DEVELOPMENT AND CHARACTERIZATION OF NANOFIBERS FROM KENAF BAST TO REINFORCE POLYMER COMPOSITES

By

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In the name of GOD

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LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
µm	Micrometer
cm	Centimeter
G	Giga
g	Gram
h	Hour
J	Joule
k	Kilo
Kg	Kilogram
KV	Kilo Volt
M	Molar
m	meter
mA	Milli Ampere
mg	Milligram
mm	Millimeter
min	Minutes
nm	Nanometer
MPa	Mega Pascal
T_{onset}	Onset decomposition temperature
T_{deh}	Dehydration temperature
T_{max}	Decomposition temperature
υ	Volume

LIST OF ABBREVIATIONS

AFM	Atomic Force Microscopy
AQ	Anthraquinon
ASTM	American Society for Testing and Materials
BC	Bacterial Cellulose
CNF	Cellulose Nanofiber
CNW	Cellulose Nanowhisker
DGEBA	Diglycidyl Ether of Bisphenol-A
DSC	Differential Scanning Calorimetry
DTG	Derivative Thermogravimetric Analysis
FETEM	Field Emission Scanning Electron Microscopy
HPC	Hydroxy Propyl Cellulose
KBr	Potassium Bromide
MCC	Microcrystalline Cellulose
Mg_2SO_4	Magnesium Sulphate
NaOH	Sodium Hydroxide
OPEFB	Oil Palm Empty Fruit Bunches
P	Passing Times
PCL	Polycaprolactone
PLA	Poly(lactic acid)
PVA	Polyvinyl Alcohol
Phr	Part per Hundred
SEM	Scanning Electron Microscopy
Soda	Sodium Hydroxide

TGA	Thermogravimetric Analysis
UT	Ultra Turax
Wt.	Weight
XRD	X-Ray Diffraction

LIST OF SYMBOLS

%	Percentage
°C	Degree Celsius
µm	Micrometer
cm	Centimeter
G	Giga
g	Gram
h	Hour
J	Joule
k	Kilo
Kg	Kilogram
KV	Kilo Volt
M	Molar
m	meter
mA	Milli Ampere
mg	Milligram
mm	Millimeter
min	Minutes
nm	Nanometer
MPa	Mega Pascal
T_{onset}	Onset decomposition temperature
T_{deh}	Dehydration temperature
T_{max}	Decomposition temperature
υ	Volume

V_f	Fiber volume fraction
V_m	Matrix volume fraction
W_f	Fiber weight fraction
W_m	Matrix weight fraction
W_d	Weight before immersion in water
W_n	Weight after immersion in water
K	Magnification
θ	Theta
λ	Lambda
ρ	Density
ρ_c	Composite density
ρ_f	Fiber density
ρ_m	Matrix density
$\rho_{theoritical}$	Theoretical density
$\rho_{experimental}$	Experimental density

LIST OF PUBLICATIONS

PEMBANGUNAN DAN PENCIRIAN NANOFIBER DARIPADA KULIT KENAF DIPERKUAT KOMPOSIT POLIMER

ABSTRAK

Tujuan kajian ini adalah untuk meneroka gabungan asid hidroklorik (HCl) hidrolisis dan penyeragaman tekanan tinggi sebagai proses baru untuk mengasingkan selulosa nanofiber (CNF). Dalam usaha untuk menyediakan CNF, pertama pempulpaan soda-anthraquinon dan alkali hidrogen peroksida pemutihan dilakukan untuk menghapuskan lignin dan hemiselulosa dan juga untuk memisahkan gentian tunggal. Selepas itu, proses hidrolisis asid dilakukan sebagai rawatan awal pada sela masa yang berbeza untuk mengurangkan saiz gentian dan mencegah dari tersumbat daripada penyeragaman ini. Kondisi hidrolisis yang terbaik telah dipilih untuk menyediakan CNF. Kemudian, pengasingan CNF menggunakan penyeragaman tekanan tinggi pada pelbagai kitaran dan kepekatan suspensi dilakukan. Analisis struktur gentian sebelum dan selepas setiap rawatan telah dijalankan oleh Belauan Sinar-X (XRD) dan Spektroskopi Inframerah Transformasi Fourier (FT-IR). Juga, sifat-sifat morfologi gentian telah dikaji dengan mikroskop imbasan elektron (SEM), mikroskopi daya atom (AFM) dan mikroskop elektron transmisi (TEM) dan ciri-ciri haba dianalisis dengan analisis Termogravimetri (TGA) dan kalorimeter pengimbasan perbezaan (DSC) . Di samping itu, hasil setiap rawatan dikira. Selepas itu, epoksi nanokomposit oleh mesin tekanan sejuk pada berbeza penambahan CNF dihasilkan. Sifat mekanikal, fizikal, permukaan patah dan kestabilan terma yang yang diperolehi dari nanokomposit terhasil dibandingkan.

Analisis FT-IR mengesahkan membuang lignin dan hemiselulosa menggunakan prosedur ini. Keputusan analisis XRD menunjukkan penghabluran telah meningkat daripada kulit kenaf mentah kepada gentian asid dihidrolisiskan mungkin kerana membuang juzuk bukan selulos dan amorfus semasa ia menurun untuk CNF mungkin kerana proses pengelupasan. Diameter CNF didapati dalam lingkungan 9-13nm. TGA dan DSC analisis menunjukkan kestabilan haba yang lebih tinggi daripada CNF. Tambahan pula, keputusan dipaparkan menunjukkan bahawa dengan meningkatkan bilangan kitaran, diameter CNF mengurangkan manakala hasil, penghabluran dan kestabilan haba meningkat. Masa hidrolisis terbaik, iaitu penggantungan kepekatan CNF dan nombor kitaran berdasarkan semua keputusan analisis adalah 2 jam masa kitaran, pada 0.1wt% dan 40, masing-masing. Data menunjukkan bahawa dengan meningkatkan jumlah CNF sifat-sifat mekanik, kestabilan terma, penyerapan air dan ketumpatan nanokomposit meningkat. Morfologi sebahagian kecil permukaan nanokomposit menunjukkan serakan agak baik daripada CNF dalam resin epoksi. Hasil kajian ini menunjukkan bahawa CNF terasing mempunyai keupayaan penguatan dan berpotensi untuk aplikasi nanokomposit.

DEVELOPMENT AND CHARACTERIZATION OF NANOFIBERS FROM KENAF BAST TO REINFORCE POLYMER COMPOSITES

ABSTRACT

The aim of this research was to explore the combination of hydrochloric acid (HCl) hydrolysis and high pressure homogenization as a new process to isolate cellulose nanofiber (CNF). In order to prepare CNF firstly soda-anthraquinon pulping and alkaline hydrogen peroxide bleaching was performed to remove lignin and hemicellulose as well as to separate single fibers. Subsequently, the acid hydrolysis was applied as a pretreatment at different time to reduce the size of fibers and to prevent from clogging of the homogenization. The best hydrolysis condition was selected to prepare the CNF. Then CNF was isolated using high pressure homogenization at various cycle and suspension concentrations. The structural analysis of the fibers before and after each treatment was conducted by X-ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FT-IR). Also, the morphological properties of the fibers was studied by scanning electron microscopy (SEM), atomic force microscopy (AFM) and transmission electron microscopy (TEM) and the thermal characteristics was analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). In addition, the yield of each treatment was calculated. Finally, epoxy nanocomposite was manufactured by cold press machine at different CNF loading. The mechanical, physical, fracture surface and thermal stability of the obtained nanocomposites were compared.

The FT-IR analysis confirmed the removal of lignin and hemicellulose using these procedures. The results of XRD analysis showed that the crystallinity was increased from the raw kenaf bast to the acid hydrolyzed fibers probably due to the removal of non-cellulosic and amorphous constituents while it decreased for the CNF might be because of peeling process. The diameter of the CNF was found to be in the range of 9-13nm.

The TGA and DSC analysis revealed the higher thermal stability of the CNF. Furthermore, the results displayed that by increasing the number of cycle, the diameter of CNF reduce whereas the yield, crystallinity and thermal stability increase. The best hydrolysis time, CNF's suspension concentration and number of cycle based on all analysis results were 2hours, 0.1wt% and 40, respectively. The nanocomposite data showed that by increasing the amount of CNF the mechanical properties, thermal stability, water absorption and density of the nanocomposites increase. The surface fraction morphology of the nanocomposites illustrated relatively good dispersion of the CNF in epoxy resin. The findings of this study exhibited that the isolated CNF has reinforcing ability and potential for nanocomposite applications.

