PREPARATION AND CHARACTERIZATION OF NANOCELLULOSE DERIVED FROM WASTE OFFICE PAPER PREPARED BY ACID HYDROLYSIS METHOD

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Submitted in accordance with the requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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I hereby, declared this report entitled “Preparation and Characterization of Nanocellulose Derived from Waste Office Paper Prepared by Acid Hydrolysis Method” is the results of my own research except as cited in reference.

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Date : 31 May 2019

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Hons.) The members of the supervisory committee are as follow:

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(TS. DR. ROSE FARAHIYAN BINTI MUNAWAR)

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(DR. TOIBAH BINTI ABD RAHIM)

ABSTRAK

Peningkatan penggunaan kertas telah membawa kepada isu-isu alam sekitar disebabkan oleh tapak pelupusan dan pembakaran. Memandangkan itu, salah satu bahan buangan utama selulosa termasuk sisa kertas pejabat. Oleh itu, untuk mengurangkan pembaziran adalah dengan mengubahnya menjadi nanokomposit selulosa yang disediakan secara mesra alam dan kos efektif. Oleh itu, kajian ini dilakukan untuk mensintesiskan nanokristal selulosa (CNCs) dari sisa kertas pejabat dengan kaedah hidrolisis asid menggunakan kepekatan asid optimum berdasarkan parameter terpilih. Setakat ini tiada kajian terperinci telah dilakukan mengenai penyediaan nanoselulosa dari sisa kertas pejabat. Selain itu, proses penyediaan nanokristal selulosa adalah lebih mudah dan juga boleh menjimatkan tenaga dan masa kerana jumlah lignin lebih sedikit berbanding sisa selulosa yang lain. Kaedah prarawatan alkali dan kaedah hidrolisis asid telah dilakukan sebelum analisa lebih lanjut dengan menggunakan analisis Belauan Sinar X (XRD) untuk menentukan indeks kehabluran kristal (CrI) dan Spektroskopi Inframerah Transformasi Fourier (FTIR) bagi memastikan bahan bukan selulosa telah dikeluarkan oleh rawatan alkali dengan kepekatan 5 wt%. Di samping itu, dengan Mikroskop Elektron Pengimbas (SEM), didapati bahawa morfologi permukaan sisa kertas pejabat yang dirawat alkali adalah lebih halus berbanding tidak dirawat. Dari hasil yang diperoleh, kepekatan asid optimum ialah 30 wt% kepekatan dengan 90 minit masa hidrolisis dan suhu 45 ° C dengan indeks kehabluran dan saiz kristalit paling tinggi iaitu 36.35% dan 32.92nm masing-masing. Pengekstrakan CNC dari sisa kertas pejabat meningkatkan kebarangkalian untuk aplikasi dalam industri nanokomposit sebagai tetulang. Oleh itu, penggunaan sisa kertas pejabat boleh dianggap sebagai bahan hijau dan sejajar dengan reka bentuk dan pembangunan mampan.

ABSTRACT

The increase of consumption of paper has led to the environmental issues due to the landfills and incineration. Considering that, one of the major cellulosic waste material are including waste office paper. Therefore, to value add this wastage is by converted it into cellulose nanocomposites that is prepared by environmental friendly and cost effective method. Hence, this study is perform to synthesize cellulose nanocrystals (CNCs) from waste office paper by acid hydrolysis method with the optimum acid concentration based on selected parameters. Nevertheless, to date no detailed studies have been done on the preparation of nanocellulose from waste office paper. Plus, the process to prepare the cellulose nanocrystals is easier and also more energy and time efficient due to the least amount of lignin compared to other cellulosic waste. The alkali pretreatment and acid hydrolysis method has been conducted before further analysis by using X-ray diffraction (XRD) in order to determine the crystallinity index (CrI) and Fourier Transform Infrared (FTIR) Spectroscopy which show the confirmation of non-cellulosic materials has been removed by alkaline treatment with the 5 wt% concentration. In addition, via Scanning Electron Microscopy (SEM), it was found that the surface morphology of alkaline treated waste office paper was smoother than untreated. From the result obtained, the optimum acid concentration is 30 wt% with 90 minutes hydrolysis time and 45°C temperature with the highest crystallinity index and crystallite size which is 36.35% and 32.92nm respectively. Extraction of CNC from waste office paper provides possible application in nanocomposites industry as a reinforcement. Thus, the use of waste office paper can be considered as green material and align with the sustainable design and development.

