PROPERTIES OF NANOFIBRILLATED CELLULOSE AND ITS LENGTH-WIDTH RATIO DETERMINED BY A NEW METHOD

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Softwood nanofibrillated cellulose (SW-NFC) was fabricated from bleached softwood Kraft pulp by using a Masuko grinder. The properties of SW-NFC were investigated by thermogravimetric analysis (TGA), X-ray diffraction (XRD) and mechanical investigation. A SW-NFC film was formed by casting on a calibrated glass dish, and was determined as having a tensile strength of 110 Nm/g and Young's modulus of 9 GPa. The width of SW-NFC was evaluated by using field emission scanning electron microscopy (FE-SEM). Additionally, an intense study was conducted on the SW-NFC length using two simple methods, namely: FE-SEM and imageJ analyses. The length-width ratio of SW-NFC is one of the most important factors for composite applications. The result indicated the length-width ratio of SW-NFC was around 90, relying on the measurement of 30 single selected SW-NFCs. These two simple assessment methods are accessible in many laboratories rather than transmission electron microscopy (TEM), atomic force microscopy (AFM), and nanoparticle analysis techniques.

Keywords: nanofibrillated cellulose, FE-SEM, imageJ analysis, length-width ratio

INTRODUCTION

In recent years, there has been a dramatic increasing interest in nanocellulose. There is a huge number of research articles on nanocellulose and nanocellulose applications.[1-4] Nanocellulose could be isolated by using chemical, such as sulfuric acid,[5-8] TEMPO,[9-13] and mechanical methods, such as a grinder or high-pressure homogenizer,[14,15] as well as by enzymatic treatment. Nanocrystalline cellulose (NCC) has a small width and very short length. In general, the higher the aspect ratio of NCC is, the better its reinforcing ability. The longer the nanocellulose fiber is, the better the selection for the composite applications. NFC can be produced by a high-pressure homogenizer, grinder, and others. Previous studies[14,16-18] have reported that NFC had a length of several micrometers and a few nanometers width. To produce sustainable and environmentally friendly products, in this research, a mechanical method was selected. Thus, our first target was to isolate NFC by using a Masuko grinder.

To evaluate the nano-sized cellulose fibers, different techniques have been proposed, such as transmission electron microscopy (TEM),[9,19,20] atomic force microscopy (AFM),[21-23] field emission scanning electron microscopy[8,24,25] (FE-SEM) and others. In the case of nanocrystalline cellulose, the length-width ratio was easy to determine by TEM, SEM and AFM. To evaluate the NFC, the width of the fibers was easy to determine, however, determining the length of the NFC is a difficult task. Many published papers on NFC have indicated that the length of the NFC was of several micrometers.[14,16,18] However, there is no suitable method to determine the length of NFC, and thus, this remains one of the greatest challenges. Hence, the target of this research work was to determine the length of the NFC using two simple methods, namely FE-SEM and imageJ analyses.

Additionally, to investigate the crystallinity index and the thermal stability of initial cellulose and isolated nanofibrillated cellulose, different methods were used, such as X-ray diffraction

(XRD) and thermogravimetric analysis (TGA). The crystallinity index is one of the factors contributing to the strength properties of materials. A large number of papers have been published concerning the crystallinity index of NFC. The higher the crystallinity is, the better the strength of the material. In this research, XRD was used to determine the crystallinity index of initial cellulose and NFC. Furthermore, the TGA was used to evaluate the thermal degradation stability of cellulose and NFC. Thermal stability is one of the important criteria for some composite applications. The higher the thermal stability is, the better the application of the reinforcing materials. Thus, the crystallinity index and the thermal degradation stability of the samples were evaluated as well.

EXPERIMENTAL

Materials and methods

Bleached softwood Kraft pulp was used for NFC production. The alpha-cellulose content and CED's viscosity was 90.4% and 16 cPs, respectively. The initial cellulose was soaked in water for at least three hours, then it was disintegrated by a disintegrator at 3000 RPM for 30 minutes.

Nanofibrillated cellulose isolation

An amount of 3 L of softwood bleached kraft pulp, with 1.5% consistency, was slowly added into the Masuko grinder funnel for isolating nanofibrillated cellulose. The intensity (2.0 A) and the revolution (1500 RPM) were adjusted and recorded. The number of passes was calculated relied on the softwood kraft pulp solution collected after each circulation. In this study, the softwood suspension was collected after it was passed through the Masuko grinder 19 times. The gap between the rotor and the stator was adjusted to -60 microns.