CHAPTER ONE

INTRODUCTION

1.1. Background

In recent decade's nanotechnology as a multidisciplinary field have been extensively developed in wide variety of areas. In line with development of nanotechnology and recent concern about environmental issues, researchers have shadowed light on potential of renewable and biodegradable materials, lignocellulosic fibers. So, this great insight to extract nanocellulose (minimum one dimension ≤ 100nm) either in whisker or fiber form (Abdul Khalil et al., 2014) for producing of sustainable and environmentally friend nanomaterials came into light as one of the widespread applications of nanotechnology. It is recognized that their unique and attractive properties such as renewability, higher strength, biodegradability, higher aspect ratio and larger surface area, can open new doors and give good insights to technological world.

In the one side of nanocellulose field there is cellulose nanowhisker /nanocrystal which can be produced by acid hydrolysis (Moran et al., 2008; Morais et al., 2013) and are rod like particles with low aspect ratio (Hubbe et al., 2008; Siqueira et al., 2010). On the other side, nanofibrillated cellulose or cellulose nanofiber, as a long fibrous material with high aspect ratio (Chakraborty et al., 2006; Siró & Plackett, 2010) is located.

Cellulose nanofibers can be prepared using mechanical processes like high pressure homogenization (HPH) (Leitner et al., 2007; Wang & Sain, 2007; Habibi et al., 2009; Jonoobi et al., 2011; Ferrer et al., 2012), grinding (Iwamoto et al., 2005; Iwamoto et al., 2007; Wang et al., 2012; Hassan et al., 2012) and ultrasonication (Johnson et al., 2009; Wang & Cheng, 2009; Frone et al., 2011; Qua et al., 2011; Wang et al., 2013; Chen et al., 2011). However, homogenization as high shear and impact energy method is considered as the most widely used method for the production of cellulose nanofiber

(Siqueira et al., 2010). In this regard higher energy consumption and clogging of the machine are two important drawbacks for this production process.

In order to tackle above drawbacks in mechanical processes, researchers employed pretreatment as a solution. Considering pretreatments issues in this field, numerous attempts was performed by researchers. For example, acetylation (Bulota et al., 2012; Jonoobi et al., 2012), carboxymethylation (Wågberg et al., 2008; Eyholzer et al., 2010; Siró et al., 2011), TEMPO oxidation (Saito et al., 2006; Lasseuguette et al., 2008; Besbes et al., 2011; Gonzalez et al., 2012), enzyme treatment (Henriksson et al., 2007; Pääkkö et al., 2007; López-Rubio et al., 2007; Siddiqui et al., 2011; Janardhnan & Sain, 2011; Tanpichai et al., 2012) and alkaline-acid-alkaline treatment (Bhatnagar & Sain, 2005; Wang et al., 2007a,b,c; Alemdar & Sain, 2008a,b) are such type of pretreatments for reducing the fibre size which would eventually reduce the energy consumption and prevent from clogging of the equipment.

Since various raw materials show different characteristics during cellulose nanofiber production processes, it is important to study about this parameter as another critical issue beside production methods. The isolated nanofibrillated cellulose from diverse cellulosic sources such as kenaf (Jonoobi et al., 2009; Jonoobi et al., 2010; Jonoobi et al., 2011), wheat straw and soy hulls (Alemdar & Sain, 2008b), algae (Imai et al., 2003), sugarcane bagasse (Bhattacharya et al., 2008; Li et al., 2012), oil palm (Jonoobi et al., 2011), potato pulp (Dufresne et al., 2000), bacterial cellulose (BC) (Yano et al., 2005; Nakagaito & Yano, 2005; Nogi et al., 2006; Ifuku et al., 2007), flax (Hrabalova et al., 2011), banana rachis (Zuluaga et al., 2009), wood (Bhatnagar & Sain, 2005; Chakraborty *et al.*, 2005; Siddiqui et al., 2011), hemp (Wang et al., 2007c), rice straw (Hassan et al., 2012) microcrystalline cellulose (Pan et al., 2013) and etc have shown remarkable thermal stability, high values of crystallinity as well as very small size. All of these mentioned characteristics make them good choice to come to industry, for example to fabricate nanocomposites for high performance applications.

As stated above one of the non-wood cellulosic fibers which can be applied in preparation of cellulose nanofiber is kenaf (*Hibiscus cannabinus* L). In addition, Malaysian government is developing usage of kenaf fiber as the next main industrial crop and as new source in order to economic growth (karimi et al., 2014). The higher cellulose content of bast fiber (55%) compared to core fiber (49%) (Abdul Khalil & Suraya, 2011) make the bast fibre as a good choice in order to prepare novel and modern materials with outstanding properties such as nanocellulose. It is worth nothing that there are limited research about isolation of kenaf either in nanocrystalls form (Zaini et a., 2013; Kargarzadeh et al., 2012; Shi et al., 2011) or nanofibrillated cellulose from bast (Karimi et al., 2014; Jonoobi et al., 2010; Jonoobi et al., 2009), core (Joonobi et al., 2010) or stem (Jonoobi et al., 2011).

In spite of cellulose nanofibers preparation methods from various sources, their applications can be considered as another important issue in nanotechnology field. They have many different applications like nanocomposites, medical stuffs, and barrier films (Chen et al., 2011), paper additives (Gonzalez et al., 2012), transparent packaging films (Aulin et al., 2010) and etc. By inserting these nanoscale compounds into polymers even in small quantities, the properties of polymers will improve (Ioelovich, 2012). Extensive researches and numerous review papers covered manufacturing of nanocomposites from various thermoplastic or thermoset polymers reinforced with cellulose nanofibers (Abdul Khalil et al., 2014; Missoum et al., 2013; Siró & Plackett, 2010; Siqueira et al., 2010). For example, nanocomposite composed of cellulose nanofibers with polyvinyl alcohol (PVA) (Bulota at al., 2012), polypyrrole (Nyström et al., 2010), hydroxypropylcellulose (HPC) (Johnson et al., 2009), polycaprolactone (PCL) (Lonnberg et al., 2011), polylactic acid (PLA) (Qu et al., 2010; Jonoobi et al.,2010), poly (styrene-co-butyl acrylate)

(Besbes et al., 2011), amylopectin (López-Rubio et al., 2007), melamine formaldehyde (Henriksson & Berglund, 2007), epoxy (Lu et al., 2008; Masoodi et al., 2011), phenol formaldehyde (Qing et al., 2012) and etc.

1.2. Problem Statement

The aim of this research was to apply mild acid hydrolysis as a ptretreatment before homogenization process to prepare kenaf bast nanofiber and using of this nanofiber to reinforce epoxy nanocomposite. Since petroleum based polymers are limited, high cost and non-biodegradable, and according to the recent world environment conservative regulations it seems necessary to find alternative for this materials. So, biodegradable, environmentally friend, renewable, low cost and high strength cellulosic fibers can be good choice to solve this problem.

In addition, the shortage of wood based cellulosic fibers is another important issue which should be considerd. So, applying kenaf bast as non-wood cellulose fibers with high cellulose content and great mechanical properties can be take into account in order to tackle the aforementioned obstackel.

Furthermore, low physical, thermal and mechanical properties of the bulk cellulosic fibers can be compensate by applying very small size, high surface area, low density, high modulus and strength as well as high thermal stability nanofibers. In addition, the evaluation of the effect of processing parameters and various pretreatments on the properties of nanofibers is another important point which neglected in the avalibale literatures. The existing researches just dedicated an effort to study the influence of mechanical pretreatments on the characteritics of kenaf bast nanofibers at constant pressure, cycle and suspension concentration. So this field need to pay more attention to obtain the best homogenization conditions based on diverse processing parameters as well as to evaluate the effect of chemical pretreatment on the properties of kenaf bast nanofibers.

Last but not least point is related to high cost of epoxy nanocomposite. So, the incorporation of low cost and high strength nanofibers can help to solve this problem and reinforce the resultant epoxy nanocomposite. In conclusions, the environmental issues, need for high mechanical and cheap reinforcement, propel me forward to apply the kenaf bast nanofibers to prepare rigid epoxy nanocomposite.

1.3. Objectives of the Study

The main objectives of the present research are as follow:

1) To extract cellulose from the raw kenaf bast fiber using soda-anthraquinon pulping and alkaline hydrogen peroxide bleaching processes and to characterize their thermal and morphological properties, crystallinity, functional groups and yield.
2) To evaluate the effect of HCL hydrolysis time on the morphology, thermal properties, yield, functional groups and crystallinity of the fibers.
3) To study the impact of suspension concentration and homogenization cycle as well as ultra turax pretreatment on the functional groups, crystallinity, yield, thermal and morphological properties of the kenaf bast nanofiber.
4) To prepare epoxy nanocomposite reinforced with various kenaf bast nanofiber loading and to analyze their mechanical, thermal and physical characteristics.