DEDICATION

Only

my beloved father, Awang bin Zakaria

my appreciated mother, Raja Azizah binti Raja Ismail

my adored supervisor, Ts. Dr. Rose Farahiyan binti Munawar

my friends

for giving me moral support, money, cooperation, encouragement and also understandings.
Thank You So Much & Love You All Forever

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LIST OF ABBREVIATIONS

CNCs	-	Cellulose Nanocrystals
CNFs	-	Cellulose Nanofibers
BC	-	Bacterial Cellulose
eCNFs	-	Electrospun Cellulose Nanofibers
CNWs	-	Cellulose Nanowhiskers
cFs	-	Cellulose Fibers
WOP	-	Waste Office Paper
MPPA	-	Malaysia Pulp and Paper Association
MCC	-	Microcrystalline Cellulose
XRD	-	X-Ray Diffraction
FTIR	-	Fourier Transform Infrared Spectroscopy
SEM	-	Scanning Electron Microscopy
TEM	-	Transmission Electron Microscopy

LIST OF SYMBOLS

h	-	hour
min	-	minute
s	-	second
wt%	-	Weight Percentage
%	-	Percent
g	-	gram
°C	-	Degree Celcius

CHAPTER 1
INTRODUCTION

This chapter explains concisely the background of study, problem statement, objectives, research scopes and the significance of this research.

1.1 Background of Study

The large use of various types of papers such as packaging paper, advertising papers, newspapers and waste office papers in our daily lives reflects that paper is an important ingredient in the world and affects human life in depth. With the advent of new computer technology and the growing popularity of personal computers, there has been an increase in paper usage regarding to all types of printers, including laser printers (Lee *et al.* 2013).

Paper use worldwide over the past four decades has increased by 400%, with the United States becoming the largest paper consumer. The same source revealed that over the last two decades, the country's consumption has grown about 126% from 92 million tons, with only representing 5% of the world's population. Based on official figures (Desdelared 2012; Semamat 2018), Mexico generates an estimated waste of approximately 111, 000 tons per day, of which 14% is waste paper. In Malaysia, about 1.9 million tons of paper and paperboard was consumed on 2015. This figure is based on the statement by Malaysia Pulp and Paper Manufacturers Association (MPPA) honorary secretary-general, Datuk Mas'ut A. Samad.

Waste paper, being a cellulose biomass gives a potential wellspring of crude material for the creation of CNCs. Previous study had found that waste paper constitute up to 70-100% of

organic parts which consists of cellulose, hemicellulose, lignin and numerous compound of lignin.

The obtained cellulose is reported to have very special properties such as crystal arrays, high level of whiteness and viscosity (MacDonald 2011). Cellulose, due to its structure, is a compound that has high potential to be used as a nanomaterial, in view of its abundance and its fibrillar nano structure. This polysaccharide has a very special feature that makes it an extraordinary material, such as high rigidity, mechanical properties, low cost and biodegradable (Beck-Candanedo *et al.* 2005).

There are four main classes of cellulose nanomaterials that differs in terms of morphology, particle size, crystallinity and some properties due to the different of sources and extraction method. Main classes of cellulose are cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), bacterial cellulose (BC), and electrospun cellulose nanofibers (ECNFs) (Yang *et al*. 2018). However, the cellulose nanocrystals (CNCs) of natural fiber have been widely used due to the advantages of its high crystallinity that can be obtained through chemical method such as acid hydrolysis.

