# PREPARATION AND CHARACTERIZATION OF CELLULOSE NANOCRYSTALS (CNC) FROM KENAF FIBER VIA ACID HYDROLYSIS

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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I hereby, declared this report entitled ―Preparation and Characterization of Cellulose Nanocrystal (CNC) from Kenaf Fiber via Acid Hydrolysis" is the result of my own research except as cited in references.

Signature : ……………………………………

Author's Name : NUR SYAHIRAH BINTI ROSNAN

Date : 22 JUN 2017

# APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The members of the supervisory committee are as follow:

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# ABSTRAK

Serat kenaf ialah serat semulajadi yang mudah didapati dan mempunyai harga yang lebih murah berbanding dengan serat semulajadi yang lain. Terdapat peningkatan minat dalam penggunaan serat kenaf sebagai bahan mentah dalam pelbagai aplikasi kerana kandungan selulosa yang tinggi di dalam tumbuhan ini. Pelbagai kajian telah dilaksanakan untuk mengkaji kaedah sintesis nanokristal selulosa (CNC). Berdasarkan kajian lepas, masih belum ada kajian yang melaporkan kaedah sintesis nanokristal selulosa serat kenaf menggunakan kaedah asid hidrolysis dengan menggunakan kepekatan asid yang optimum. Oleh itu, dalam kajian ini, proses sintesis nanokristal selulosa serat kenaf dengan menggunakan kepekatan asid yang optimum di kaji secara menyeluruh. Selain itu, kesan kepelbagaian kepekatan asid terhadap morfologi dan penghabluran nanokristal selulosa serat kenaf juga dinilai. Analisis penghabluran nanokristal selulosa ditentukan dengan menggunakan analisis XRD. Untuk rawatan alkali, analisis XRD menunjukkan indeks kristal meningkat selepas rawatan dan keputusan ini disokong melalui analisis FTIR yang mendedahkan bahawa tiada kehadiran puncak untuk lignin dan hemiselulosa di spektra fiber selepas rawatan alkali. SEM mikrograf untuk serat kenaf sebelum rawatan dan selepas rawatan dibandingkan dan fiber dengan rawatan daripada 6 wt.% NaOH mempunyai permukaan yang bersih tetapi kelihatan bergerigi dan kasar bila disentuh. Untuk proses asid hidrolisis, index kristal CNC meningkat jika kepekatan asid yang digunakan meningkat tetapi jika masa hidrolisis dipanjangkan, indeks kristal akan menurun. Keputusan eksperiment menunjukkan bahawa kepekatan asid yang optima ialah 30 wt.% dengan 90 minit dan suhu setinggi 45 ºC. Melalui penghasilan CNC daripada serat kenaf, kajian ini telah menyumbang untuk masa depan aplikasi didalam industri nanokomposit sebagai bahan pengikat untuk komposit polimer. Oleh itu, penggunaan CNC daripada serat kenaf boleh dikatakan sebagai produk hijau dan selari dengan trend rekaan dan perkembangan kemampanan.

# ABSTRACT

Kenaf fibre is a one of the natural fibre that is commercially available and there is a growing interest in the use of kenaf fibre as a raw material in many applications due to its high content of cellulose in plant. Numerous studies have investigated the synthesizing of cellulose nanocrystals (CNC) from kenaf fibre by using chemical treatment such as acid hydrolysis. Based on the previous study, there is no study has been reported on optimum acid concentration as a parameter of using hydrolysis method. Therefore, in this study, the process of synthesizing cellulose nanocrystals by using acid hydrolysis method with optimum acid concentration is comprehensively studied. In addition, the influence of different acid concentration on the morphology, crystallinity of cellulose nanocrystals and crystallite size were also evaluated. The crystallinity analysis of cellulose nanocrystals kenaf fibre is determined by using X-ray diffraction (XRD) analysis. For the alkali treatment, the XRD analysis shows that the crystalinity index (CrI) of the alkali treated fiber increased and this result is confirmed by FTIR analysis which reveals that peaks for lignin and hemicellulose at were absent from the spectra of the alkali-treated fibers. The SEM micrograph of the untreated fiber and alkali treated fiber is then compared and the 6 wt. % NaOH treated fiber has a cleaner surface but looks jagged and feels rougher when touched. For acid hydrolysis, it can conclude that the CrI of the CNC will increase if the concentration of acid used increased but if the hydrolysis time is prolonged, the crystallinity index of the CNC will decreased. From the result obtained, it shows that the optimum acid concentration is 30 wt. % with 90 minutes hydrolysis time and 45 ºC temperature. By producing the CNC from kenaf fiber, this research contributes in future for the application in nanocomposites industry as reinforcing material for polymer composite. Hence, the use of CNC from kenaf fiber can be considered as green material and align well with the global trends of sustainability design and development.