1.4. Organization of Thesis

This thesis has been divided into 7 respective chapters.

Chapter 1: Introduction, concentrated on research background, major gaps, problem statement and objectives of this thesis.

Chapter 2: Literature review, focused on literature surveys of cellulose nanofiber pre-treatments and production processes, kenaf nanofibers and cellulose nanofiber reinforced nanocomposites.

Chapter 3: Explains about method of extraction of cellulose from raw kenaf bast, their characterization, results and discussion, final conclusion.

Chapter 4: Describes about acid treatment of bleached kenaf, study about influence of various acid treatment times, their characterization, results and discussion, final conclusion.

Chapter 5: Focused on nanofibrillation of acid treatmented kenaf, evaluate effect of three different parameters, their characterization, results and discussion, final conclusion.

Chapter 6: Explains about fabricating of nanocomposite from epoxy and two different kenaf nanofiber loading, study their properties, results and discussion, final conclusion.

Chapter 7: Summarizes the overall conclusions and recommendation for future research of this study.

CHAPTER TWO

LITERATURE REVIEW

2.1. Natural Fibers

In general, depend on origins, natural fibers can be classified into three categories, vegetable, animal and mineral fibers (Bismarck et al., 2005). Vegetable fibers are called plant or cellulosic fibers (Sequeria, 2010) because they are basically composed of cellulose. Furthermore, plant fibers can be subdivided into seed, fruit, bast, leaf, wood (hard wood and soft wood) and stalk (Kalia et al., 2009). Classification of natural fibers according to their origin is displayed in figure 2.1.

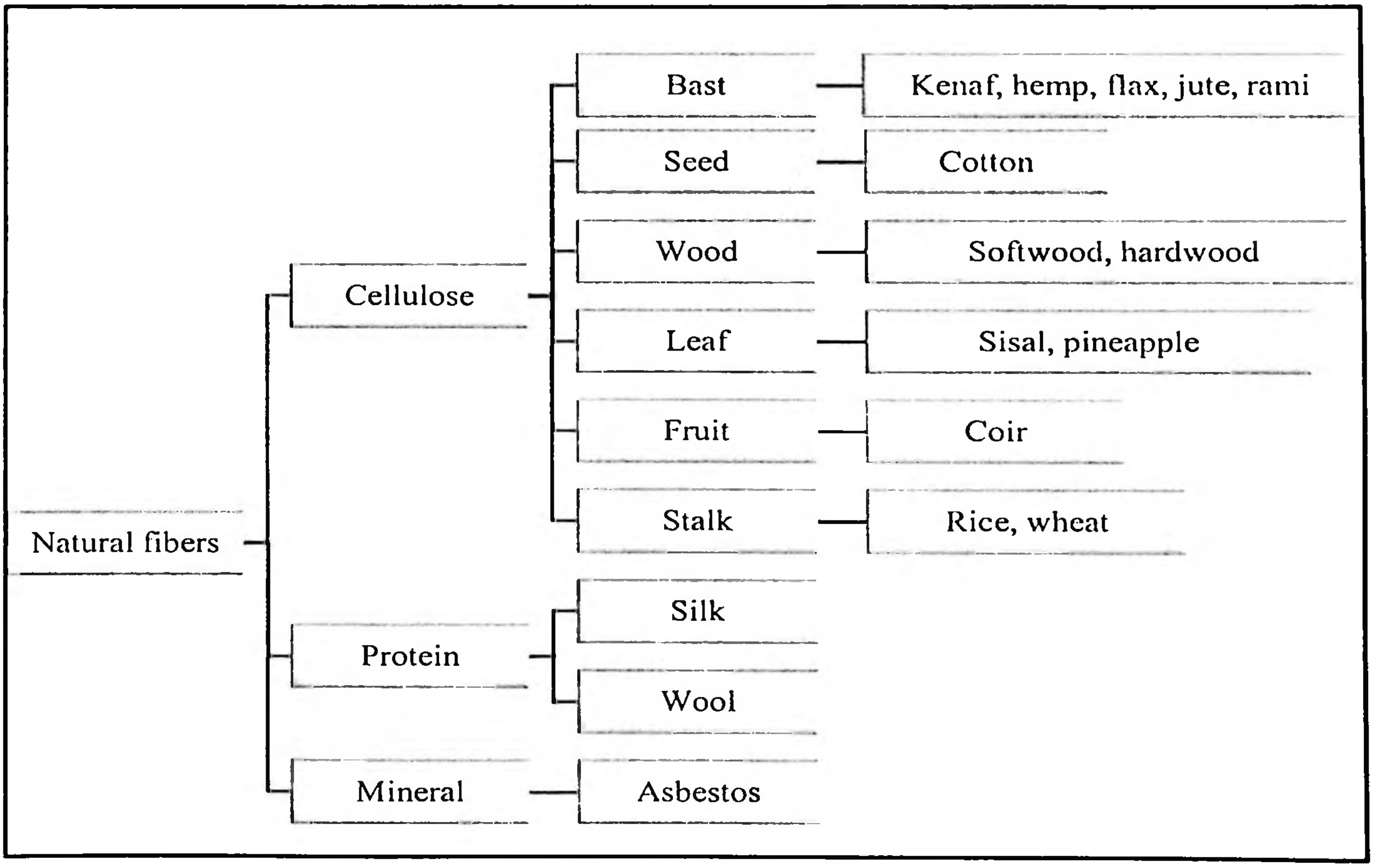

Figure 2.1: Classification of natural fibers (Bismarck et al., 2005)

In spite of good properties of cellulosic fibers inclusing renewability, biodegradability, low cost, high mechanical strength, low density and etc (Kamel, 2007), they suffer from some drawbacks such as hydrophilic nature which is difficult to disperse in hydrophobic matrix and high moisture absorption (Kalia et al., 2009). In order to overcome problems of cellulosic fiber various types of modification such as silylation, acetylation, incorporating surfactants can be used (Frone et al., 2011).

2.2. Cellulose

Cellulose as the most abundant and natural biopolymer exists in various and numerous living species such as plants, some bacteria and animals (Lima & Borsali, 2004). Since cellulose is the main component of plants and is renewable natural source, from environmental point of view it can be very good alternative for petroleum based materials which are limited (Beck et al., 2011; Ma et al., 2011). Over 7.5 × 10^{10}tons of cellulose are produced annually (Habibi et al., 2010). Cellulose (figure 2.2) as a linear homo-polysaccharide comprised of β-D-glucopyranose units connected by β-1–4-linkages and with repeating unit of cellubiose (Abdul Khalil et al., 2014).

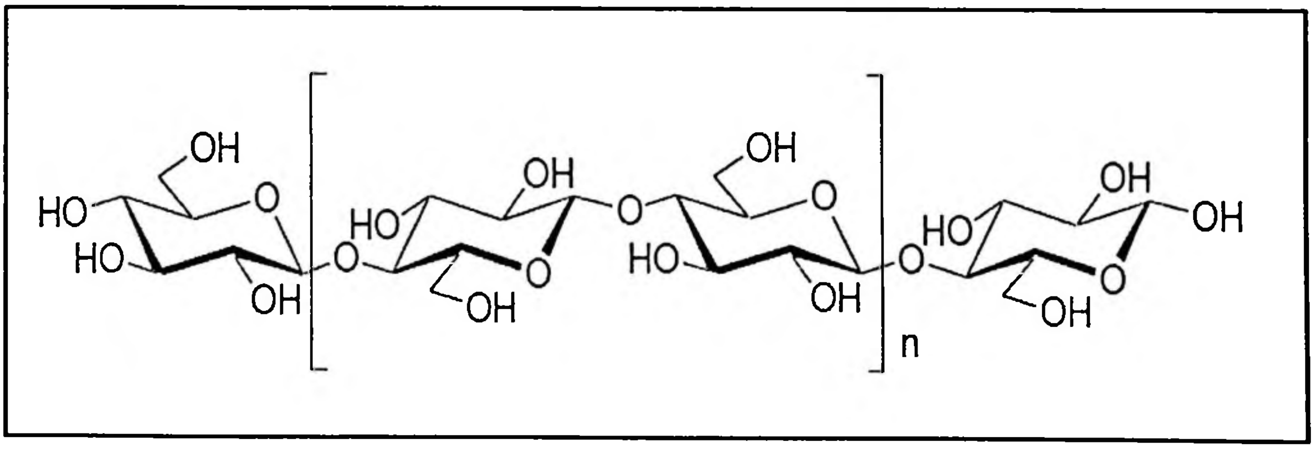

Figure 2.2: Chemical structure of cellulose (Siqueira et al., 2010)

Each glucose monomer of cellulose consists of three hydroxyl groups that can form hydrogen bonding and therefore can play a critical role in physical properties and crystalline packing of cellulose (John & Thomas, 2008). Cellulose is consists of both crystalline and amorphous domains. In the nature, cellulose does not exist as individual molecule and it can be found as assemblies of single cellulose chain which form fiber cell wall. Essentially, the cell wall in a cellulosic fibers is not homogenous and it is made up of primary (thin outer layer) and secondary wall which this secondary wall is composed of three layers (Thomas et al., 2013).

