**Research on Cleaner Production Process of Nano-cellulose and Its Application in Paper Strengthening**

Qijun Ding¹, Ping Zhang²

¹Foshan Polytechnic, Foshan, Guangdong, China
²School of Business Administration, Foshan Polytechnic, Foshan, Guangdong, China

Abstract: This experiment initially explored the clean production process of nanocellulose fibrils (NFC) using commercial softwood pulp as raw materials, and selected appropriate biological enzyme pretreatment to prepare NFC₁ with a higher concentration. Compared with NFC₂ obtained by TEMPO oxidation method, it is found that the diameter of NFC₁ obtained by enzymatic pretreatment method (10-30nm) is similar to that of NFC₂ (20-30nm). But the length of NFC₁ (1-4μm) is much longer than the length of NFC₂ (400-600nm). In addition, the influence of two kinds of NFC on the physical strength of paper is also explored. Experimental results show that: NFC₁ is better than NFC₂ in enhancing the physical strength of paper. And when cationic starch and NFC act synergistically, the enhancement effect is obviously better than using NFC alone or cationic starch alone. When the addition amount of NFC₁ is (1.5±0.5)%, the tensile index, burst index, and tear index of the resulting paper increase by (43±3)%, (55±1)%, (37±2), respectively %. When the amount of NFC₂ added is (1.5±0.5)%, the paper tensile index is (29±2)%. When the amount of NFC₂ added is about (3±1)%, the paper's bursting index and tearing index growth rate are (29±1)% and (33±1)% respectively.

1. Introduction

Nanocellulose fiber (NFC) is an ultrafine fiber with a diameter of less than 100nm. Compared with ordinary cellulose fibers, NFC has many excellent characteristics, such as high specific surface area, high strength, high Young's modulus, high strength, light weight, biocompatibility etc. It is used in papermaking, construction, cosmetics and electronic products. Medical equipment and other fields have huge application prospects. NFC with the above excellent properties can be prepared by mechanical method, chemical-mechanical method, enzyme treatment method, and biological method [1,2,3]. Among them, the chemical-mechanical method (TEMPO oxidation method) is currently a more mature preparation method.

In recent years, a large number of research reports have shown that NFC is suitable for the papermaking process of paper, thereby improving the physical strength of paper [4,5,6,7]. The main reason for strengthening the paper is that NFC has a large aspect ratio and strong physical interweaving with pulp fibers, which improves the bonding force between pulp fibers, thereby increasing the physical strength of the paper. Many researchers use the TEMPO oxidation method to prepare NFC and explore its effect on the physical strength of paper. However, these two methods have the disadvantages of serious environmental pollution and high energy consumption in the process of preparing NFC, so they are not economically feasible, and are not suitable for large-scale application in the paper industry as a
paper strengthening agent. Therefore, it is necessary to research and develop a clean production process that is economically feasible and environmentally friendly, so as to realize the industrial application of NFC.

The enzymatic treatment method uses cellulase to selectively enzymatically hydrolyze the amorphous area of cellulose, which directly acts on the fiber surface to produce many branches on the smooth fiber surface, thus playing the role of fibrillation. In this process, the fiber surface may be corroded, peeled, and fibrillated and cut[8]. The preparation process of enzymatic hydrolysis is mild and specific, and the reagent enzymes and cellulase used are both renewable resources, so it is of great significance to the sustainable development of society. In this experiment, biological complex enzymes were used to pretreat cellulose raw materials to explore the clean production process of enzymatic preparation of NFC and analyze the morphology of NFC1 prepared by enzymatic method and NFC2 obtained by TEMPO oxidation method. In addition, the NFC1 prepared by the biological enzyme pretreatment method and the NFC2 obtained by the TEMPO oxidation method were used as papermaking aids to compare and analyze the influence of different NFC on the physical strength of paper. It is expected that NFC1 can replace NFC2 to realize the large-scale application of NFC in the papermaking field.

