their yield was analyzed, comparing the results for the CNFs isolated from different cellulose resources.

## EXPERIMENTAL

The raw materials used in this research were cotton linter (CO, 99.5% alpha cellulose content), bleached hardwood Kraft pulp mixture, which was a mixture of aspen and poplar from Canada (HW, 87% alpha cellulose content) and recycled deinked paper (DIP, 75.4% alpha cellulose content). TEMPO, sodium bromide (NaBr), NaClO, and HCl were purchased from Sigma-Aldrich. NaOH was acquired from Daejung Chemical Co., South Korea. HW was kindly provided by Chungnam National University, Department of Bio-based Materials. The recycled deinked paper, *i.e.* copy and printing paper waste (DIP), was kindly donated by Daeha Paper Co., Ltd., South Korea.

### Preparation of cellulose nanofibers

Dried HW and CO (5 g of cellulose) were soaked in water for a day before being disintegrated by a food mixer for 10 minutes. CNF isolation was prepared according to Saito *et al.*<sup>24</sup> In brief, a total of 400 grams of diluted emulsion was made by mixing cellulose (5 g), TEMPO (0.0625 g) and sodium bromide (0.625 g). To this emulsion, 17 ml/g<sub>cellulose</sub> of 10-15% NaClO was added under magnetic stirring at room temperature. The reaction starts when the NaClO is added to the emulsion. A pH of 12 was maintained by adding 0.5M NaOH. To measure the pH, a pH meter (Orion Star A211, Thermo Scientific) was used. After 4 h, the reaction process was stopped by adding 0.5 M HCl to adjust the pH to 7. The oxidized cellulose was first filtered through filter paper (0.45 μm, Millipore) and then continuously washed with 1000 ml of water by filtration. After that, the oxidized cellulose was mechanically disintegrated using a digital homogenizer mixer (T25, IKA) for 10 minutes. The mixed cellulose emulsion was sonicated with a sonicator (SONOPULS 2200, 200 Watt) at 35% power for 5 minutes. The suspension was then separated by using a centrifuge (Supra 22K, Hanil, Korea) at 11000 rpm for 20 minutes to separate the un-isolated large fibers from the suspension.

In the case of DIP, 3.3% wet slurry pulp, received from Daeha Paper Co., was used as received. For TEMPO oxidation, 5 grams in dried weight of DIP was used and the same TEMPO oxidation for HW and CO was carried out.

### Characterization

AFM was carried out for the isolated CNFs. A drop of 0.005% CNF suspension was poured onto a microslide glass, followed by drying in air. The dried samples were then analyzed using an AFM (3100, Veeco). The tapping mode was used for amplitude. The length and width of the CNFs were determined using the AFM images and ImageJ software (version V1.50i).

TGA was carried out to investigate the thermal properties of the CNFs (TG 209F3, NETZSCH), using an Al<sub>2</sub>O<sub>3</sub> crucible, under N<sub>2</sub> gas flow, with the temperature range of 30-600 °C. The sample weight was 7 mg.

XRD analysis of the CNFs was performed on an X-ray diffractometer (RINT-2000, Rigaku) with a wide angle goniometer installed. X-Ray diffraction analysis was carried out at 40 kV/100 mA, with a 5-40° scanning angle and a 0.02° step size. The *CrI* was calculated using the following equation:

$$CrI(\%) = \frac{I_{200} - I_{am}}{I_{200}} \times 100 \quad (1)$$

where  $I_{200}$  is the intensity of the maximum crystalline peak between  $2\theta = 22^\circ$  and  $23^\circ$ ,  $I_{am}$  is the intensity of the minimum peak between  $2\theta = 18^\circ$  and  $19^\circ$ .

The FT-IR spectra of the initial cellulose samples and the oxidized CNFs were investigated using an FT-IR spectrometer (VERTEX 80V, Bruker), in the range between 400 and 4000  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

### Morphology

To investigate the morphology of CNFs, AFM images were taken in tapping mode. Figure 1 shows AFM images of HWCNF, COCNF and DIPCNF. Left and right images for each case represent the height and amplitude found in tapping mode. The results show that the width of CNFs is  $20 \pm 4.5$ ,  $20 \pm 6.0$  and  $30 \pm 7.8$  nm for HWCNF, COCNF and DIPCNF, respectively. Also, in order to analyze the length of CNFs, a drop of a diluted emulsion of 0.005% CNF was deposited on a micro-slide glass. In this study, the length of CNFs was found to be in the range of  $660 \pm 216$ ,  $850 \pm 273$ , and  $614 \pm 203$  nm for HWCNF, COCNF and DIPCNF, respectively. This result is similar to those reported by other research groups.<sup>3,9-11</sup> The long and narrow aspect of the CNFs gives rise to aspect ratios as high as of 30-50.