Primary cell wall is containing 9-25% cellulose microfibrils, 25-50% hemicellulose and 10-35% petins (Bhatnagar & Sain, 2005). Secondary cell wall is derivative of primary walls and is composed 40-80% cellulose, 10-40% hemicellulose and 5-25% lignin (Bhatnagar & Sain, 2005). The cellulose microfibril is elementary structural constituent of cellulose and diameter of each single microfibrils is around 2-20nm (Siqueira et al., 2010). They are helically wound framework (Kamel, 2007) which locate in the secondary cell wall and have various directions in secondary cell wall layers (Mossello et al., 2010). Microfibrillar aggregates allow formation of crystalline or highly ordered domains (Azizi Samir et al., 2005). The hierarchical structure of cellulose is displayed in figure 2.3.

Since crystalline organization can determine mechanical properties of cellulosic fibers and this characteristic in each cellulose fibers is different, so the mechanical properties of these fiber are different from each other (Bledzki & Gassan, 1999). The mechanical characteristics of some plant fiber is abbreviated in Table 2.1. As can be seen in this table, different fibers have various mechanical properties. For example, kenaf and flax fibers have the highest tensile strength. Besides, hemp has the highest tensile modulus. The density of various cellulosic fibers are in the close range.

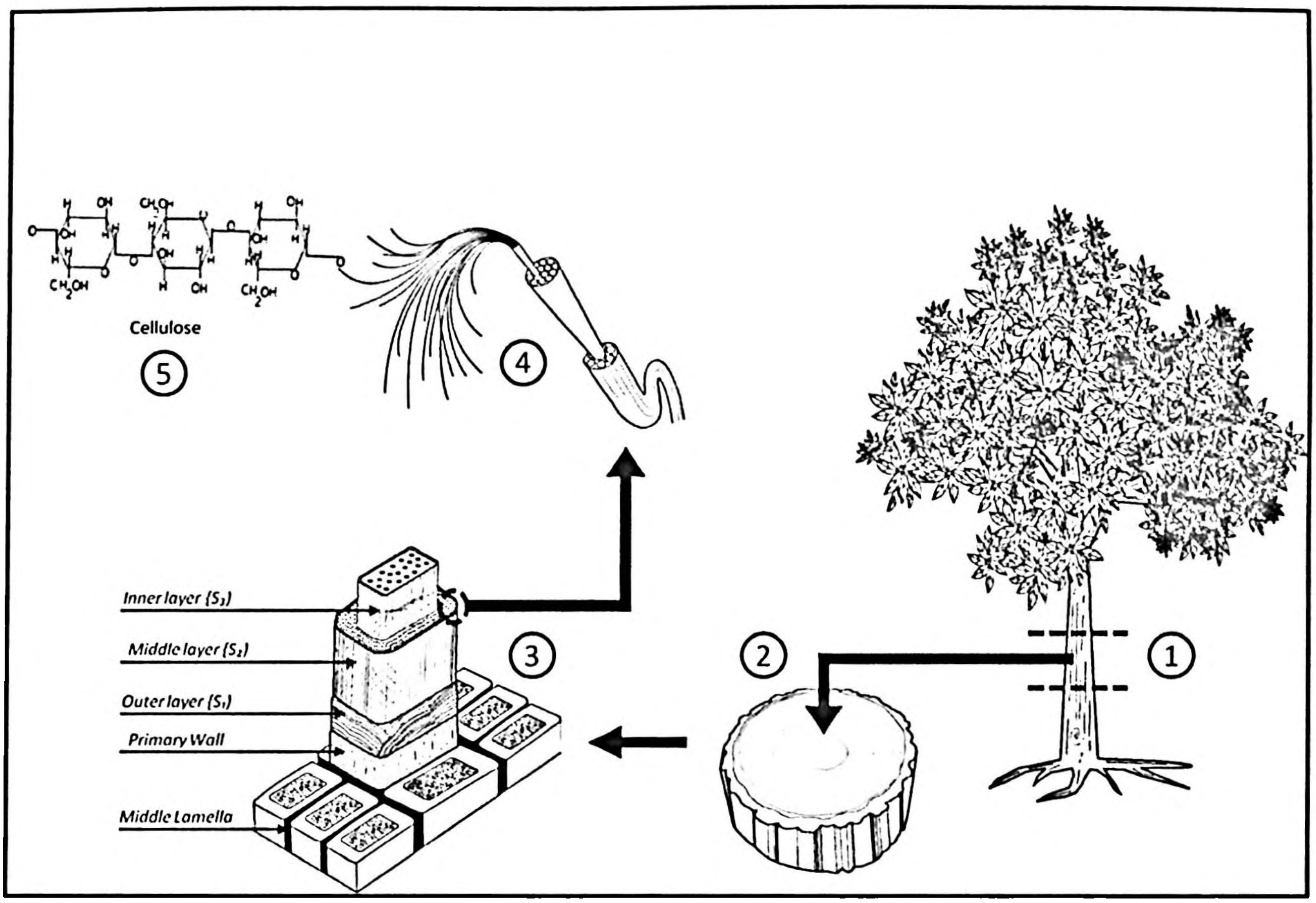

Figure 2.3: Schematic drawing of cellulose hierarchical structure (Abdul Khalil et al., 2014)

Table 2.1: Density and mechanical properties of natural fibers (Abdul Khalil & Suraya, 2011)

Type of fibers	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	Density (g/cm^3)
Bagasse	290	17	-	1.25
Bamboo	140-230	11-17	-	0.6-1.1
Banana	500	12	5.9	1.35
Cotton	287-597	5.5-12.6	7-8	1.5-1.6
Flax	345-1035	27.6	2.7-3.2	1.5
Hemp	690	70	1.6	1.48
Jute	393-773	26.5	1.5-1.8	1.3
Kenaf	930	53	1.6	-
Oil palm	248	3.2	25	0.7-1.55

Naturally occurring cellulose (cellulose I) crystallizes is composed of two polymorphs named Iα (triclinic structure) and Iβ (monoclinic structure) (Moon et al, 2011). Cellulose Iα is a metastable form and can be converted into the Iβ form by an alkaline treatment (Saxena & Brown, 2005). Cellulose II the most stable allomorph has been hardly ever found in the nature but it can be synthesized from cellulose I by mercerization or regeneration (Moon et al., 2011). It differs from cellulose I in unit cell dimensions and probably in chain polarity (Moon et al., 2011). Other allomorphs of cellulose such as cellulose III and IV are known but rare and intensively reviewed by Habibi et al. (2010). Conversion of cellulose to various polymorphs can be seen in figure 2.4.