2. Experiment

2.1 Experimental materials and instruments

softwood pulp: beating degree 13.5°SR; cellulase (from Trichoderma reesei), enzyme activity 250FPU/ml; Banzyme 2900; citric acid-sodium citrate buffer solution: 0.05mol/L, pH=4.8; TEMPO reagent; NaBr; NaClO; NaOH.

PFI refiner (HAMJERN MASKIN 621); water bath; nano refiner (domestic); ultra-high pressure homogenizer (Nano DeBEE); Kaiser method (RK3AKWT); Canadian freeness meter (PTIME-13); Atomic Force Fiber Mirror (AFM); Tensile Strength Tester (L&W CE062); Tear Strength Tester (L&W 009); Bursting Strength Tester (L&W CE180).

2.2 Preparation of NFC1

In the experiment, commercial softwood pulp was used, and NFC1 was prepared through processes such as refining, enzymatic hydrolysis, nano-refining, and high-pressure homogenization. In the refining section, two process methods, 20% (w/v) thick refining and 10% (w/v) thick refining are used. Enzymatic treatment of the two slurries with beating enzyme and cellulose complex enzyme respectively. The pulp concentration during enzyme treatment is 5% (m/v).

2.3 Papermaking

NFC1 papermaking: According to the pulp dry ratio of 0, 0.5%, 1%, 1.5%, 2%, 3%, 5%, it is added into the pulp for papermaking. The basis weight of the paper is 60g/m². The physical properties of the paper after drying were tested.

The specific process is that the pulp is decomposed for 5000r, then NFC1 is mixed with the pulp and stirred for 30 minutes. Add 1.5% (relative to the bone-dry pulp) of cationic starch to the mixed slurry and continue stirring for 30 minutes. Finally, the mixed slurry is decomposed for 10000r and papermaking is carried out.

NFC2 papermaking: According to the pulp dry ratio of 0, 1%, 1.5%, 2%, 3%, 4.5%, 10%, it is added to the pulp for papermaking. The basis weight of the paper is 60g/m². Test the physical properties of the paper after drying. The specific process is that mixing NFC2 with pulp and decomposing 10000r, then adding 1.5% (relative to the bone dry pulp) cationic starch to the mixed slurry. Finally, continue to parse 10000r and make paper.

2.4 Analysis and testing

NFC morphology analysis: Dilute the NFC to a concentration of one hundred thousandths of five parts
after ultrasonic dispersion. Then drop on the mica sheet to dry and observe its shape under AFM.

The tensile strength, burst strength and tear strength of the paper were tested according to the national standards GB/T 26460-2011, GB/T 465.1-2008, and GB/T 455-2002.

3. Results and discussion

3.1 Morphological analysis of NFC1

Figure 1 shows the AFM diagram of NFC1. Among them, a, c, and e are the AFM pictures of NFC1. The scanning range of the probe is 1μm, 2μm and 5μm respectively. b, d, f are the AFM diagrams of NFC1. The scanning range of the probe is 2μm, 2μm and 4μm respectively. From Figures a and b, the diameter of NFC1 can be measured in the range of 10-30nm. The diameter of NFC1 is in the range of 20-60nm. This shows that the diameter of the NFC obtained under high-concentration refining and high-concentration homogenization is smaller and more uniform than that of low-concentration refining and low-concentration homogenization. This may be due to the strong mechanical shearing force on the fiber directly contacting the disc mill in the state of low concentration and high pressure refining, and the less force on the non-contact fiber. This phenomenon of uneven force leads to uneven distribution of NFC1 filament diameter. On the contrary, the mechanical shearing force acting on the fiber under the high concentration and low pressure refining state is relatively small, mainly relying on the friction between the fibers to promote the uniform dispersion of the fibers into NFC filaments.