# DEDICATION

Dedicated to
my beloved father,
Rosnan Bin Jaafar
my appreciated mother,
Juwahir Binti Jaffar
my adored siblings,
Nur Syafikah, Mohd Syariq and Nur Syuhada
my respected lectures and my friends for
giving me moral support, encouragement, cooperation and also understanding.
Thank you so much.

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| | | |
|---|---|---|
| AC | - | Activated carbon |
| BC | - | Bacterial cellulose |
| C-H | - | Carbon – hydrogen bond |
| $CH_3CO$ | - | Acetyl group |
| CNCs | - | Cellulose nanocrystals |
| CNFs | - | Cellulose nanofibers |
| C-O | - | Carbon – oxygen bond |
| C-O-C | - | Ester |
| CrI | - | Crystallinity index |
| DOE | - | Design of experiment |
| FHWM | - | Full- Width at Half Maximum |
| FTIR | - | Fourier Transform Infrared |
| H+ | - | hydrogen ion |
| $H_2SO_4$ | - | Sulphuric acid |
| HCl | - | Hydrochloric acid |
| HPA | - | Heteropoly acid |
| KBr | - | Potassium bromide |
| KDC | - | Kenaf- derived- cellulose |
| KFRC | - | Kenaf fibre - reinforced composite (KFRC) |
| NaOH | - | Sodium hydroxide |
| OH | - | Hydroxyl groups |
| PFA | - | Polyfurfuryl alcohol |
| PLA | - | Poly-lactic acid |
| PMMA | - | Polymethylmethacrylate |
| SEM | - | Scanning electron microscope |
| TEM | - | Transmission Electron Microscopy |
| XRD | - | X-ray diffraction |

# LIST OF SYMBOLS

| | | |
|---|---|---|
| % | - | Percent |
| °C | - | Degree Celsius |
| µm | - | Micrometre |
| cm | - | Centimetre |
| GPa | - | Giga Pascal |
| $H^+$ | - | Hydronium ion |
| K | - | Kelvin |
| kg | - | Kilograms |
| kN | - | Kilo newton |
| kv | - | Kilo volt |
| m | - | Metre |
| mm | - | Millimetre |
| mm/min. | - | Millimetre per minute |
| MPa | - | Mega Pascal |
| nm | - | Nanometre |
| rpm | - | Revolution per minute |
| w/v | - | weight per volume |
| wt. % | - | Weight per cent |
| β | - | Betha |
| λ | - | Wavelength |
| Ө | - | Angle |

# CHAPTER 1

## INTRODUCTION

This chapter details describe the background, problem statement, objectives, scope and significant of study.

### 1.1 Background of Study

Kenaf fiber or its scientific name Hibiscus *cannabinus* is a one of the natural fiber that is easily available and economical amongst other natural fiber. This kenaf fiber is extracted via chemical treatment from the bast or core of a plant. It consists of cellulose (56–64 wt. %), hemicellulose (21–35 wt. %), lignin (8–14 wt. %) and small amounts of extractives and ash. Due to high contents of cellulose in kenaf plant, many studies have investigated the use of cellulose as a raw material for many new applications such as building materials, absorbents, paper products and animal feeds.

Previous research has established that cellulose can be categorized into cellulose nanofibers (CNFs), cellulose nanocrystals (CNCs) and bacterial cellulose (BC) via mechanical, chemical or enzymatic treatment (Abitbol *et al*., 2016). Recently, the cellulose nanocrystals (CNC) of natural fiber have been widely used due to the advantage of its high crystallinity that can be obtained through chemical method such as acid hydrolysis. Joonobi *et al*. (2016) reported that the CNCs are a sustainable resource that accounts for more than 50 % of the abundant plant resources in the world. Moreover, it has many great characteristics which make it suitable as reinforcing agent.