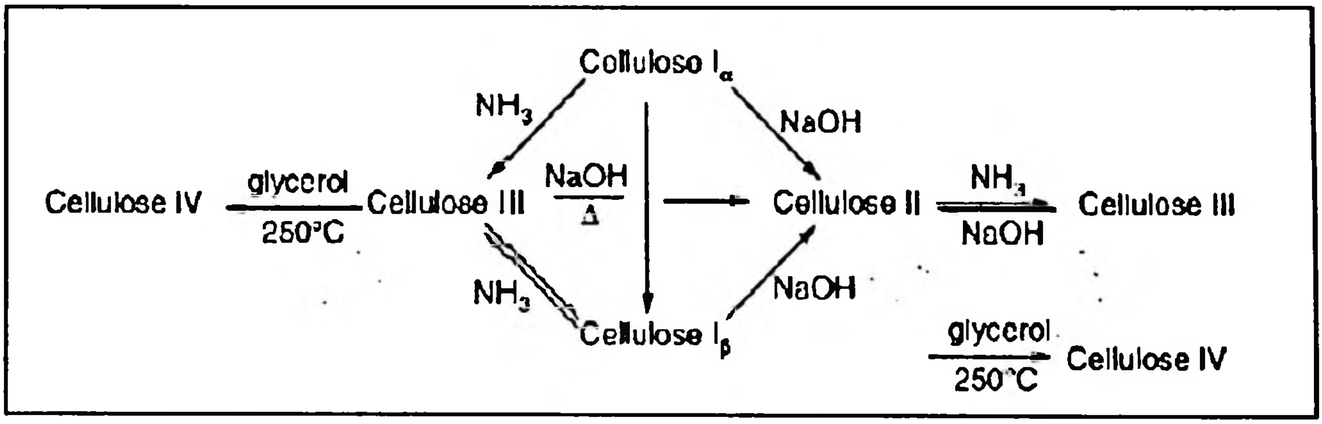

Figure 2.4: Conversion of cellulose into its different polymorphs (Kamel et al., 2008)

2.3. Other Constituents of Cellulosic Fibers

Basically, the structure of natural fibers are quite complex and they are constituted of cellulose, lignin and hemicellulose, ash and extractives. Essentially, rigid cellulose microfibrils are embedded in soft matrix consisting of lignin and hemicellulose (Kukle et al., 2011). Different cellulosic fibers have various chemical compositions related to their origin. Table 2.2 exhibits the chemical composition of some natural fibers (Li et al., 2007).

Lignin can be defined as three dimension and complex polymer which comprised of propyl–phenol groups connected together by C-C bonds and ether (Serrano-Ruiz & Dumesic, 2012). It provides rigidity to fibers using holding them together. In better words, lignin as a sealant besides stiffening cellulose fiber protect it against biological attack (Thielemans & Wool, 2005). On the other hand Hemicellulose is low molecular weight, amorphous and heterogeneous polysaccharides linked with cellulose and lignin in plant fiber's cell walls and consists of xyloglucans, xilans, mannans and glucomannans (Ochoa-Villarreal et al., 2012). Hemicellulose as compatiblizing agent form interface between hydrophobic lignin and hydrophilic cellulose (Thielemans & Wool, 2005). Depend on various sources, lignin and hemicellulose are usually formed 15–25%, 20-30% of chemical composition of cellulosic fibers (Serrano-Ruiz & Dumesic, 2012).

Table 2.2: Chemical composition of some natural fibers (Li et al., 2007)

Type of fibers	Cellulose (%)	Lignin (%)	Hemicellulose (%)
Bast fiber			
Fiber flax	71	2.2	18.6-20.6
Seed flax	43-47	21-23	24-26
Kenaf	31-57	15-19	21.5-23
Jute	45-71.5	12-26	13.6-21
Hemp	57-77	3.7-13	14-22.4
Ramie	68.6-91	0.6-0.7	5-16.7
Core fiber			
Kenaf	37-49	15-21	18-24
Jute	41-48	21-24	18-22
Leaf fiber			
Abaca	56-63	7-9	15-17
Sisal	47-78	7-11	10-24
Henequen	77.6	13.1	4-8

2.4. Kenaf Bast Fibers

Increasing attention to kenaf as non-wood cellulosic fibers is related to ability to absorb phosphorus and nitrogen in the soil as well as its ability to high rate accumulation of carbon dioxide (Aji et al., 2009). Kenaf (*Hibiscus cannabinus* L.) is an agricultural crop of the Malvaceae family and history of kenaf fiber cultivation is date back to Africa (Shi et al., 2011). Kenaf can be grown in severe and various weather conditions; for instance, even in moderate conditions of ambient, it can grow to higher than 3m in 3 months with 25 to 51 mm diameter of stem diameter (Aji et al., 2009). Basically, Kenaf can grows in subtropical and tropical areas. Generally, kenaf fiber whole stalk can be divided to bast (outer layer) and core (inner layer). Kenaf fiber is comprised of long bast (35 wt%) and short core (65 wt%) fibers (Abdul Khalil et al., 2010). The higher cellulose content of bast fiber (55%) compared to core fiber (49%) (Abdul Khalil, & Suraya, 2011) make the bast fibre as a good choice to prepare novel and modern materials with outstanding properties such as nanocellulose. The physical properties and chemical composition and of kenaf bast compare to kenaf core are tabulated in Table 2.3 and Table 2.4, respectively.

Figure 2.5: Kenaf bast fiber

Table 2.3: Physical properties of kenaf bast and core fibers (Akil et al., 2011)

Physical properties	Bast	Core
Fibril length, L (mm)	2.22	0.75
Fibril width, W (μm)	17.34	19.23
L/W	128	39
Lumen diameter (μm)	7.5	32
Cell wall thickness (μm)	3.6	1.5

Table 2.4: Chemical composition of kenaf bast and core (Abdul Khalil & Suraya, 2011)

Constituents	Bast (%)	Core (%)
α-Cellulose	55	49
Holocellulose	86.8	87.2
Lignin	14.7	19.2

2.5. Pulping

Pulping also known as delignification is a process to produce fiber mass from cellulosic materials and can be classified into two general subsections including chemical and mechanical pulping (Mossello et al., 2010). Mechanical pulping applies mechanical instruments such as refiner to detached fibers with yield of up to 95% and low strength pulp whereas in chemical process lignin degrade using alkaline or acid and produce higher strength pulp with low yield around 40-50% (Mossello et al., 2010). It is worth mentioning here from environmental point of view pulping using sulphite and sulphate produce pollution and therefore researcher's attention turned to use eco-friendly method such as soda (alkaline) (Jime'nez et al., 2009). In some cases researchers used anthraquinone (AQ) combine with soda to do pulping process. Some reasons like improve delignification rate and carbohydrate stabilization as well as reduction of kuppa number and increasing yield are stated by researcher to apply AQ in soda pulping (Mossello et al., 2010).

2.5.1. Soda-AQ Pulping of Kenaf Bast Fibers

There are a lot of research about soda-AQ pulping of kenaf bast fibers. For example, based on study conducted by Hart et al., (1993) using 0.1% AQ, 14% soda, at 170°C and for 2h kappa number of kenaf bast pulp reduced from 34.1 to 25.2 but yield didn't change (Hart et al., 1993). In 2002, Khristova et al., evaluated the effect of different pulping processes including soda-AQ, alkaline sulfite-anthraquinone-methanol (ASAM) and alkaline sulfite-anthraquinone (AS-AQ) on the kenaf whole stalk, core and bast. They concluded that AS-AQ method exhibits higher yield, brightness, viscosity and strength for kenaf bast and whole stalk than soda-AQ pulping. Also the yield of kenaf bast fiber using 0.1% AQ, 15% alkali, at 165°C and for 2h was 54.1% (Khristova et al., 2002).

Ang et al., identified that 0.1% AQ, liqur to materil ratio of 7:1, 19.4% NaOH, cooking temperature 160°C and 2h cooking at this temperature are optimized conditions for soda-AQ pulping of kenaf bast with yield of 52.7% (Ang et al., 2010). Also, they concluded that soda-AQ kenaf bast pulp resulted in comparable or higher handsheet properties in comparison with kraft pulps. In addition, they mentioned that by increasing cooking temperature and active alkali percentage, delignification and carbohydrate degradation will increase while these factors will reduce with increasing liqur to fiber ratio. The effect of 20 and 25% NaOH and cooking time 30-180 min on the soda-AQ and soda pulping of kenaf bast are examined by Shakhes and his coworkers (Shakhes et al., 2011). They found that using 0.2% AQ, screening rejects and kappa number of pulps decrease whereas its yield increase. Furthermore, they showed that strength and handsheets' properties of soda-AQ pulp are better than soda pulp. Comparison between pulping of whole kenaf stem, kenaf bast and core using 12, 13.5 and 15% alkali, 0.1% AQ, at 160°C for 30-90min was done by Mossello et al., (2010). They found that cooking of bast is relatively easier than core and its yield also is higher (56.2%) than core fibers (51.8%) whereas whole stem properties was between bast and core fibers.

2.6. Bleaching

Bleaching treatment improves the appearance of fibers and makes them brighter (Wang & Ramaswamy, 2003) as well as can be used to more defibrillation of fibers (Karimi et al., 2014). From environmental point of view, nowadays researchers more concentrate on using chlorine free bleaching processes and good substitute for chlorine agents in bleaching processes is hydrogen peroxide which has been applied for cellulose pulps intensively (Rodriguez et al., 2011). Kenaf pulps bleaching processes using hydrogen peroxide studied by various researchers (Mohta et al., 2003; Ashuri, 2006; Salam et al., 2007; Zinali et al., 2009).

