OPTIMIZATION OF NANOPAPER PREPARATION FROM TROPICAL PIONEER SPECIES

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Abstract— **This study shows about optimization of nanopaper preparation from tropical pioneer species in Peninsular Malaysia like Mahang wood which by adding nanocrystalline cellulose (NCC) into paper. The first outline is this research need to extract desired structure of nanocellulose, NCC from Mahang wood sample as a main raw cellulose material that was obtained from Forest Research Institute Malaysia (FRIM). The outline want to optimize the extraction on desired structure from nanocellulose in the Mahang. Secondly, the NCC were extracted from the bleached pulps must by cellulase hydrolysis rather than acid treatments and had been analyzed for their physical, mechanical and optical properties. The purpose using the enzyme is to reduce using of harsh and unfriendly chemicals towards environment. Thirdly, selected amount of NCC need to undergo fluorescent grafting process with different fluorescein concentrations and pH conditions for determine the degree of substitution fluorescein in NCC suspension under fluorescent microscope. Then, there will be different amount of NCC yield mix with same pulp in different condition of nanopaper preparation. This outline want to show effectiveness of NCC as an additive to give advantages toward paper. The result of the study is the effect of enzymatic hydrolysis in NCC extraction and the optimum pH for grafted NCC to use in nanopaper preparation. The desired structure obtained in the study is NCC with average length of the NCC is 514.9nm and the yield is 12.06%. The optimum pH for grafted NCC is ph11. There are six samples of grafted NCC nanopaper with different concentrations, 0%, 0%, 1%, 2.5%, 5%, and 10% respectively. The tensile strength of Sample 1, 2, and 3 is decrease linearly, 1.64kN/m, 1.52kN/m, 1.424kN/m then the tensile strength of Sample 4, 5, 6 is increase linearly, 1.744kN/m, 2.072kN/m, 2.44kN/m.**

Keywords— enzyme, fluorescent nanocellulose, nanocrystalline cellulose, nanopaper

I. INTRODUCTION

Nanotechnology is a rising territory of science and technology that will revolutionize use in the 21st century. The moderately unrefined and unsophisticated technology on which we presently depend will be replaced with very productive and environmentally friendly nanotechnologies (Wegner & Jones, 2009). The finding of novel materials, procedures, and phenomena at the nanoscale and the development of new experimental and theoretical techniques for research give crisp chances to the improvement of creative nanosystems and nanostructured materials (Bharat, 2010).

The papermaking application of employing nanoparticle systems has evolved to become more of a "properties" management system during papermaking, and beyond the mill at converting operations and printers. Nanotechnology developments in areas of fiber science, minerals and other additives will give papermakers the means to put order and structure into the designs of a sheet (Innova, 2004). NCC has the capability of turning into an imperative class of renewable nanomaterials, which could discover numerous helpful applications. The main application of NCC is for the reinforcement of polymeric matrix in nanocomposite materials (Peng, Dhar, Liu, & Tam, 2011). Besides that, NCC can improves barrier properties in nanocomposite. In particular, food packaging materials require both mechanical strength and barrier for such molecules as gases (mainly oxygen), moisture migration, flavour and aroma control. Barrier property investigations of NCC-improved materials have mainly focused on water vapour transmission and oxygen permeability (Brinchi, Cotana, Fortunati, & Kenny, 2013).

The addition of NCC in papermaking process has been identified as a method to improve physical and mechanical properties of paper, however there is a possibility that some of the NCC added are lost in the whitewater due to its small size. This results in significant property improvement. Hence, there is a need to identify the optimum papermaking process protocol which retains most of the NCC to be effective as an additive.

Nanocellulose- Cellulose structure with commonly size at least one dimension in nanoscale (1–100 nm) are referred to as nanocellulose. Depending on the production conditions, which influence the dimensions, composition and properties, nanocellulose can be split up into two main cate-gories: (i) cellulose nanocrystals (NCC) or cellulose whiskers and (ii) cellulose nanofibrils (CNF), also known as nanofibrillated cellu-lose (NFC), microfibrillated cellulose (MFC) or cellulose nanofibers (Nechyporchuk, Belgacem, & Bras, 2016).

