

A STUDY OF ACID HYDROLYSIS BASED SYNTHESIS OF MICROCRYSTALLINE AND NANOCRYSTALLINE CELLULOSE FROM LOCAL LIGNOCELLULOSIC MATERIALS

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Declaration by the Candidate

I do hereby declare that this thesis or part of it has not been submitted elsewhere for the award of any degree or diploma.

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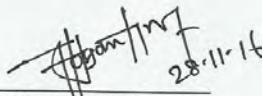
**A STUDY OF ACID HYDROLYSIS BASED SYNTHESIS OF MICROCRYSTALLINE AND
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BY**

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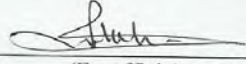
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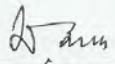
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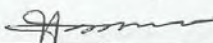
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**DEDICATED TO
MY BELOVED MOTHER**

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Mst. Shahanaz Yeasmin

Abstract

Cellulose is one of the most important substances among natural and synthetic polymeric materials. Fibrous cellulosic materials are capillary porous disperse systems with high specific surface areas. The degraded (low molecular weight product) micro and nano cellulose is highly renewable. Because of their inherent renewability and sustainability and unsurpassed quintessential physical and chemical properties, microcrystalline cellulose (MCC) and nanocrystalline cellulose (NCC) have a great attention to the researcher. The highly crystalline cellulose can be prepared by selective methods based on the source of the cellulose. MCC and NCC can be derived from number of process like reactive extrusion process, enzyme mediated process, the steam explosion process and acid hydrolysis process etc. Out of this process acid hydrolysis process is most suitable to prepare the low cost degraded micro and nanocellulose. In this study, cotton based waster cloths and commercial wood pulp, which were collected from local shop, hosiery industry and paper industry, were used to prepare MCC and NCC by acid hydrolysis and ultrasound assisted acid hydrolysis process, respectively.

Since the cellulose contains both amorphous and crystalline structures, MCC and NCC is derived by severe acid hydrolysis to remove the amorphous portions of cellulose, yielding low molecular weight micro and nano particles. In this study cellulosic materials were hydrolyzed in different concentration of HCl (2.5-10N) at different temperatures (80-110)⁰C to optimize the preparation condition for the preparation of MCC powder from local waste lignocellulosic materials. It was observed that the formation of MCC depends upon the source of cellulose and the reaction conditions of hydrolysis. On the other hand, the stable suspension of cellulose nanocrystals was prepared by sulfuric acid hydrolysis followed by ultrasound. For that purpose the optimum conditions for the formation of transparent gel of NCC were established for the local cotton cloths. Set of experiments were performed to examine the optimum condition viz. temperature, time and concentration of acid for the preparation of NCC. The optimum condition of hydrolysis was: concentration of acid 63-65 % (w/w), temperature 60°C and time 35 minutes.

Surface morphology and particle size were investigated through Field Emission Scanning

Electron Microscopy (FESEM). The analysis showed that the average diameter of prepared MCC was about 5-10 μm and length was about 50 μm and the average fiber diameter of NCC was less than 20 nm with a length of 100 nm to few micrometers. Comparison of commercial MCC and prepared MCC of FTIR confirmed the preparation of typical microcrystalline cellulose. The FTIR analysis of NCC was also observed. The results of chemical analysis, XRD confirmed the crystallinity of MCC and NCC. Thermogravimetric analysis results showed the stability of the prepared MCCs from different sources. Thermogravimetric analysis results showed that MCC have higher thermal stability than NCC.

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CHAPTER 1

INTRODUCTION

1. Introduction

Cellulose is the most abundant organic polymer with the formula $(C_6H_{10}O_5)_n$. It is a carbohydrate polymer made up of repeating β -D glucopyranose units and consists of three hydroxyl groups per anhydroglucose unit (AGU) giving the cellulose molecule a high degree of functionality [1]. The knowledge of the molecular structure of cellulose is of prime importance as it explains the characteristic properties of cellulose, such as hydrophilicity, chirality, biodegradability and high functionality. As a renewable material, cellulose and its derivatives have been widely studied, focusing on their biological, chemical, as well as mechanical properties. The materials based on cellulose and its derivatives have been used for more than 150 years in a wide variety of applications, such as food, paper production, biomaterials and pharmaceuticals [2]. Cellulose is a relatively stable polymer [3], due to the hydrogen bond network, which does not dissolve in common aqueous solvents [4] and has no fixed melting point. In contrast with mineral fibers (glass, carbon fibers), the cellulose fibers have a good flexibility and elasticity, these properties allowing them to maintain a high aspect ratio in the process of manufacturing.