For instance, Zinali et al., (2009) evaluated the effect of two level of NaOH (2 and 3%) and three level of H_2O_2 (3, 4 and 5%) on kenaf bast soda pulp properties. They reported that bleaching using 5% H_2O_2 and 2% NaOH with initial cheation give highest yield of 95% and brightness of 70% and nominated as the best condition. Also, Ashori et al., (2006) evaluated the effect of totally chlorine free bleaching sequences on properties of kenaf. In his bleaching sequences alkaline-peroxide bleaching was done using 3% NaOH and 3% H_2O_2. Jonoobi et al., did bleaching process on kenaf bast soda-AQ pulp in three stages known as DEpD (Jonoobi et al., 2009). They used sodium chlorite and acetic acid in D stage and 1.5% NaOH and 1% H_2O_2 in Ep stage. The results showed that bleached pulp have higher cellulose content (92%) compare to unbleached pulp (81.5%). All in all, researchers apply a wide variety of bleaching processes in order to remove remaining lignin after pulping and therefore to obtain higher cellulose content in the fibers and higher crystallinity and thermal stability.

2.7. Nanocellulose

Nanotechnology as a multidisciplinary field have been extensively developed in wide variety of areas. One of the widespread applications of nanotechnology is in the extraction of nanocellulose (minimum one dimension ≤ 100nm) either in whisker or fiber form (Abdul Khalil et al., 2014). It is recognized that their unique and attractive properties such as renewability, higher strength, biodegradability, higher aspect ratio and larger surface area, can open new doors and give good insights to technological world. In general, nanocellulose materials are calssified to two major families' whisker and fiber. They have different size, morphology and production methods. Cellulose nanowhisker (CNW) also known as nanocrystals are rod-like and usually extractes by acid hydrolysis process (Siqueira et al., 2010). They have low aspect ratio with typical diameter and length of 2-20nm and 100-600 nm, respectively (Hubbe et al., 2008; George & Ramana, 2011).

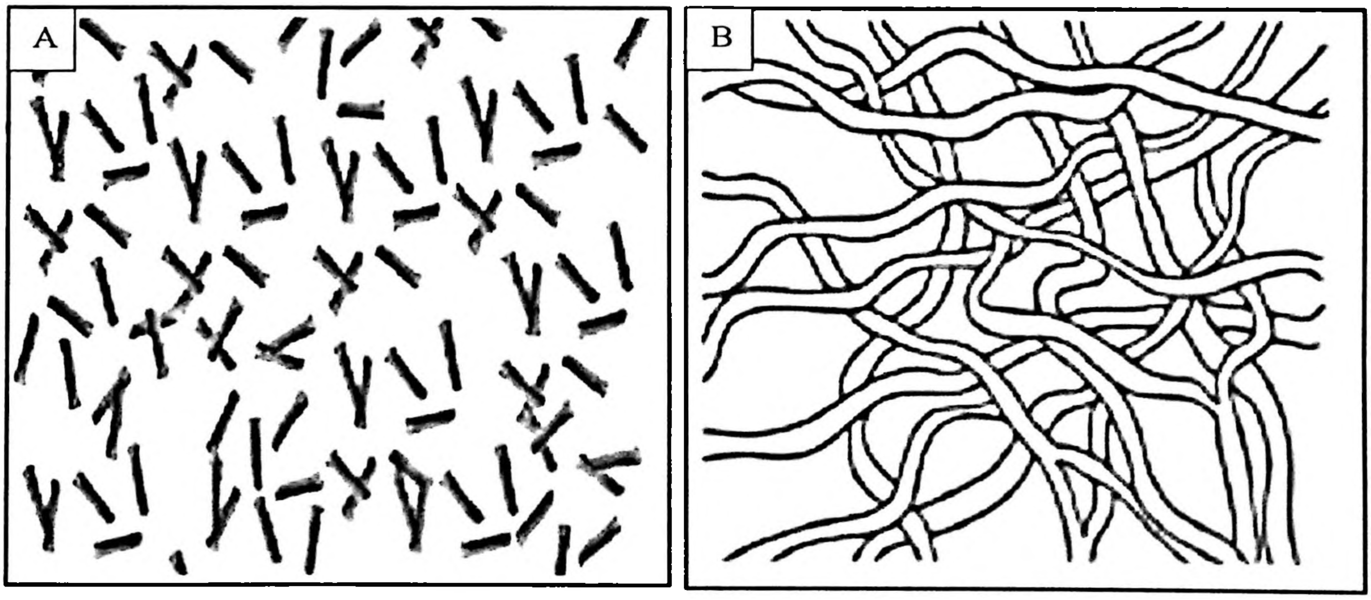

Figure 2.6: Schematic drawing of (A) CNW (B) CNF

Table 2.5: Comparison between nanocelluloses (Abdul Khalil et al., 2014)

Type of nanocellulose	Synonyms	Typical sources	Average size
Cellulose nanocrystal (CNC)	Nanocrystalline cellulose (NCC), whiskers, rod like cellulose	Wood, cotton, hemp, flax, wheat straw, MCC, algae, tunicin, bacteria, etc	Diameter:5-70nm Length: 100-250nm
Nanofibrillated cellulose (NFC)	Nanofibrils, nanofibrillated cellulose, microfibrillated cellulose	Wood, sugar beet, potato tuber, hemp, flax, etc	Diameter:5-60nm Length: several microns

Cellulose nanofiber (Bhatnagar & Sain, 2005), cellulose nanofibril (Ahola et al., 2008) or microfibrillated cellulose (Siró &Plackett, 2010) are terms which used for long and entangled networks of cellulose nanofibers (Chakraborty et al., 2006). Figure 2.6 illustrates schematic drawing of CNW and cellulose nanofiber (CNF) morphology. This figure clearly shows rod like structure of CNW and fibrillar structure of cellulose nanofiber. Furthermore, synumymes, size and some sources of CNW and cellulose nanofiber are tabulated in Table 2.5 (Abdul Khalil et al., 2014).

2.8. CNF's Sources

Since various sources have different characteristics in isolation process of CNFs, so it is important to consider this issue. CNFs can be prepared from kenaf (Jonoobi et al., 2010), wheat straw (Alemdar, & Sain, 2008a), algae (Imai et al., 2003), sugarcane bagasse (Li et al., 2012; Bhattacharya et al., 2008), oil palm (Jonoobi et al., 2011), sugar beet pulp (Dufresne et al., 1997), flax (Hrabalova et al., 2011), wood (Chakraborty et al., 2006; Siddiqui et al., 2011), potato pulp (Dufresne et al., 2000), hemp (Wang et al., 2007), microcrystalline cellulose (Pan et al., 2013), banana rachis (Zuluaga et al., 2009).

2.9. CNF's Isolation Methods

CNFs can be extracted using wide variety of methods such as high pressure homogenization (HPH) (Malainine et al., 2005, Habibi et al., 2009; Zimmermann et al., 2010;), refining (Nakagaito & Yano, 2004; Karande et al., 2011), grinding (Iwamoto et al., 2007, Wang et al., 2012; Hassan et al., 2012), microfluidization (Lee et al., 2009; Ferrer et al., 2012), ultrasonication (Johnson et al., 2009; Chen et al., 2011; Kamphunthong et al., 2012), steam explosion (Cherian et al., 2010; Abraham et al., 2011; Kaushik & Singh, 2011) and electrospinning (Ohkawa et al., 2009; Montaño-Leyva et al., 2011). Figure 2.7 shows the morphology of CNF produced by various methods and from different cellulose fiber sources.