Nechyporchuk et al. (2016) found the extraction of NCC utilizing acid hydrolysis of cellulose strands dispersed in water were initially created by Rånby (1949). In this method as usual, concentrated sulfuric acid is regularly utilized, which degrades amorphous regions of cellulose and leaves in place the crystalline ones. By such treatment, rod-like rigid NCC with sulfate groups at their surface are produced. Their morphology generally relies on upon the source of cellulose. Ordinarily, NCC with a measurement of 3–35 nm and a length of 200–500 nm are created. However, there is enzymatic way as pretreatment of cellulose for obtaining NCC. According to Brinchi et al. (2013), limited literature has yet been published for ways to introduce enzymes in the preparation process of NCC. In recent study, Beltramino et al. (2015) introduced cellulase in the preparation of cotton linters NCC. The objective using cellulase in the study was to evaluate the effect of this pretreatment on the characteristics showed by final product and to make a first trial to establish working parameters in order to partially replace the use of harsh chemicals, by this environmentally friendly catalyst (Beltramino, Roncero, Vidal, Torres, & Valls, 2015).

Enzymatic hydrolysis- Commonly, mostly researchers extracting NCC from cellulose using acid hydrolysis compare to enzymatic hydrolysis because acidic hydrolysis produces both high quality and crystallinity compare to the enzymatic treatment. The more extensively used method to obtain these crystalline regions consists of a controlled hydrolysis with sulfuric acid, basically due to the stability of the resulting suspensions (Abitbol et al., 2013; Habibi et al., 2010). During this reaction, amorphous domains are attacked preferentially, while crystalline regions present higher resistance to acid attack (Habibi et al., 2010). However, the enzymatic hydrolysis is an environmental-friendly treatment which is less toxic to the environmental compared to the acidic hydrolysis treatment. A recent study has shown that enzymatic hydrolysis have been used for extracting NCC from local fast–growing pioneer timber species such as Mahang and Acacia. A high recovery of 80% was achieved via enzymatic hydrolysis compared to acidic hydrolysis which is 40%. This study shows that enzymatic hydrolysis produces NCC with higher yield but lower crystallinity compared to acid hydrolysis (Adnan & Jasmani, 2016).

II. METHODOLOGY

A. Materials

Raw materials that used in this experiment are sodium hydroxide (NaOH), sodium chlorite ($NaClO_2$), hydrochloric acid (HCl), cellulase and fluorescein. These raw materials are purchased from local chemical suppliers. The main raw material for NCC extraction is Mahang wood are obtained from FRIM campus.

B. Methods

Soda pulping is carried out using a 16L Rotary Digester with fibre to liquor ratio of 1:6 NaOH charge 25%, with temperature of 170˚C and total time of 3.5 hour. The resulting pulp is washed and screened to remove shives.

In **pulp bleaching** process, the pulp is bleached by 5 stages of elementary chlorine free process (ECF) using chlorine dioxide (D) and alkali extraction (E) according to the following Table 1. 100g OD equivalent of pulp is bleached in polyethylene bags for each set.

	D1	E1	D2	E2	D3
Chemical & charge (%)	ClO_2 3	NaOH 2	ClO_2 3	NaOH 2	ClO_2 3
Pulp consistency (%)	10	10	10	10	10
Time (min)	120	60	90	60	90
Temperature (˚C)	70	70	70	70	70