Meanwhile, major element in lignocellulosic biomass which mostly localized in plant cell walls about 35% - 50% is cellulose. Cellulose not only has been found in plant cell such as hemp, cotton, flax, jute and wood, cellulose also can be found in agricultural residues such as sugarcane bagasse, tunicate, algae and sea animals that consist of protein and carbohydrate. The common extraction method in order to obtain the nanocellulose are by chemical treatments, mechanical treatments or both combination of chemical and mechanical treatments (Souza *et al.* 2017).

However, acid hydrolysis is a famous method used in producing a stable colloidal suspension of cellulose nanocrystals (Phanthong *et al*. 2018). In this method, the acid help in degrading the amorphous region of hemicellulose and lignin thus, the crystal cellulose become the domain structure. The essential parameters such as temperature correlation, hydrolysis time and acid concentration must be considered in the acid hydrolysis as it could affect the result of

nanocellulose obtained. In order to make the cellulose more accessible and effective hydrolysis, chemical pretreatment is always being a prior for the hydrolysis method. The most common pretreatment used is alkali pretreatment in which, the cellulose fiber is subjected into bases solution (Orue *et al.* 2017)

The reason of this study is to prepare and characterize the nanocellulose derived from waste office paper by acid hydrolysis (H_2SO_4) method with the optimum condition consider the temperature correlation, hydrolysis time and acid concentration. This is due to the lack of the previous study that use waste office paper that includes any waste paper either printed or no printed paper as the raw materials for the extraction of cellulose nanocrystals with the complete study. The cellulose nanocrystals that obtained will be further analyzed and characterized by using selected tools such as X-ray diffraction (XRD) analysis, Fourier Transform Infrared (FTIR) Spectroscopy and Scanning Electron Microscopy (SEM). Therefore, a definite cellulose crystals structure and crystallinity can be evaluated due to the optimum condition of hydrolysis focusing on the effect of hydrolysis time and concentration.

1.2 Problem Statement

This study focuses on the preparation and characterization of nanocellulose waste office paper prepared by acid hydrolysis method which is has high crystallinity and stable colloidal suspensions of cellulose nanocrystals. In order to synthesize this cellulose nanocrystals from waste office paper, several method need to be done starting with the extraction of CNCs from the waste office paper by alkaline treatment before subjected with the acid hydrolysis treatment. The selection of waste office paper in this study is due to some tremendous advantages of lignocellulosic fibers that being an attention among the researchers. In addition, this study can help in reducing the potential of environment problem that cause from waste paper such as waste office paper, newspaper and printed paper that is highly use nowadays. This waste paper must be disposed of by landfills or incineration. Considering that, one of the major cellulosic waste material are including waste office paper that is comes from printed office waste. Therefore, to give value added to this wastage is by converting it into cellulose nanoparticles and

nanocomposites that are prepared by environmental friendly and cost effective method by using waste office paper as the raw material. Although using waste office paper as a raw material in producing an application is not the only answer to the garbage issues, somehow it will be as a partial solution in reducing the issues.

Nevertheless, to date no studies have been done on the preparation of derived nanocellulose from waste office paper and its characterization with the effect of hydrolysis time, temperature correlation and its optimum concentration has not yet exploit. So that, this study is fully conducted on preparation and characterization of nanocellulose waste office paper via acid hydrolysis method. Meanwhile, waste office paper had been going through many process in a papermaking so that the lignin contains in waste paper had been reduces and the amount had been decreased compared to other cellulosic wastage like banana trunk and kenaf fiber. Thus, the process in order to prepare the cellulose nanocrystals will be easier and also can save the energy and time. Even though, waste paper can be recycle, but due to the several process that has been done and reduce the lignin, the waste paper can be value added in extraction of cellulose nanocrystals. Several problem might been faced during the study in order to get an accurate result. However, the problems must be improved by designing the correct parameter for the acid hydrolysis treatment.