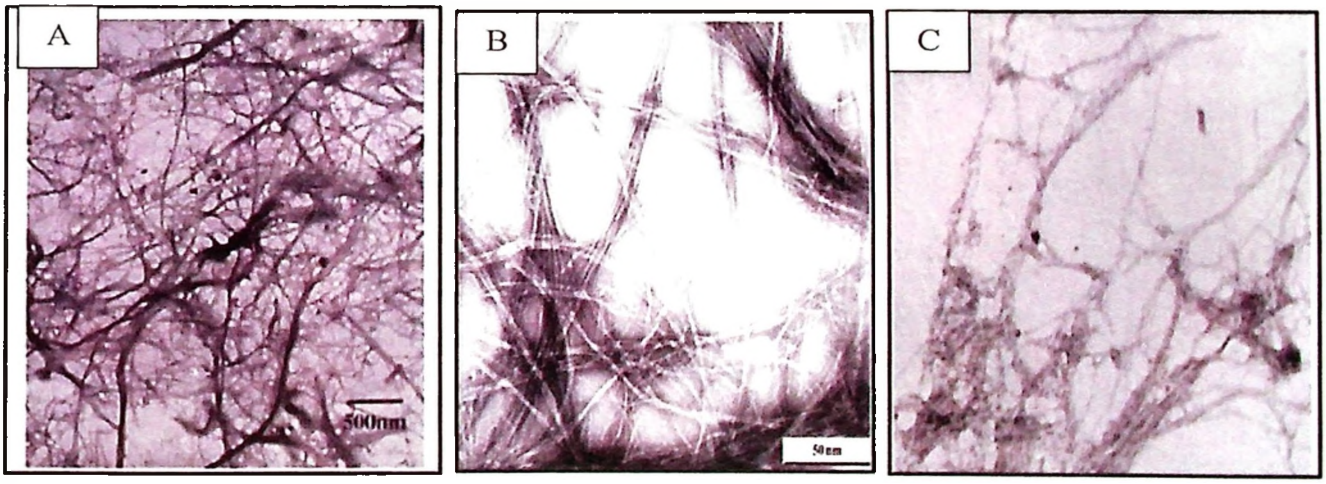

Figure 2.7: TEM micrographs of CNF by (A) ultrasonication (Wang & Sain, 2007a, 2007b) (B) homogenization (Habibi et al., 2009) (C) steam explosion (Kaushik & Singh, 2011)

For example, in electrospinning process finding a solvent which can dissolve cellulose directly is very difficult and most of researchers are using cellulose derivatives. Cryo-crushing and refining usually applied in combination of homogenization in order to increase efficiency of production process. Higher efficiency and defibrillation rate can be obtained by combination of ultrasonication-homogenization (Wang and Chen, 2009) and steam explosion-homogenization (Kaushik & Singh, 2011) compare to each of these methods solely. It is worth nothing that homogenization is most widely mechanical process used in order to isolate CNFs from various sources.

2.9.1. High Pressure Homogenization (HPH)

In homogenization instrument cellulosic fiber suspension passes through a small orifice with high pressure. Effective parameters in diminishing the size of the fibers to nanoscale in this process include high shear and impact forces along with high pressure and velocity on fluid which generate shear on the stream (Abdul Khalil et al., 2012). Some of the most important parameters which affect the properties of obtained nanofibers are pressure, different passing times through machine and concentration of suspension.

Herrick and Turbak in 1983, for first time applied this method to isolate CNF from wood fiber (Herrick et al., 1983; Turbak et al., 1983). Although homogenization is very simple process without needs to organic solvents (Keeratiurai & Corredig, 2009) but clogging is one of the most important issues related to application of this instrument because of its small orifice. To overcome this problem, researchers used various pretreatments like refining and cryocrushing (Jonoobi et al., 2009), and milling (Zimmermann et al., 2010) to reduce the size of fibers. It is worth noting that, another main drawback of homogenization is high energy consumption.

In this regard, application of some chemical pretreatments including, enzyme treatment (Henriksson et al., 2007; Pääkkö et al., 2007; Janardhnan & Sain, 2011) and alkaline-acid treatment (Bhatnagar & Sain, 2005; Alemdar & Sain, 2008a,b), ionic liquids (Li et al. 2012) utilized by researchers to decrease the amount of energy for production of CNF. As Siro and Plackett (2010) mentioned, using such chemical or enzymatic pretreatments energy consumption in mechanical processes can be diminished from 20,000 to 30,000 kWh/tonne which is common in these kinds of methods to 1000 kWh/tonne.

Figure 2.6 shows the transmission electron microscopy (TEM) images of alkaline treated wheat straw (Alemdar & Sain, 2008b), enzyme treated softwood pulp (Pääkkö et al., 2007) and ionic liquid treated sugarcane bagasse (Li et al., 2012). As can be seen in this figure, the diameter of wheat straw reached to after alkaline treatment the diameter of wheat straw was 9 μm and after mechanical isolation it reached to 30-40nm (figure 2.8A) whereas diameter of enzyme treated fiber (figure 2.8B) was around 5 nm and circular shape nanoparticle with diameter of 10 to 20nm produced from ionic liquid treatment of sugarcane bagasse (figure 2.8C). Apart from the production process of CNF by homogenization, their final application is also critical issue. Because of hydrophilic nature of CNF, incorporation and dispersion of them with common polymers, which are hydrophobic, are very critical issues. Low interfacial adhesion between these two parts in composite leads to reduce the mechanical and other properties of the final product. Thus, a wide variety of modifications like acetylation (Jonoobi et al., 2012; Bulota et al., 2012), carboxymethylation (Siró et al., 2011; Eyholzer et al., 2010), 2, 2, 6, 6-tetramethylpiperdine-1-oxyl (TEMPO) oxidation (Saito et al., 2006; Lasseuguette et al., 2008) and silylation (Andresen et al., 2006; Qua et al., 2011) designed to overcome this problem.

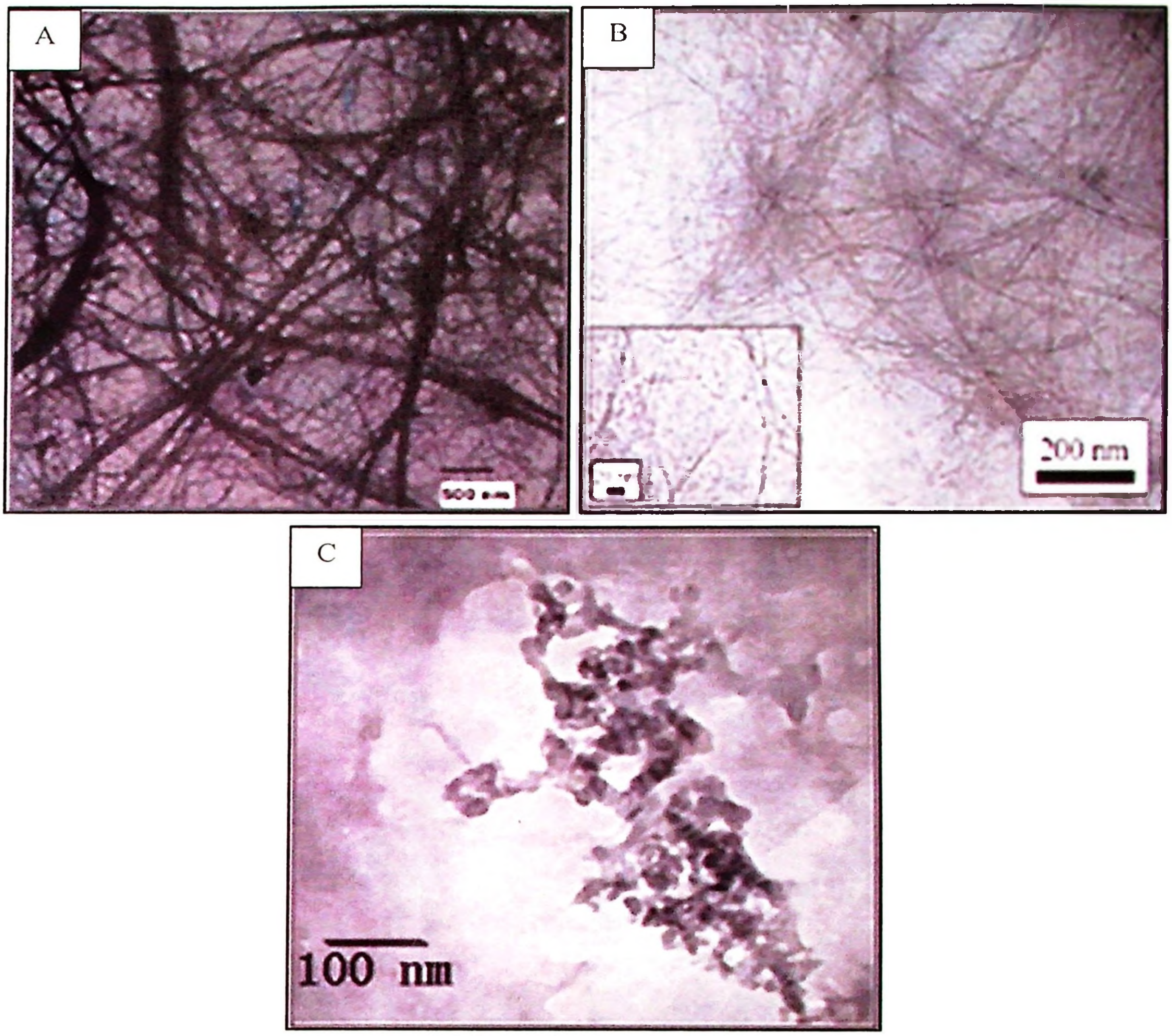

Figure 2.8: TEM images of (A) alkaline treated wheat straw (Alemdar & Sain, 2008b) (B) enzyme treated softwood pulp (Pääkkö et al., 2007) (C) ionic liquid treated sugarcane bagasse (Li et al., 2012)

2.10. Acid Hydrolysis Pretreatment before HPH

Actually acid hydrolysis by removing hemicellulose as amorphous regions of cellulosic fibers can help to increase crystallinity of fibers. In this regard there are just three researches which applied acid hydrolysis as pretreatment before homogenization in order to reduce the size of fibers and therefore reduce energy consumption as well as prevent from blocking of the HPH machine. Henriksson et al., (2007) compared effect of enzyme, mild HCl hydrolysis (1M, 1h) and strong acid hydrolysis (2.5M, 2h) before homogenization on wood fiber (figure 2.9).