### Yields of CNFs

The yield of CNFs is important for production. Therefore, it was calculated by the following formula:

$$Yield(\%) = \frac{M_3}{M_0} \times 100 \quad (2)$$

where  $M_0$  is the weight of the starting cellulose materials,  $M_3 = M_1 \times M_2$ , where  $M_1$ : the weight of supernatant after centrifugation,  $M_2$ : the concentration of supernatant determined in oven dry state.

Yields of CNFs for hardwood, cotton and DIP were found to be 59.3, 34.7 and 41.9%, respectively. The HWCNF showed the highest yield among them. According to a previous study,<sup>24</sup> the yield of dried native cellulose was reported to be 17%. Also, they reported that after a three-cycle treatment of CNFs, the yield of the dried cellulose reached up to 27, 52 and 99% by adding 2.5, 3.8 and 6.3 NaClO mmol/g with 2 h reaction time. In our research, the reaction time was 4 h, followed by 10 min of mechanical homogenization and 5 min of power sonication. It indicates that longer reaction time could enhance the yield of CNFs. Thus, a higher yield of CNFs can be achieved for dried cellulose samples by subjecting it to repeated treatment, which enables energy and chemicals savings.

### Crystallinity indices

To evaluate the *CrI* of CNFs, XRD analysis was carried out on the raw materials (HW, CO, DIP) and the isolated CNFs. Figure 2 illustrates the XRD results. The peaks of all the cellulose samples at around  $2\theta = 16^\circ$ ,  $22.7^\circ$ , and  $34^\circ$  correspond to the (110), (200) and (040) planes of cellulose I.<sup>23</sup> Also, the peak at  $14.5^\circ$  is assigned to the (101) crystal plane for CO only. The peak at  $18^\circ$  is due to the amorphous structure of the cellulose. The *CrI* of the initial cellulose materials and cellulose nanofibers were calculated using Equation 1.

In addition, the XRD patterns of DIP and DIPNFC present an additional peak at around  $30^\circ$ . It is believed that the peak at  $30^\circ$  is assigned to precipitated  $\text{CaCO}_3$ .<sup>25,26</sup> Also, according to M. E. Fortuna, precipitated  $\text{CaCO}_3$  has high thermal stability.<sup>26</sup>