It can be seen from the figures c, d, e, and f that when the scanning range of the probe is 2 μm, neither NFC1 nor NFC1 can present a complete single filament. When the scanning range of the probe is expanded to 4-5 μm, a complete single NFC1 and NFC1 filament can be shown in the figure. This shows that the length of the NFC prepared by the enzymatic method has reached the micron level and is about 1-4 μm. This may be due to the enzyme treatment destroying the surface structure of the fiber and the non-crystalline area. The loose fiber inside the fiber is easy to absorb water and swell. Under the action of mechanical force, the fiber surface is easier to split into filaments, and longer nanofibrils are obtained.

Figure 1 AFM diagram of NFC1. a, c, e are NFC1.1 diagrams. The scanning range of the probe is 1μm, 2μm and 5μm respectively. b, d, and f are NFC1. The scanning range of the probe is 2μm, 2μm and 4μm respectively.
3.2 NFC2 morphological analysis

Figure 2 shows the AFM diagram of NFC2. Figure a The probe scanning range is 1μm. The scanning range of the probe in Figure b is 2μm. From Figure a, the diameter distribution range of NFC2 can be measured to be 20-30nm. From Figure b, the length distribution range of NFC2 can be measured to be 400-600nm. In this experiment, the degree of oxidation of TEMPO is relatively light, but the aspect ratio of the obtained NFC2 is not high. This may be due to too many homogenization times in the subsequent high-pressure homogenization process. The cutting effect of NFC2 is more significant, resulting in a serious decrease in length. However, as the number of homogenization increases, the size of NFC2 is relatively uniform.

![AFM diagram of NFC2](image)

Figure 2 AFM diagram of NFC2. The scanning range of the probe in Figure a is 1μm. The scanning range of the probe in figure b is 2μm.

3.3 The enhancement effect of NFC1 and NFC2 on paper

Because NFC1,1 has a more uniform structure. Therefore, the NFC1 obtained by the enzymatic method (hereinafter referred to as NFC1) and the NFC2 obtained by the TEMPO oxidation method are selected as the papermaking additives to be used in the papermaking process. Compare and analyze the influence of NFC obtained by different preparation processes on the physical strength of paper.

The experimental results are shown in Figure 3. Figures a, e, and f show the influence of NFC1 on the tensile index, bursting index and tear index of paper. Figures b, d, and g show the influence of NFC2 on the tensile index, burst index and tear index of paper. It can be seen from a-f that adding cationic starch can significantly improve the strengthening effect of NFC on paper. No matter NFC1 or NFC2. After blending with softwood pulp, the physical strength is improved. However, the effect of paper enhancement is unstable under different addition levels. This may be due to the fact that NFC itself is easy to agglomerate and is unevenly dispersed in the process of blending with pulp. It may also be due to the instability of NFC retention rate during the sheet forming process.

It can be seen from Figure a that when the amount of NFC1 added is (1.5±0.5)% and the amount of cationic starch added is 1.5%, the growth rate of the tensile index of the paper is (43±3)%. When only cationic starch is added, the growth rate of tensile index is only (12±2.5)%. It can be seen from Figure b that when the amount of NFC2 added is (1.5±0.5)% and the amount of cationic starch added is 1.5%, the growth rate of the tensile index of the paper is only (29±2)%. This shows that the NFC1 prepared in this experiment is better than NFC2 in enhancing the tensile strength of unbeaten softwood pulp. This may be due to the length-to-diameter ratio of NFC1 prepared by the enzymatic method in this experiment is greater than the length of NFC2. It has a strong interweaving effect with fibers in the process of paper mixing. It is also possible that the interaction time between NFC1, slurry and cationic starch in the
process of NFC1 and paper mixing in this experiment is longer than NFC2, which makes the combination of the three more stable.