Table 1: Bleaching condition

Next for the **NCC extraction**, 20g OD (oven dry) of cellulose is obtained from part is placed in 1000mL flask. Then, 400mL 0.05M sodium acetate buffer solution and 1mL enzyme is added into the flask. The 0.05M sodium acetate needs to prepare by diluting 4.1g sodium acetate salt in 1000mL distilled water. After the sodium acetate and enzyme are added, stir the mixture before adding the cellulose. Then, the flask is placed in rotary digester at 150rpm, room temperature for 48 hours. At the end of stated hydrolysis period, the cellulose is quickly filtered. The filtrate is removed into a bottle and keeps in refrigerator. The solid is transferred back into the beaker and 750mL of boiling distilled water is added and stirred for 10 minutes. The hydrolyzed cellulose is then washed and rinsed with 1000mL distilled water twice by using filter funnel with porosity 2 (pore size of 400-100μm). After the hydrolyzed cellulose is filtered, the retentate is transferred into homogenizer for shear homogenization for 2 hours. The suspension is transferred into a bottle and sonicated for 30 minutes. The concentration of suspension is determined using oven drying method. The suspension is adjusted to 1wt% and kept in refrigerator for further used. The hydrolysis yield is calculated based on the starting material of the 20g OD of cellulose. Finally, the analyses is carried out, particle size, AFM (Atomic force microscope), and TEM (Transmission electron microscope).

The next step is **fluorescent grafting of NCC**. About 0.2g of NCC at 1wt% concentration is mixed with acid/alkali solution to adjust its pH, (5,7,11) before fluorescein reagent is added with concentration 1%, 1.5%, 2%, 5%). The mixture is left in the dark at room temperature with constant stirring and with time, 24 hours. The reacted mixture is centrifuged and washed with distilled water three times to remove unreacted fluorescein. The final NCC is kept in 1% suspension before further analysis. Results are evaluated to identify the optimum condition to be repeated. Table 2 is referred for experimental conditions. The degree of substitution is determined for all runs using calibration curve of fluorescein under fluorescence microscope.

No.	pH	Fluorescein concentration (%)	Fluorescein weight (g)	Grafting hours (hours)
1	5	2	0.004	24
2	7	2	0.004	24
3	11	2	0.004	24
4	11	1	0.002	24
5	11	1.5	0.003	24
6	11	5	0.010	24

Table 2: Experimental conditions for fluorescein grafting

The final step is **nanopaper preparation**. Standard 60±3 gsm laboratory handsheets are prepared according to TAPPI T205 method. For NCC incorporation, some modifications are made.

12g OD pulp are disintegrated with NCC in 1L of water. The mixture is transferred to the stock divider and enough water is added to make 4L stock. Alum is added and the stock pH is recorded. For control handsheets, sulphuric acid or NaOH is added if the pH range is not within 5.5-6.5. 1L mixture is taken out for CFS measurement. 4L of water is added to the remaining stock and continuously mixed. 1L of stock solution is taken out for weight correction. Water is added or removed accordingly. After correction, 1L stocks are taken out for handsheet making. Table 4 is referred for list experimental runs.

The pulp freeness, zeta potential and drainage time are recorded. Physical mechanical and optical properties of handsheet prepared are determined. The NCC retention contents are determined using fluorescent microscope.

No.	Pulp	pH	Alum (%)	Alum weight (g)	NCC Concentration (%)	NCC weight (g)
1	Mahang bleached soda	-	0	0	0	0
2		5.5-6.5	2	0.28	0	0
3		5.5-6.5	2	0.28	1	0.12
4		5.5-6.5	2	0.28	2.5	0.30

5		5.5-6.5	2	0.28	5	0.60
6		5.5-6.5	2	0.28	10	1.20

III. RESULTS AND DISCUSSION

A. The effect of enzymatic hydrolysis in NCC extraction

There were ten bottles of NCC collected and with weight total 9.0545g. The NCC were extracted by hydrolyzed with cellulase from *Thricoderma reesei* (ATCC 26921). The amount of pulp used 20 g OD which mean 74 g AD (air dry). The yield for the NCC is 12.06% which is very low. According to local recent study, the enzymatic way got higher yield but lower crystalinity compare to the harsh chemical way [2].