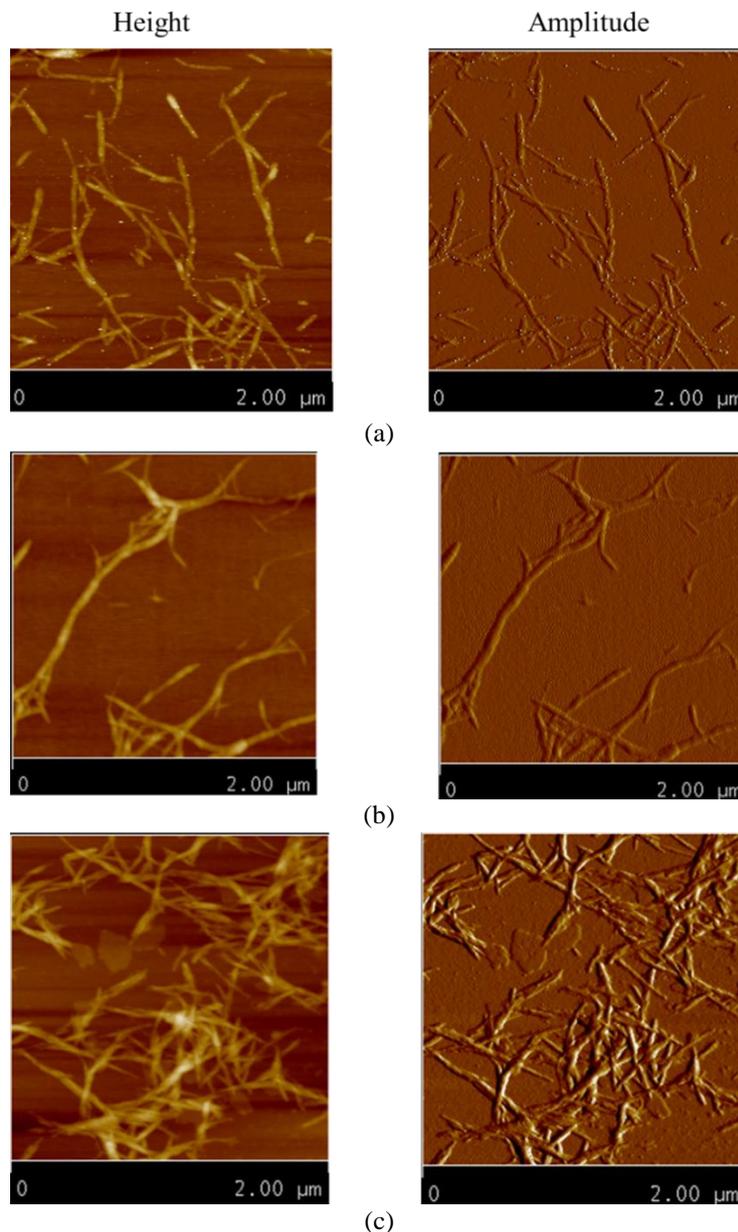


Figure 1: AFM images of CNFs isolated from various cellulose resources: (a) hardwood cellulose nanofibers (HWCNF), (b) cotton linter cellulose nanofibers (COCNF) and deinked paper cellulose nanofibers (DIPCNF); (scale bar 2 x 2  $\mu\text{m}$ )

In general, the ash content from paper contains different types of fillers, such as  $\text{CaCO}_3$ , clay and others. The investigation indicates that the ash content of DIP was 19.24%, and only around 0.1% for the CO and HW samples. Hence, this could be due to the fact that residuals, such as clay and nano-sized  $\text{CaCO}_3$ , contributed to the thermal stability of DIPCNF that was discussed in the TGA section.

CrI was calculated according to Equation 1. Table 1 indicates the CrI of all the CNFs, in comparison with that of the initial cellulose samples. Crystallinity indices of the initial cellulose samples are higher than those of the isolated CNFs. DIPCNF shows the largest CrI reduction, of about 50%, compared to its corresponding initial cellulose, whereas COCNF exhibits the highest CrI. The decrease of CrI can be explained by long reaction times, sonication and long homogenizer treatment.<sup>3</sup> Large crystallinity index reduction could be one of the factors that contribute to lowering the thermal degradation of CNFs, which will be discussed later in the thermogravimetric analysis.