Process of extraction nanocellulose or cellulose nanocrystals (CNC) from the cellulose which contains the cementing material such as lignin and hemicellulose can be done by alkali treatment (Ng *et al*., 2014). The alkaline treatment is important in order to obtained highly purified cellulose fiber prior to extraction of cellulose nanocrystals. Selected fibres were immersed in 6% concentration of NaOH for 24 hours at room temperature. According to Azwa (2013), alkaline treatment will enhance the mechanical strength of the composite and also could reduce the crystallinity ratio of the cellulose.

In order to obtain cellulose nanocrystals kenaf fiber, acid hydrolysis treatment needs to be conducted by following several conditions. The hydrolysis treatment can be used to isolate CNC with a high degree of crystallinity by eliminating the amorphous part of the cellulose material. According to Ng *et al.* (2014), the process of hydrolysis will release hydronium ion (H+) for hydrolytic cleavage of glycosidic bonds in cellulose molecular chains. It also changes within amorphous region along the cellulose fibrils. In addition, the acid hydrolysis will breaking down the structure of the nano-fibril bundles into crystalline nanocrystals.

The hydrolysis process condition such as acid concentration, temperature, hydrolysis and acid per fiber ratio plays an important role in producing cellulose nanocrystals material. Thus, this project investigates the optimum acid concentration used during the hydrolysis treatment towards the development of cellulose nanocrystal of kenaf fiber. The temperature will be considered as the constant parameter but the acid hydrolysis time is varied depends on the concentration of sulfuric acid used.

There have been several studies in the literature reporting about the usage of cellulose nanocrystals material. Martin *et al.* (2015) reported that, cellulose nanocrystals have been used as reinforcing fillers into many type of polymer matrixes including segmented polyurethanes due to their appealing intrinsic properties. Zaini *et al.* (2013) also found that cellulose nanocrystals can act as effective reinforcing materials because of their perfect crystalline arrangement. The finding is consistent with findings of past studies by Abitbol *et al.* (2016) which described that the used of cellulose nanocrystals as filler in thermoplastic polymer matrices can produce economical green nanocomposites material.

As stated above, numerous studies have investigated the synthesizing of cellulose nanocrystals kenaf fiber by using chemical treatment such as acid hydrolysis. There is no study has been reported on optimum acid concentration as a parameter of using hydrolysis method. Therefore, the main objective of this study is to synthesize cellulose nanocrystals (CNC) from kenaf fiber via acid hydrolysis method with optimum concentration of acid used and to characterize their properties. The influence of different acid concentration on the morphology, crystallinity and crystallite size were also evaluated.

## 1.2 Problem Statement

This research is emphasizing on the synthesizing and characterization of cellulose nanocrystals from kenaf fiber via chemical treatment. In order to synthesize this cellulose nanocrystals from kenaf fiber, several procedure need to be done which start from the extraction of the CNCs from the plant by using alkaline treatment followed by the acid hydrolysis treatment. The results of this treatment are depending on the parameters that have been chosen such as the concentration of the acid used, temperature and the acid hydrolysis time.

The main challenge faced by many experiments is the accurate result may not be obtained if the acid concentration used is not suitable. Therefore, this current problem must be improved by designing the correct design parameter for the acid hydrolysis treatment. Different set of experiment which contains different parameter is used during the hydrolysis process of synthesizing the cellulose nanocrystals from kenaf fiber.

However, recent studies on extraction of nanocellulose via acid hydrolysis only focused on the optimum hydrolysis time to get the best crystal structure of nanocellulose kenaf fiber. Nevertheless, to date no study has been done on the optimum concentration of acid used during hydrolysis treatment. Hence, it is important for this study to investigate the effect of acid concentration on crystallinity and crystallite size of the cellulose nanocrystals kenaf fiber as these cellulose nanocrystals will be used as new class of bio-based reinforcing material due to its sustainable ability.