There is a way to identify the extracted component known as NCC is by testing under zeta potential test. The zeta sizer result for the NCC:

Z-Ave (d.nm)			
1	2	3	Average
547.1	505.0	492.7	514.9

The average length of the NCC is 514.9nm. This result shows that the extracted NCC quite same with past study which the length ordinarily 200–500 nm [6].

So the extracted product is NCC but the yield is low. The problem occur maybe from the low activity of the enzyme because the activity of the enzyme never tested before starts the experiment and maybe some of the NCC had missing during filtration process.

B. The optimum pH for grafted NCC to use in nanopaper preparation

The fluorescent grafting method is to know the best condition by observing the degree of substitution of fluorescein in NCC under a fluorescence microscope. There are several picture were captured by the microscope:

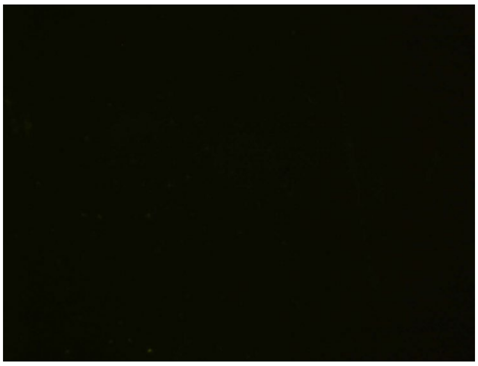


Figure 1: No. 1 (ph 5, 2% fluorescein concentration)

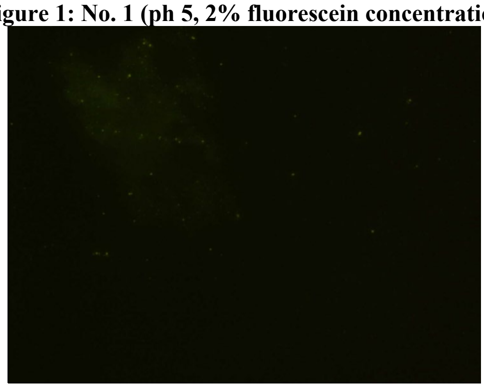


Figure 2: No. 2 (ph 7, 2% fluorescein concentration)

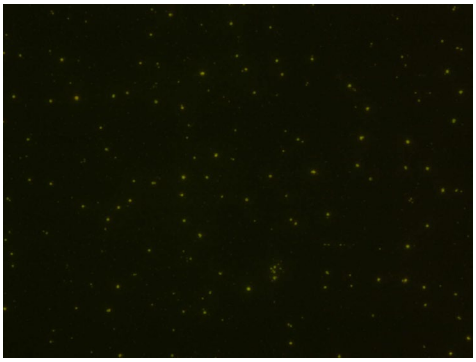


Figure 3: No. 3 (ph 11, 2% fluorescein concentration)

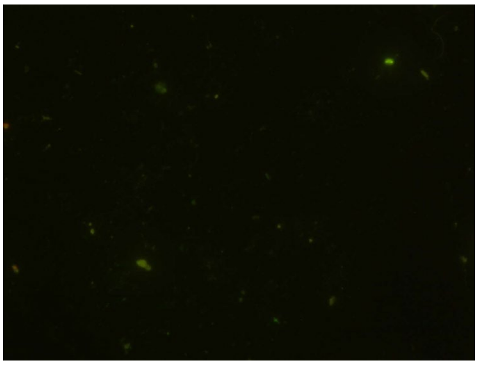


Figure 4: No. 4 3 (ph 11, 1% fluorescein concentration)

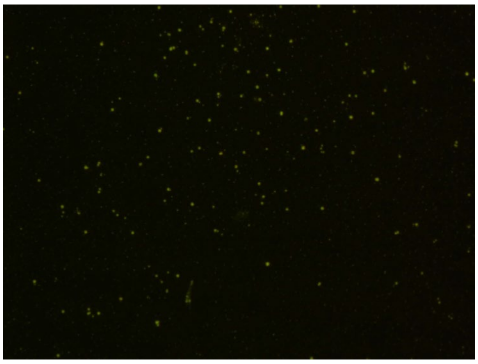


Figure 5: No. 5 (ph 11, 1.5% fluorescein concentration)