It can be seen from Figure c that when the addition amount of NFC1 is (1.5±0.5)% and the addition amount of cationic starch is 1.5%, the paper's bursting index growth rate is (55±1)% When only cationic starch is added, the growth rate of burst resistance index is only (16±2)%. It can be seen from Figure d that when the amount of NFC2 added reaches (3±1)%, the paper's bursting index growth rate is only (29±1)%. It can be seen from Figure e that when the amount of NFC1 added is (1±0.5)% and the amount of cationic starch added is 1.5%, the growth rate of the tear index of the paper is (37±2)% When only cationic starch is added, the growth rate of tear index is only (17±1)%. It can be seen from Figure f that when the amount of NFC2 added is (3±1)% and the amount of cationic starch added is 1.5%, the growth rate of the tear index of the paper is (33±1)%. This shows that the NFC1 prepared by the enzymatic method in this experiment has a more obvious strengthening effect on the paper when the addition amount of (1.5±0.5)%. The addition of NFC2 needs to be (3±1)% to enhance the paper significantly. The enhancement effect of NFC2 on paper in this experiment is basically the same as that of NFC made by TEMPO oxidation in the literature.

Figure 3. The effects of NFC1 and NFC2 on the physical strength of paper. Figures a, c, and e are the effects of NFC1 on the paper's tensile index, burst index, and tear index, respectively. Figures b, d, and f are the effects of NFC2 on the tensile index, bursting index, and tearing index of paper.

4. Conclusion
1. In this experiment, NFC1 was prepared by enzymatic method. When the enzyme dosage is 50g/kg pulp, the NFC1 yield is (90±2)% when the treatment time is 15h, the diameter is 10-30nm, and the length is 1-4μm. Has a higher concentration and a larger aspect ratio;
2. The NFC1 prepared by the enzymatic method has a significant enhancement effect on the physical strength of unbeaten softwood pulp;
3. When cationic starch is added, it can significantly improve the enhancement effect of NFC on pulp. When the addition amount of NFC1 is (1.5±0.5)%, the growth rate of the tensile index, breaking index and tearing index of the paper are (43±3)%, (55±1)%, (37±2), respectively. When the amount of NFC2 added is (1.5±0.5)%, the paper tensile index is (29±2)%. When the amount of NFC2 added is about (3±1%), the paper's bursting index and tearing index growth rate are (29±1)% and (33±1)% respectively.

Acknowledgement.
Supported by Guangdong Basic and Applied Basic Research Foundation (2019A1515110708).
References

[1] Williams W S, Cannon R E. Alternative environmental roles for cellulose produced by acetobacter xylinum[J]. Applied and Environmental Microbiology, 1989, 55(10): 2448-2452.

[2] Henriksson M, Henriksson G, Berglund L A, et al. An environmentally friendly method for enzyme-assisted preparation of microfibrillated cellulose (MFC) nanofibers[J]. European Polymer Journal, 2007, 43(8): 3434-3441.

[3] Delgado-Aguilar M, González I, Tarre’s Q, Pe ‘lach MA’, Alcala M, Mutje´ P (2016) The key role of lignin in the production of low-cost lignocellulosic nanofibres for papermaking applications. Ind Crops Prod 86:295–300.

[4] Eriksen O, Syverud K, Gregersen O (2008) The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. Nord Pulp Pap Res J.23(3):299–304.

[5] González I, Boufi S, Pe ‘lach MA, Alcala´ M, Vilaseca F, Mutje´ P (2012) Nanofibrillated cellulose as paper additive in eucalyptus pulps. BioResources 7(4):5167–5180.

[6] Syverud, K., Gregersen, Ø., Chinga-Carrasco, G. and Eriksen, Ø. (2009): The influence of microfibrillated cellulose, MFC, on paper strength and surface properties, In: l’Anson, S.J. (ed.), Advances in pulp and paper research, Oxford 2009, Volume 2, Pulp and Paper Fundamental Research Society, Bury, 899-931.

[7] Madani, A., Kiiskinen, H., Olsson, J. and Martinez, M. (2011): Fractionation of microfibrillated cellulose and its effects on tensile index and elongation of paper, Nord. Pulp Paper Res. J., 26:(3), 306-311.

[8] Ahola, S., Österberg, M. and Laine, J. (2008): Cellulose nanofibrils – adsorption with poly(amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive, Cellulose, 15(2), 303-314.