## 1.3 Objective

The objectives of the study are listed as below:

1. To synthesize cellulose nanocrystals (CNCs) from kenaf fiber using acid hydrolysis method with optimum acid concentration
2. To determine the crystallinity of cellulose nanocrystals (CNCs) kenaf fiber by using X-ray diffraction (XRD) analysis and Fourier Transform Infrared (FTIR) Spectroscopy.
3. To characterize the morphology of kenaf fiber before and after the alkali treatment.

## 1.4 Scope

The aim of this study is to synthesize the cellulose nanocrystals (CNC) from the cellulose of kenaf fiber using acid hydrolysis method with optimum acid concentration and to study the crystallinity and characterization of the cellulose nanocrystals. In order to achieve the aim of this study, the research will be performed based on several scopes. The treatment that is used to extract the cellulose fiber is alkaline treatment followed by the acid hydrolysis treatment for the preparation of cellulose nanocrystals. Alkaline treatment is used to eliminate the lignin and hemicellulose in order to obtain highly purified cellulose.

For the first objective, the potential of synthesizing cellulose nanocrystals via acid hydrolysis will be explored. Acid hydrolysis method was chosen to extract the cellulose nanocrystals. This is because acid hydrolysis is the most effective method for breakage the glycosidic bonds in cellulose and it has lower energy consumption. The parameters that will be optimized in this method are the concentration of the acid used, temperature and the acid hydrolysis time. Sulfuric acid ($H_2SO_4$) with different concentration is used in this study and the temperature of the experiment is fixed at 45ºC. However, the acid hydrolysis time is varied due to the concentration of sulfuric acid used.

Then, the crystallinity of cellulose nanocrystals kenaf fiber is studied by using X-ray diffraction (XRD) analysis as mention in second objective. The XRD analysis is used to study the crystallinity of the CNC by calculating the crystallinity index (CrI) and crystallite size. Next, the result of the experiment is supported by the Fourier Transform Infrared Spectrometry (FTIR) analysis. FTIR spectrometry is used to reveal the presence of lignin and hemicellulose structure after the acid hydrolysis treatment is done. Finally, the result of the experiment is used to study the morphology and structure of cellulose nanocrystals kenaf fiber which would be the third objective of this study. The Scanning Electron Microscopy (SEM) is used to study the surface morphology of kenaf fiber before and after the alkali treatments.

## 1.5 Significant of the Study

The research on preparation of cellulose nanocrystals from kenaf fiber is done to determine the crystallinity of cellulose nanocrystals kenaf fiber. Research on the other optimum hydrolysis condition such as hydrolysis time, temperature and cellulose/acid ratio is recently studied. However, to date no study has been done on the use of suitable acid concentration during hydrolysis. Thus, the studies of extraction nanocellulose kenaf fiber will be conducted by optimizing the best concentration of acid used during the hydrolysis process. The best crystal structure with a needle-like structure will indicate the property of their reinforcing abilities. Due to good reinforcing abilities, the cellulose nanocrystals from kenaf fiber are widely used as reinforcing material for polymer composite. In addition, the use of natural fiber also provides several advantages including impressive mechanical properties associated with low density and high aspect ratio.

Furthermore, increase attention has been concentrated towards the use of ―green" material as the raw material. The use of kenaf fiber can save the environment because this material has good properties which make it a good potential to be an alternative material to synthetic material. Besides, the use of this green material, align well with the global trends of sustainability design and development, energy efficiency and water preservation. The production process of natural fiber would not emit the greenhouse gases into the atmosphere which will cause the global warming. However, the production processes of synthetic fiber such as glass fiber or carbon fiber contribute to the emission of carbon dioxide that can cause ozone thinning.

Thus, it is clearly to be seen that the use of natural fibers such as kenaf fiber have low impact on the human health and environment and it is important to increase the research on the use of natural materials for current and future applications. In other words, the research on use of natural materials can be consider as a long life learning process for the current and future generation. Throughout this process of long life learning, more improvement can be achieved in the use of green technology.