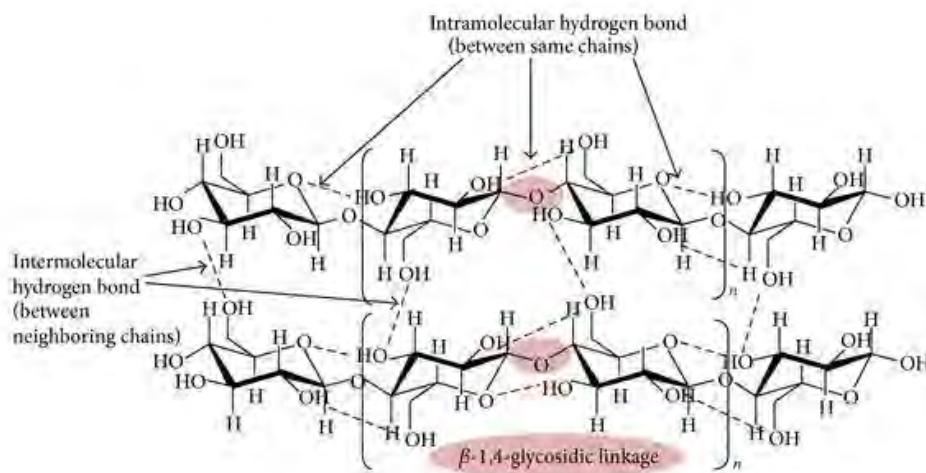


Fig: 1.1: Chemical Structure of cellulose chain.

In the world, approximately 10^{15} Kg/yr. is synthesized and degraded and it is found in plenty in nature in the form of cotton, hemp, jute, flax etc. A good percentage of wood also consists of cellulose. Cellulose has an extremely high degree of crystallinity and this is due to the formation of several hydrogen bonds originating from its hydroxyl groups. Its high stereo regularity is also

a contributory factor for its high crystallinity. Pure cellulose, also known as α -cellulose, is a material insoluble in 17.5% NaOH. β -cellulose and γ -cellulose are not true cellulose. β -cellulose believed to be degraded. It has low degree of polymerization cellulose and is insoluble in 17.5 % NaOH; γ -Cellulose is completely soluble at any pH and is thought to be hemicelluloses such as xylans, mannas, galactansetc [5-6]. Pretreatment is required to alter the structure of cellulosic materials to make cellulose more accessible to reactants and is a necessary element in bioconversion of lignocellulosic materials to fuels and chemicals. Pretreatment methods are either physical or chemical, some methods incorporate both. Chemical treatments with acids or bases promote hydrolysis and improve the yield of crystalline cellulose from cellulosic materials by removing hemicelluloses or lignin during pretreatment. The most commonly used acid and base are H_2SO_4 and NaOH, respectively; however, nitric, hydrochloric acid and phosphoric acid have also tested.

Cellulosic material is one of the most abundant important substances because of its renewability, biodegradability and non-toxicity [7]. The important value added part of cellulosic materials is the crystalline cellulose in microcrystalline and nanocrystalline form. Microcrystalline cellulose (MCC) represents a novel state of commercial cellulose widely applied as excipient in drugs/pharmaceuticals, fillers in special type of papers, emulsifier and bulking agent in food production, cosmetics and other industries. On the other hand, nanocrystalline cellulose (NCC) is a material composed of nanosized cellulose crystals with a high aspect ratio, an emerging renewable nanomaterial that holds promise in many potential applications, such as in electronics, nanocomposite films, drug delivery, emulsion, dispersion, oil recovery, protein immobilization, metallic reaction template, regenerative medicine in pharmaceuticals, cosmetics, chemicals, foods, and personal cares [8-13]. Compared to cellulose fibers, NCC possesses many advantages; such as nanoscale dimension, high specific strength and modulus, high surface area, unique optical properties, etc [2,14-15]. These amazing physicochemical properties and wide application prospects have attracted significant interest from researcher, scientists and industrialists. By appropriate modification of NCC, various functional nanomaterials with outstanding properties or significantly improved physical, chemical, biological, as well as opto-electronic properties can be developed.

Since lignocellulosic materials contain both amorphous and crystalline parts, the highly crystalline cellulose can be prepared by different selective methods based on the source of cellulose. Among them MCC is derived by acid hydrolysis to remove the amorphous parts (lignin, proteins), yielding particles consisting microcrystals [16]. On the other hand, the NCC can be prepared by vigorous acid hydrolysis or by the combination of acid hydrolysis [17] and ultrasonic treatment [18]. Acid hydrolysis followed by ultrasonic treatment is also reported for the preparation of transparent aqueous gel of NCC [19].