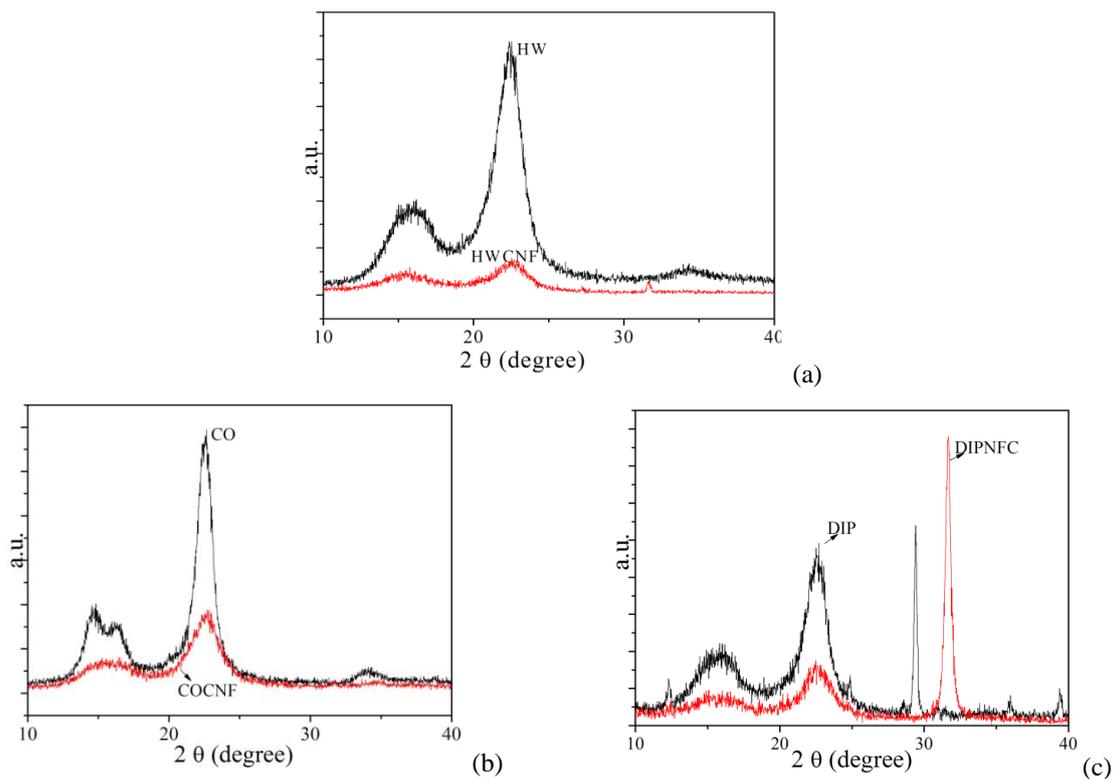


Figure 2: X-ray diffraction patterns of various initial cellulose and CNF samples

Table 1  
Crystallinity indices of initial cellulose samples and isolated CNF samples

| Sample        | Initial cellulose | CNFs |
|---------------|-------------------|------|
| Hardwood      | 75.3              | 54.0 |
| Cotton        | 82.4              | 62.4 |
| Deinked paper | 70.6              | 36.9 |

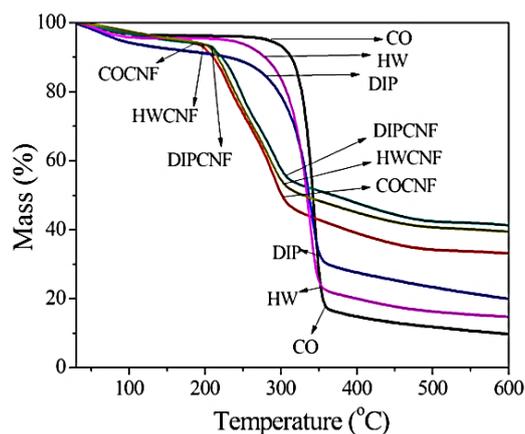


Figure 3: Thermogravimetric analysis of initial cellulose and CNF samples

### Thermal properties

Thermal properties of hardwood, cotton and recycled deinked paper, as well as those of their isolated CNFs, were analyzed by TGA and the results are presented in Figure 3. In the initial CO, HW and DIP samples, 10% weight loss was observed at 312, 275 and 221 °C and the final degradation occurred at 358, 355 and 353 °C, respectively, the samples showing constant weight thereafter. In addition, at 400 °C, the residual weight of the CO, HW and DIP samples was 14.79, 20.08 and

27.62%, respectively, the highest residual weight being recorded for DIP, which means that this sample has the highest thermal stability.

To understand the thermal stability of the CNFs, additional analysis was carried out. It was observed that 10% weight loss occurred at 220, 215 and 208 °C for DIPCNF, HWCNF and COCNF, respectively. Cellulose nanofibers quickly degrade with increasing temperature, compared with the initial cellulose samples. The thermal degradation temperature sharply decreased from 275 and 312 °C to 215 and 208 °C for HW and CO, respectively. The greatest drop of thermal degradation occurred for COCNF, while DIPCNF exhibited the lowest thermal degradation drop.

Note that the thermal degradation of DIP at 221 °C switched to 220 °C for DIPCNF. This indicates that the thermal degradation of DIP and DIPCNF are about the same. The final thermal degradation was 302, 306 and 310 °C for COCNF, HWCNF and DIPCNF, respectively. DIPCNF shows higher thermal resistance than COCNF and HWCNF. At 400 °C, the residual weight was 47.79, 45.15 and 39.11% for DIPCNF, HWCNF and COCNF, respectively. It means that DIPCNF has the highest thermal stability among the samples. The results show that recycled DIP and DIPCNF have higher thermal stability than the other samples, which is different from the results we expected.

To understand the factors contributing to the high thermal stability of DIP and DIPCNF, the ash contents of HW, CO and DIP were measured and found to be 0.10, 0.06 and 19.24%, respectively. The ash contents of HW and CO were much lower than that of DIP. The large ash content of DIP is associated with a large amount of fillers in the recycled DIP resource. The ash content of DIP might be affected by the recycled sources, for example, clay,  $\text{CaCO}_3$  and other components could be found in the composition of the recycled DIP. XRD and FT-IR curves of DIP and DIPCNF shown in Figure 2 and Figure 4 reflect the presence of  $\text{CaCO}_3$ . The fillers in DIP possibly contribute to the high thermal stability of the material. We believe that the fillers could be dissolved in the DIPCNF emulsion, so as to coat the surface of DIPCNF.