# CHAPTER 2

## LITERATURE REVIEW

A literature review of previous research work which is related to this research is presented in this chapter. Related information of previous studies are extracted as references and discussion based on their research about nanocellulose fiber, kenaf fiber, the preparation of cellulose nanocrystals from kenaf fiber, the material characterization and analysis of the cellulose nanocrystals kenaf fiber.

### 2.1 Nanocellulose Fiber

All natural fibers are cellulosic in nature which are generally is a composition of cellulose, hemicellulose, lignin and pectin. Generally, cellulose can be found naturally in the most of the plant cells such as cotton, hemp, flax, jute, ramie and wood. The cellulose also can be found in agricultural residues such as sugarcane bagasse, jute, ramie, banana and corncob. In addition, cellulose can also be found in various bacterial species, tunicates, algae and sea animals that consists of proteins and carbohydrates.

According to Mahjoub *et al.* (2014), cellulose is a semi-crystalline polysaccharide hydrophilic component consisting of a linear chain of anhydroglucose units, which contain alcoholic hydroxyl groups as shown in Figure 2.1. In recent years, there has been an increasing interest in study of cellulose fibers due to its availability of cellulose sources. Most research on nanocellulose has been carried out because of the use of natural fibers for making new environment friendly and biodegradable composite materials.

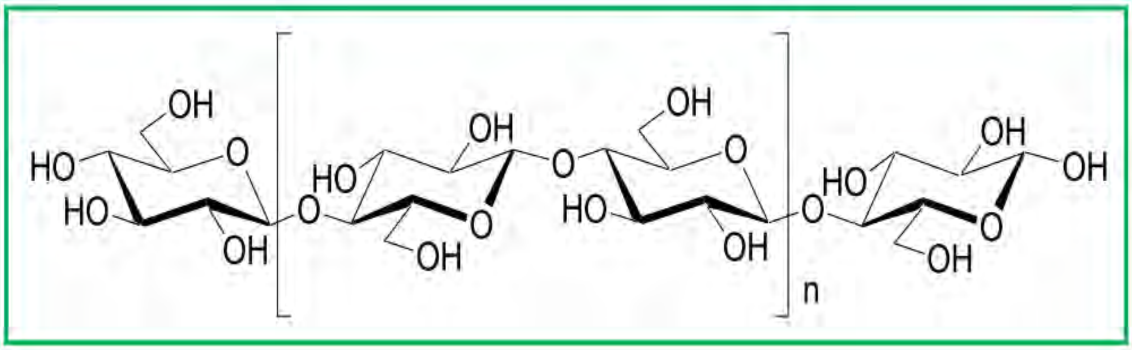

Figure 2.1: Basic chemical structure of cellulose (Siqueira *et al*., 2010)

### 2.1.1 Types and structure of nanocellulose

Previous research has established that nanocellulose can be characterized to three types of materials which are cellulose nanofibrils (CNFs), cellulose nanocrystals (CNCs) and bacterial cellulose (BC) as shown in Figure 2.2. However, the different categories of cellulose will give specific structure of its nanocrystals and also exhibit distinct properties.

The cellulose nanofibrils (CNFs) are long and have tangled bundles of cellulose molecules that are stabilized by hydrogen bonds. This CNFs or microfibrils have around 20nm wide and several lengths. CNF have higher aspect ratio than CNCs and easily connected to produce rigid web-like fibrils networks. According to Abitbol *et al.* (2016), the extraction of CNFs from cellulosic fibers can be achieved by three types of processes which are chemical treatments, mechanical treatments and combination of chemical and mechanical treatments.

Meanwhile, the CNCs generally have size differ from 100 to 1,000 nm in length and 4 to 25 nm in diameter but the size is varies based on the source from which they are generated. Many different terms is used to describe these rod-like nanoparticles such as cellulose nanowhiskers (CNWs), nanocrystalline cellulose (NCC), microfibrils and microcrystal. For the bacterial cellulose (BC) it can be characterized by average diameters of 20–100 nm. According to study by Mihaela *et al*. (2016), bacterial cellulose nanowhiskers are prepared by acid hydrolysis of BC pellicles. In addition, they also studied about the use of bacterial cellulose as reinforcements in hydrophobic polymer matrices like polylactic acid (PLA) or polyhydroxyalkanoates for biomedical applications.