In order to handle the problems, two main phase of chemical treatment were conducted in this study that involve the waste office paper in producing cellulose nanocrystals. The alkali pretreatment was used to extract the purified cellulose waste office paper. Next, to convert purified cellulose in term of cellulose nanocrystals, acid hydrolysis process were conducted. The main chemical treatment in this study was acid hydrolysis that were conducted based on selected parameters such as acid concentration, hydrolysis time and temperature correlation. Thus, the parameter was designed conventionally with the temperature correlation was fixed to 25°C in order to find the optimum condition for nanocellulose waste office paper with the highest crystallinity.

1.3 Objectives

The objectives of the study are listed as below:

a) To synthesize cellulose nanocrystals (CNCs) from waste office paper by acid hydrolysis method with the optimum acid concentration based on selected parameters.
b) To determine the crystallinity of cellulose nanocrystals (CNCs) waste office paper by using X-ray diffraction (XRD) analysis and Fourier Transform Infrared (FTIR) Spectroscopy.
c) To characterize the surface morphology and structure of nanocellulose waste office paper by using method Scanning Electron Microscopy (SEM).

1.4 Researches Scopes

The study focusing on the preparation nanocellulose in term of cellulose nanocrystals that derived from waste office paper by using sulphuric acid (H_2SO_4) via acid hydrolysis method with optimum condition and to study the crystallinity and characterization of the cellulose nanocrystals. The scope was focused to extract the cellulose nanocrystals from printed and no printed waste office paper. In order to achieve the aim of the study, several experiments will be conducted in different conditions based on several scopes to find the optimum condition in producing high crystallinity cellulose nanocrystals waste office paper. The treatment that is used for the preparation of the cellulose nanocrystals are alkaline treatment for the extraction of cellulose wastepaper followed by acid hydrolysis treatment for the preparation of cellulose nanocrystals. The used of alkaline treatment is to eliminate the lignin and hemicellulose in order to obtain highly purified cellulose.

For the first objective, acid hydrolysis is the method suggestion in this research. One of the main process in order to synthesize nanocellulose from cellulosic materials are via acid hydrolysis. The combination parts of cellulose chain which are ordered and disordered region can be easily hydrolyzed by acid. In this term, acid will hydrolyzed the disordered region and

left the remaining parts of ordered region. The alkali treatment were performed to the office waste paper to disrupt hydrogen bonding in the structure between cellulose chain to make sure the acid hydrolysis process were effective in extraction of cellulose nanocrystals. In order to obtain purified cellulose, the office waste paper were treat with alkali treatment via sodium hydroxide (NaOH) before performed the acid hydrolysis method that will be conducted in different condition such as hydrolysis time, temperature correlation and the acid concentration. In this process, sulphuric acid (H_2SO_4) is used as the agent of acid hydrolysis as it can produce a stable colloidal suspension of cellulose nanocrystals compared to other type of acids. The temperature correlation are fixed to 45°C. However, the concentration and hydrolysis time were varied since they were correlated to each other.

Then, as to perform the second objectives which is to determine the crystallinity of cellulose nanocrystals (CNCs) waste office paper, the X-ray diffraction (XRD) analysis is used. The XRD analysis is used to evaluate the crystallinity index (CrI) and crystallite size. Furthermore, the effect of elemental chemical composition for different chemical stages and thermal stability were studied by Fourier Transform Infrared (FTIR) Spectroscopy. FTIR spectroscopy is used to reveal the presence of hemicellulose structure and lignin after the acid hydrolysis is performed. After that, the result of the experiment is used to study the surface morphology and structure of cellulose nanocrystals waste office paper as mention in third objective. The final analysis that will be used is Scanning Electron Microscopy (SEM) to study the effectiveness of alkali treatment of sodium hydroxide (NaOH) that evaluated through surface morphology.

1.5 Significant of the Study

Waste office paper, being a cellulose biomass provides a potential source of raw material for the production of CNCs. Since nanocellulose that are extracted from the waste office waste paper has not being exploited yet, it is significant to study about the suitable method in order to produce nanocellulose in term of cellulose nanocrystals which is derived from the waste office