Nanofibrillated cellulose evaluation

Nanofibrillated cellulose morphology was observed using a Cold type Field Emission Scanning Electron Microscope (FE-SEM-4800 Hitachi – Japan). Diluted NFC suspension was deposited on a mica disk of 1 mm, air dried and coated with Pt for 50 s for FE-SEM analysis. FE-SEM scans were taken with 3-5 kV and a scale bar of 2 to 5 microns. An intense study on the length to width ratio was carried out using FE-SEM and imageJ analyses. These two selected methods were used to study the length of the 30 selected SW-NFCs.

Thermogravimetric analysis (TGA)

The thermal degradation of the bleached softwood Kraft pulp and isolated SW-NFC sample was investigated using thermogravimetric analysis (TGA Mettler Toledo). The sample was tested at a heating rate of 10 °C/min in the range of 30 °C to 500 °C, under a nitrogen atmosphere.

X-ray diffraction (XRD)

XRD (XPERT-PRO) was used to measure the crystallinity index of the SW and SW-NFC samples. For the crystallinity index assessment, the initial cellulose and isolated NFC were dried at 60 °C. The measurements were carried out over a range from 5° to 40° with a step size of 0.1050422°. The XRD was operated at 40 kV and 30 mA.

Tensile testing

The nanofibrillated cellulose suspension was cast on a glass dish setup on a calibrated table to form the NFC film. The dried NFC film was then kept in the conditioning room (23 °C, 50% RH – relative humidity) for two days. The NFC film was cut to the length-width size of 150 mm x 15 mm. The speed of the tester was set to 30 mm/min. The length between two grips was 100 mm. The testing load capacity was 250 kgf. The thickness of the samples was determined by a digital micrometer. Tensile strength and Young's modulus were calculated using a Universal Testing Machine, UTM Micro 350 tester (Testometric Co. Ltd., England).

RESULTS AND DISCUSSION

Evaluation nanofibrillated cellulose

The NFC was diluted to 0.005% for FE-SEM and imageJ evaluation. Length-width ratio analysis was performed on 30 single fibers selected. The FE-SEM images of the NFC were magnified from 2 to 5 microns for length investigation. Also, the same images of the SW-NFC were magnified up to 500 nm for the width investigation. The result shows that the length to width ratio of SW-NFC is almost 90 (Table 1). The FE-SEM evaluation and imageJ investigation do not present differences in length. Thus, to evaluate the length of the NFC, it would be possible to use imageJ analysis. It is a simple, easy and available to many research laboratories tool for determining the length without difficulty. Also, it is not always possible to operate FE-SEM or TEM for a sufficiently long time to evaluate the length of a certain number of NFC samples. Thus, using imageJ for evaluating nanofiber length from FE-SEM, TEM as well as AFM images, is convenient, cheap and easy.

When using FE-SEM, the length of NFCs was indicated on the images and easily defined. Each time, FE-SEM could determine the length of as many NFCs as were visible in the image. However, to have the full length of the NFC fibers, additional calculation should be done. The

length of each part can be calculated at the end of the process by Excel or manual calculation. In the case of using imageJ analyzer, the full length of the fiber will be determined automatically on a data sheet.

Details of NFC length-width ratio are shown in Figure 1. The images indicate clear full-length isolated SW-NFCs. In the case of the 5-micrometer magnification, the measurement was not used to detect the NFC width. At first, the length of the NFC was detected, then the NFC width was investigated by an additional high-magnification process. Individual NFCs were magnified from 1 micron to 500 nm and the width was determined. Thus, using these two simple methods, the length-width ratio of NFC was investigated.

Thermogravimetric analysis (TGA)

The thermal degradation stability of SW-NFC and initial cellulose was evaluated. The results indicate that the isolated SW-NFCs have their thermal degradation start at a little lower temperature value than that of the initial cellulose. NFC started to degrade at almost 305 ^{o}C, compared to around 310 ^{o}C for the initial one. It shows that the grinding treatment had a little adverse effect on the thermal degradation stability of SW-NFC. Furthermore, it is interesting to point out that SW-NFC presented higher thermal stability in the range of 370 to 500 ^{o}C. Also, the degradation residue of SW and SW-NFC were of 20 and 35%, respectively.