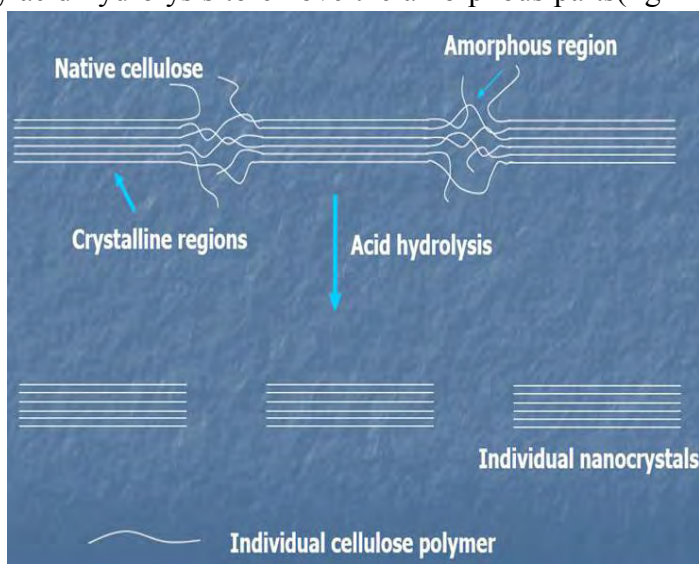


Fig.1.2. Degradation of amorphous region of cellulose by acid hydrolysis

When lignocellulosic materials are subjected to harsh sulphuric acid treatment, the hydronium ions migrate to the amorphous regions since they have lower density compared to the crystalline regions. The hydronium ions cleave the glycoside linkages hydrolytically thereby releasing the individual crystallites. Acid hydrolysis is dependent on different parameters, such as acid concentration, time of reaction, temperature of reaction and the specific acid used for the treatment [19]. Another important characteristic of NCC is that the individual crystallite has negative charges on their surface due to the formation of sulphate ester groups during sulfuric acid treatment. The negatively charged NCC forms stable aqueous suspensions due to the electrostatic repulsion between the individual crystallites. On the other hand, acid hydrolysis with hydrochloric acid does not produce as many negative surface charges on NCC, resulting in less stable NCC suspensions [20]. Therefore, sulfuric acid is mostly used in the preparation of NCC. On the other hand, both sulfuric acid and Hydrochloric acid treatment for the preparation of MCC is available in literature [21-27]. The nano and micro crystalline cellulose derived from acid hydrolysis of native cellulose possesses different morphologies depending on the origin and hydrolysis conditions.

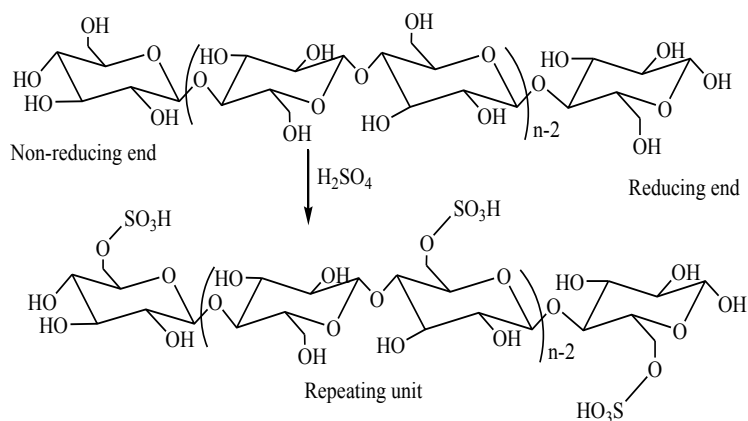


Fig. 1.3. Hydrolysis of lignocellulosic materials with H_2SO_4

However, the properties of the final products are very much dependent on the reaction conditions [23], type of acid and its concentration, combination of chemical and mechanical techniques and moreover the source of cellulose [24]. As a result, there is a huge future impact of research on the extensive studies on preparation condition of MCC and NCC for the next generation biodegradable nanopolymer & nanocomposites from lignocellulosic materials especially from local available waste lignocellulosic source. As a consequence, this research project is aimed at the development of preparation condition of MCC by acid hydrolysis technique and preparation of NCC by acid hydrolysis followed by ultrasonic treatment using local cotton based cloths and commercial wood pulp as the source of lignocellulosic materials.