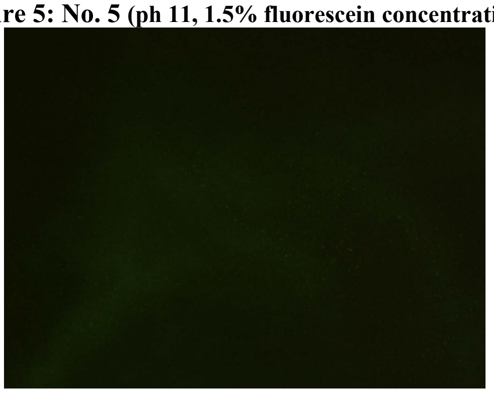
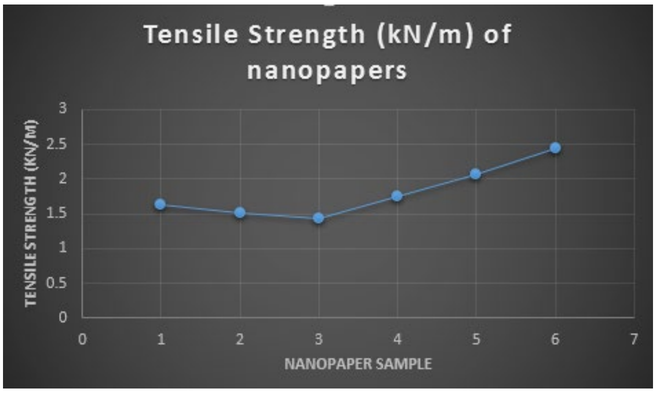


Figure 6: No. 6 (ph 11, 5% fluorescein concentration)

From all the pictures above, No. 3 and No. 5 are clearly observed the grafted NCC with high quantity and brightness compared to No. 1, No. 2, No. 4, and No. 6. So the optimum pH for grafted NCC to use in nanopaper is in pH 11 bacause the high degree substitution of fluorescein in NCC which the NCC later give advantage as an additive towards paper when it disintegrated with pulp. The pH value is same with recent study by Tiffany Abitbol (2013) which had mentioned the optimum pH in grafting the NCC [1]. The NCC also were proposed as optical markers for the dispersion quality of NCC-loaded polymer composites.

C. *The effect of NCC as an additive toward nanopaper*



There are six samples of grafted NCC nanopaper with different concentrations, 0%, 0%, 1%, 2.5%, 5%, and 10% respectively. From the graph above, the tensile strength of Sample 1, 2, and 3 is decrease linearly, 1.64kN/m, 1.52kN/m, 1.424kN/m then the tensile strength of Sample 4, 5, 6 is increase linearly, 1.744kN/m, 2.072kN/m, 2.44kN/m. The Sample 3 should get higher tensile strength compare to the Sample 1 and 2 because the Sample 3 is added with 1% of NCC while none NCC added in Sample 1 and 2. Fact, the NCC should give extra strength towards the paper. This problem occur maybe because the leaking in stock divider while making the paper. However, the Sample 4, 5, and 6 proved that the NCC can give extra strength and be good as an additive to give physically advantage toward paper.

IV. Conclusion

The conclusion of this study is the possibility for extracted NCC yield is low because of the enzyme does not give optimum impact towards pulp in enzymatic hydrolysis for NCC extraction due to its low activity. However, this study obtained the optimum condition for NCC used in nanopaper is in alkaline condition with pH 11 and proved that the NCC contributed its strength and good as an additive to give physically strength toward paper. The result may not quite satisfied but further improvement will needed in future especially in NCC extraction.

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