Table 1
Length to width ratio analysis (average value of 30 nanofibrillated cellulose samples)

	FE-SEM	imageJ
Length	4532 ± 2557 nm	4451 ± 2512 nm
Width	50.3 ± 14 nm	50.3 ± 14 nm (FE-SEM)
Ratio	90.2	88.6

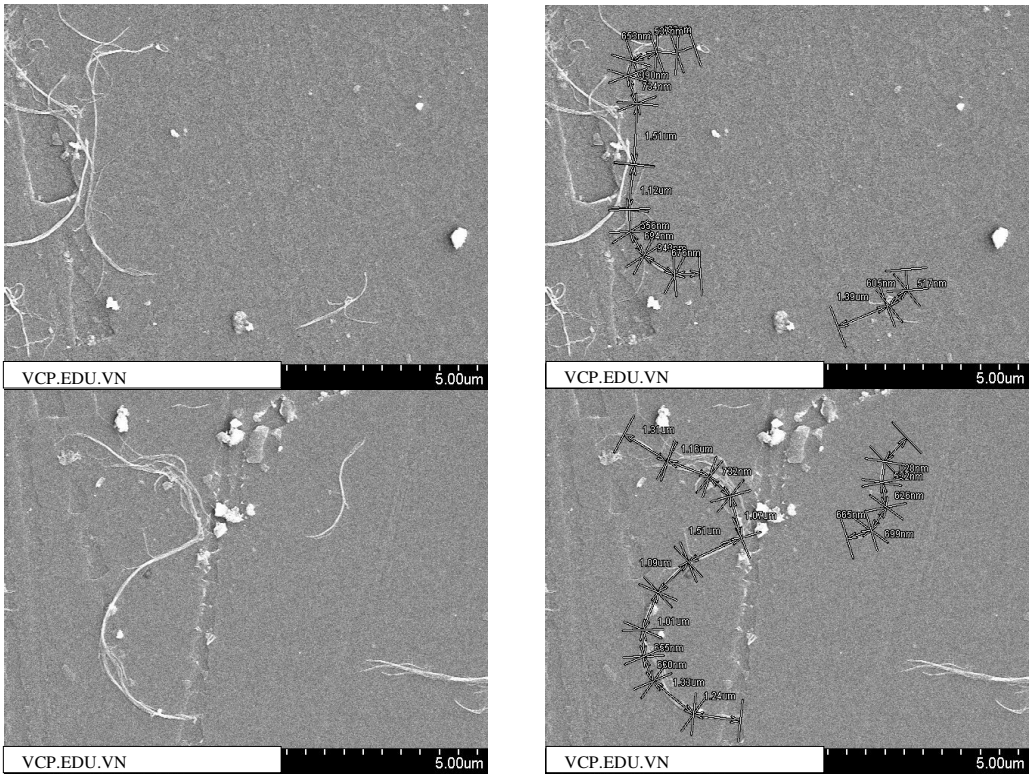

Figure 1: FE-SEM and imageJ analyzer were used to investigate SW-NFC length

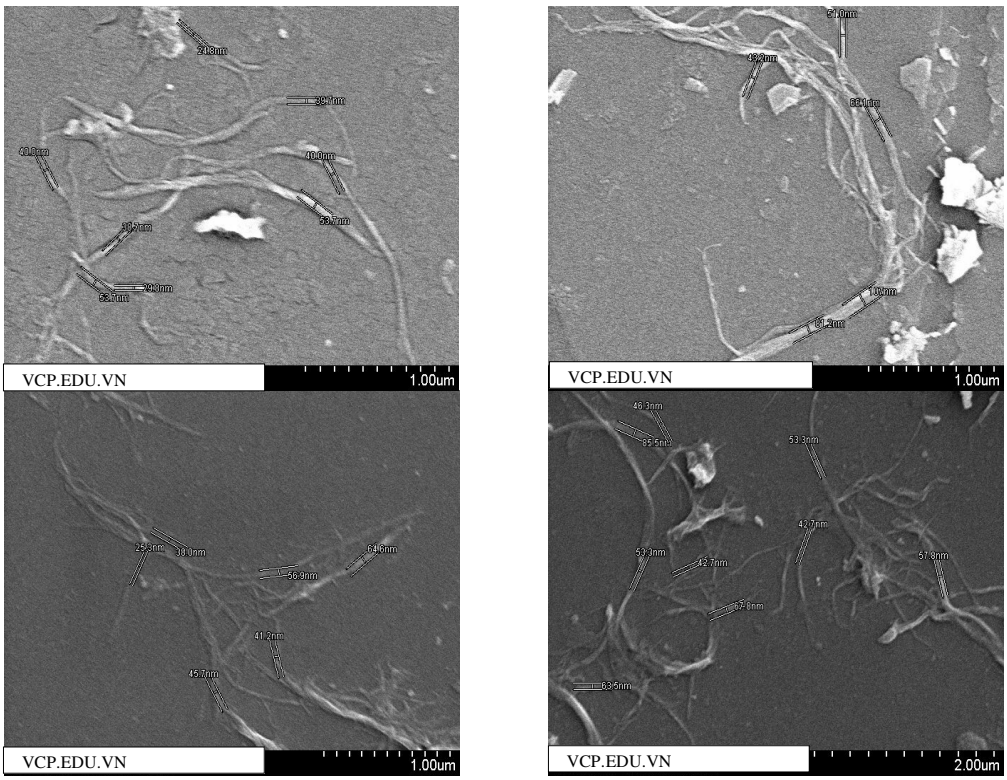

Figure 2: FE-SEM images used to evaluate the width of isolated SW-NFCs

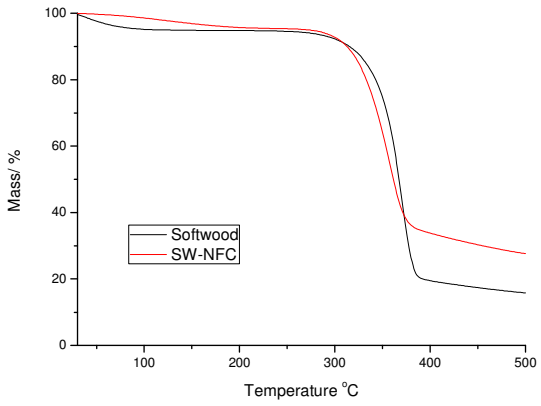

Figure 3: Thermogravimetric analysis of initial SW and isolated SW-NFC

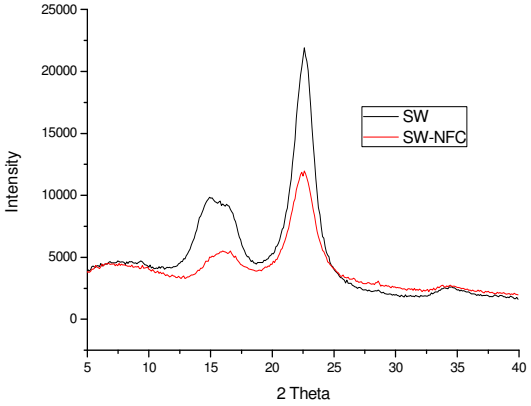

Figure 4: X-ray diffraction of initial SW and isolated SW-NFC

X-ray diffraction (XRD)

The crystallinity index of initial SW and SW-NFC was investigated. As a result, the crystallinity index of SW-NFC was decreased by the grinding treatment. More specifically, the crystallinity index dropped from 79.4% to 67.2%. The crystallinity index of the initial cellulose and isolated SW-NFC is shown in Figure 4. For the amorphous area, a 2 Theta value of 18.5^{o} was observed, while the crystallinity peak was around 22.5^{o}. Similar results regarding a decreased CrI% were reported by Tonoli.[17]

Tensile testing of SW-NFC film

The nanofibrillated cellulose suspension was cast on a calibrated glass to form a film for investigating its mechanical properties. The results show that the SW-NFC had high tensile strength and Young's modulus, as compared to its pristine cellulose source. The tensile strength

index of SW-NFC was 110 Nm/g, while it was only 20 Nm/g for the initial cellulose. Otherwise said, the tensile strength index is five times higher for SW-NFC than for initial cellulose. Young's modulus of SW-NFC was 9 GPa. This result is in agreement to that reported by Siro and Plackett.[26] The high strength development in the nanofibrillated cellulose may be explained by higher bonding within the nanofibrillated cellulose and improved individual nanofiber interaction within the cellulose films.

CONCLUSION

SW-NFC was successfully isolated using a Masuko grinder. By two simple methods, namely imageJ analysis and FE-SEM, the length to width ratio of nanofibrillated cellulose was evaluated. High magnification images were utilized for determining the width, while low magnification ones were used to assess the length of the fiber. The length-width ratio of the SW-NFC was around 90. The grinding treatment to obtain nanofibrillated cellulose was noted to have an adverse effect on its crystallinity index. However, the thermal stability of the isolated NFC did not appear to be negatively affected by the grinding treatment, on the contrary, NFC showed much better thermal stability in a high temperature range. Also, the SW-NFC film presented high tensile strength and Young's modulus.

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