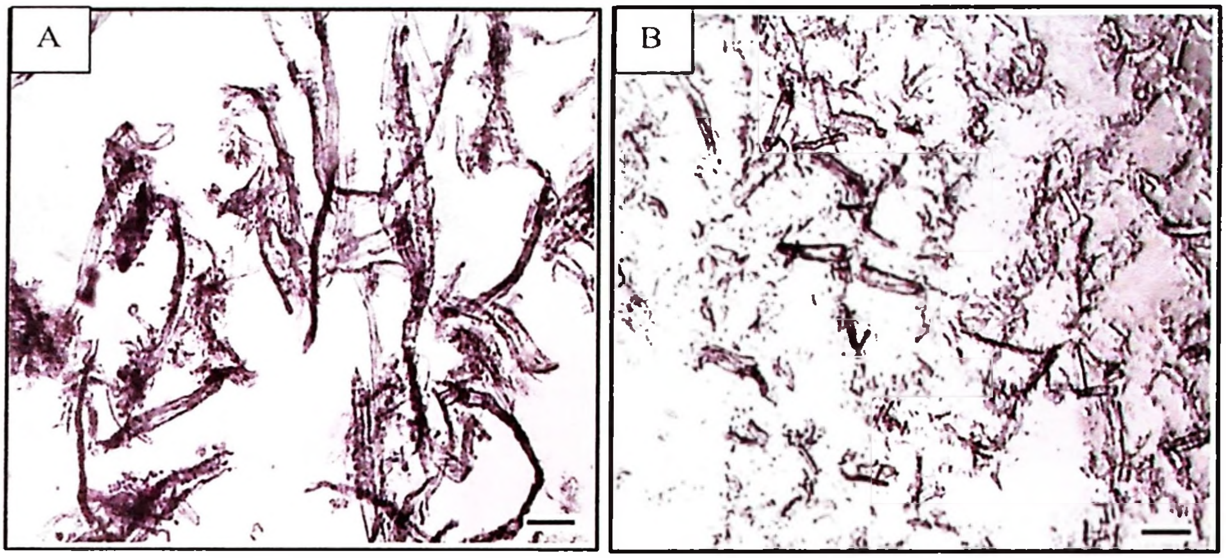

Figure 2.9: Optical image of fiber treated with (A) enzyme (B) strong acid (Henriksson et al., 2007)

Henriksson et al., (2007) found that treated fibers using mild acid can not be homogenize. They reported that compare to strong acid hydrolysis, enzyme treatment facilitate disintegration, and produce nanofiber with larger aspect ratio and higher molar mass. Their results also illustrated nonhomogeneous distribution of nanofiber as well as large number of thick fragments. It is worth nothing that in this paper just degree of polymerization and morphology of molecular weight distribution of enzyme treated and acid treated nanofibers were compared and other properties such as thermal and crystalline characteristics were neglected. In another work, Qua et al., (2011) evaluated the effect of three pretreatments including H_2SO_4 hydrolysis (20 wt%), mercerization and silylation on the properties of nanofibers obtained by microfluidizer from flax (figure 2.10). They found that overally the crystallinity of flax nanofiber increased but thermal stability decreased. They reported that thermal stability of nanofibers after multimple passing through microfluidizer was strongley effected by alkaline and acid. Generally they concluded that both acid and alkaline pretreatments boost thermal stability of nanofiber besides increasing cycles through microluidizer.

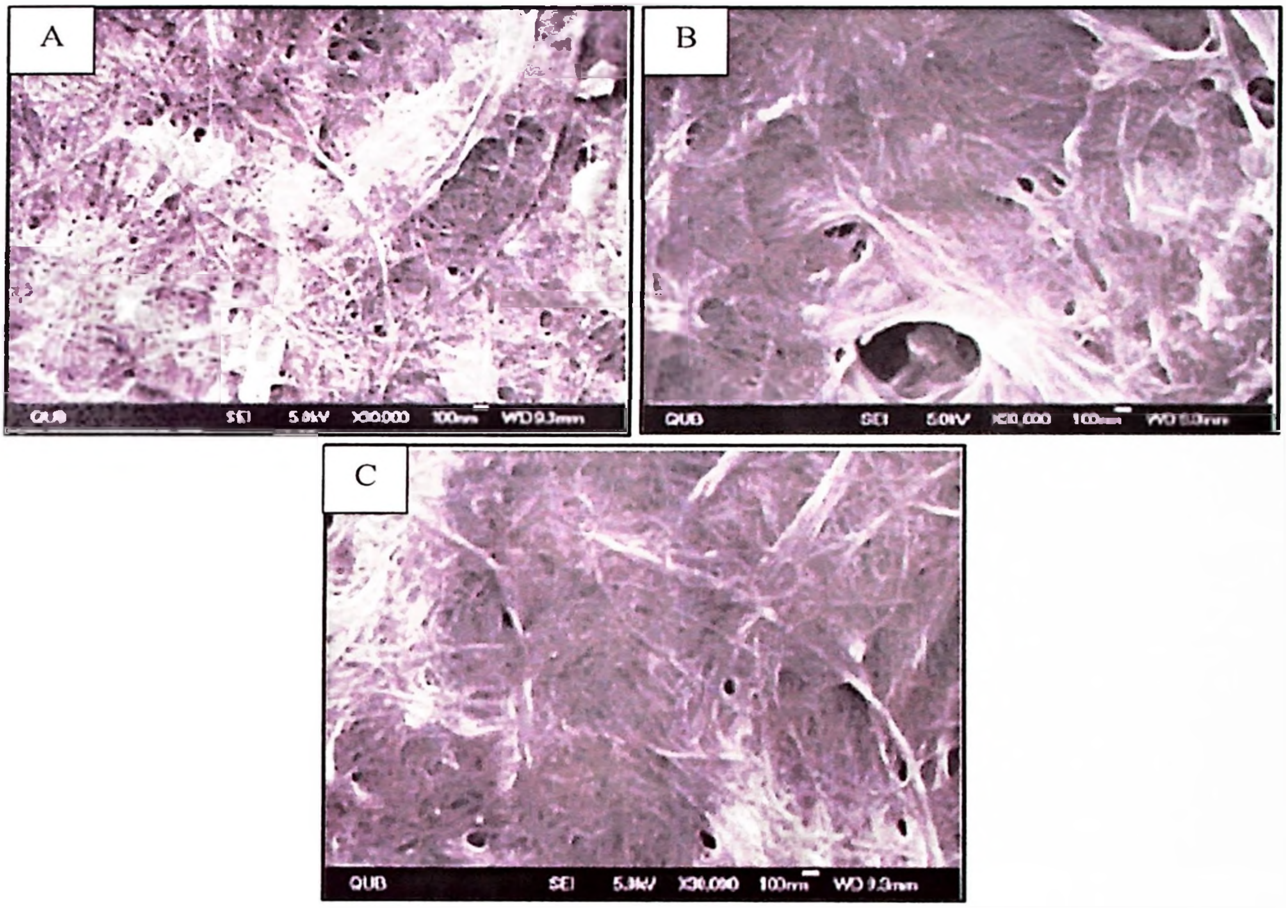

Figure 2.10: SEM images of flax CNF produced by (A) acid (B) alkaline (C) silane treatment (Qua et al., 2011)

The last research using combination of acid hydrolysis and homogenization was conducted by Pan et al., (2013). They studied the effect of time, H_2SO_4 concentration and temperature of acid hydrolysis on chemical properties and geometry of nanocellulose from MCC (figure 2.11). Their nanocellulose's length, diameter and aspect ratio was 199-344nm, 11-33nm and 10-18, respectively and because of these characteristics they called it CNW not CNF. They reported that during hydrolysis some breakage of hydrogen bond and intramolecular bonds happened. They concluded that increasing concentration