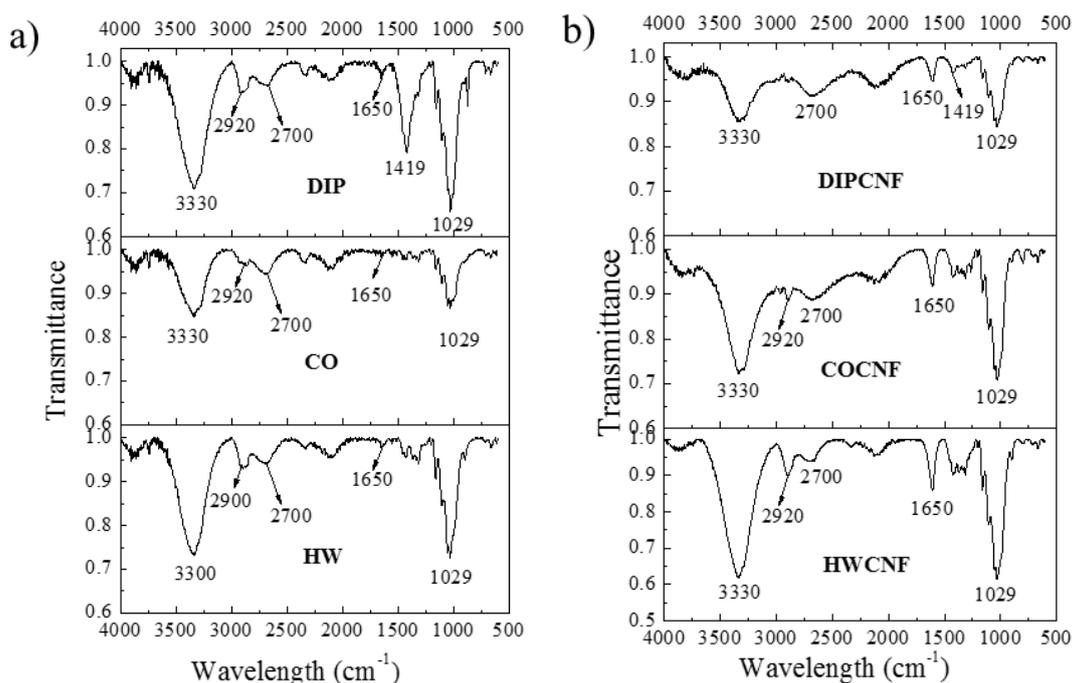


Figure 4: FT-IR spectra for (a) initial cellulose samples and (b) isolated CNF samples

### FT-IR spectroscopy

The FT-IR spectra of the initial cellulose samples and isolated CNFs are shown in Figure 4. The spectra of HW, CO and DIP exhibited peaks at 1029, 2700, 2920, 3330  $\text{cm}^{-1}$ . The peaks at 1029, 1650 and 3330  $\text{cm}^{-1}$  correspond to C-O, C-C and O-H stretching vibration, respectively. In addition, the band in the region of 2700-2920  $\text{cm}^{-1}$  is due to C-H stretching. The peak at 3330  $\text{cm}^{-1}$  is assigned to O-H stretching vibration.<sup>23</sup> However, an additional sharp peak at 1419  $\text{cm}^{-1}$  is noted only in the spectrum of the DIP sample. This peak corresponds to  $\text{CaCO}_3$ . We discussed above regarding the highest ash

content of the DIP sample, while its FT-IR analysis confirms the presence of CaCO<sub>3</sub> in its composition.

## CONCLUSION

Cellulose nanofibers were successfully isolated from hardwood, cotton and recycled deinked paper by TEMPO oxidation with the support of mechanical stirring and sonication. Cellulose nanofibers obtained from recycled deinked paper (DIPCNF) showed the highest thermal stability, while those isolated from hardwood presented the highest yield among all the samples. Cellulose nanofibers obtained from cotton (COCNF) exhibited the highest CrI%. However, the crystallinity indices of all the isolated cellulose nanofibers were lower than those of the initial cellulose resources. The nanofibers from native and recycled resources showed similar morphology. However, the filler content of the recycled paper contributed to the higher thermal stability and residual weight of DIP and DIPCNF. Therefore, it may be concluded that recycled deinked paper has great potential as a source of cellulose nanofibers with comparative properties with those obtained from native cellulose.

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