1.2 Outline of Methodology

The cotton based cloths were collected from local shop and from hosiery industry. The commercial wood pulp was collected from a paper industry. All the raw cellulosic materials were first washed and bleached to remove the dirt and colors. The samples were further treated with NaOH. The samples were then hydrolyzed in different concentrations of HCl in the range of 2.5N to 10N at different temperature to prepare the MCC. The pretreatment, hydrolysis reaction time, temperature of hydrolysis was optimized in separate experiments. After the hydrolysis, the sample was washed carefully to complete removal of dissolved materials and chlorides. For the preparation of NCC, the materials were hydrolyzed by sulphuric acid at different temperature, time and concentration. After the hydrolysis, the sample was subjected to the ultrasonic

treatment for further depolymerization with subsequent washing and high speed centrifugation. The time, temperature and concentration were optimized by the observation of gel formation. The effect of crystallinity of the MCC with different reaction conditions were analyzed from XRD data. The shift of absorption peak and intensity change in the FTIR was given additional information about the optimum hydrolysis condition. The thermal stability and degradation was analyzed by TG. The particle size was analyzed with Field Emission Scanning Electron Microscopy (FESEM).

1.3 Objectives

The main objectives of this work were to (i) develop an optimum condition of acid hydrolysis of local cellulosic materials (cotton linter and wood pulp) to prepare commercial grade MCC (ii) develop a preparation method for the NCC from the cotton linter and (iii) Characterize the prepared MCC and NCC to justify the optimum preparation condition.

1.4 References

- [1] Klemm, D., Heublein, B., Fink, H.P., Bohn, A., "Cellulose: Fascinating Biopolymer and Sustainable Raw Material". *Angewandte Chemie International Edition*, 44(22): pp 3358-3393. 2005.
- [2] De Souza Lima, M. M., & Borsali, R., "Rod like cellulose microcrystals: structure, properties and applications," *Macromolecular Rapid Communications*, 25, pp.771-787. 2004.
- [3] Whistler, R.L., BeMiller, J. M., "Cellulosic in Carbohydrate Chemistry for Food Scientists." *American Association of Cereal Chemists, Inc.*: vol. 7, p155. Minnesota 1997.
- [4] Coffey, D. G., Bell, D. A., Henderson, A., "Food Polysaccharides and their Applications," *Marcel Dekker*, New York 1995.
- [5] Chauhan, Y. P., Sapkal, R. S., Sapkal V. S., and Zamre, G. S., "Microcrystalline cellulose from cotton rags (waste from garment and hosiery industries)" *Int. J. Chem. Sci.*: 7(2), pp 681-688, 2009.
- [6] Gowarikar, V. R., Viswanathan, N. V. and Sreedhar Jaydev, "Polymer Science," *New Age International (P) Limited*, New Delhi, 1986.
- [7] Nevell, T. P., Zeronian, S. H., "Cellulose Chemistry and its application" *E. Horwood*, Chichester 1985.
- [8] Valo, H., Kovalainen, M., Laaksonen, P., Hakkinen, M., Auriola, S., Peltonen, L., Linder, M., Jarvinen, K., Hirvonen, J. & Laaksonen, T., "Immobilization of protein-coated drug nanoparticles in nanofibrillar cellulose matrices--enhanced stability and release." *J Control Release*, 156(3): 390-7. 2011.
- [9] Zimmermann, T., Bordeanu, N., & Strub, E., "Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential" *Carbohydrate Polymers*, 79(4): 1086-1093. 2010.
- [10] Turbak, A. F., Snyder, F. W. & Sandberg, K.R., "Microfibrillated cellulose, a new cellulose product: properties, uses and commercial potential." *Journal of Applied Polymer Science: Applied polymer symposia*, 37, pp 815-827. 1983
- [11] Nogi, M., Iwamoto, S., Nakagaito, A. N., & Yano, H., "Optically Transparent Nanofiber Paper." *Advanced Materials*, 21(16), pp 1595-1598. 2009.
- [12] Syverud, K., & Stenius, P., "Strength and barrier properties of MFC films." *Cellulose*, 16(1), pp 75-85. 2009.

- [13] Favier, V., Chanzy H., &Cavaille,J. Y., “Polymer Nanocomposites Reinforced by Cellulose Whiskers,” *Macromolecules*, pp 28, 6365-6367. 1995.
- [14] Ping Lu, You-Lo Hsieh,“Preparation and properties of cellulose nanocrystals: Rods, spheres, and network.”*CarbohydredPolymer*, 82, pp329-336. 2010.
- [15]Heux, L.,Chauve, G.,&Bonini, C., “Nonflocculating and Chiral-Nematic Self-ordering of Cellulose Microcrystals Suspensions in Nonpolar Solvents.” *Langmuir*, 16 (21), pp 8210–8212, 2000.
- [16]Nada, A. M. A., El-Kady, M. Y., El-Sayed, E. S. A. And Amine, F. M.,“Preparation and Characterisation of microcrystalline cellulose”,*BioResources*4(4), pp 1359-1371, 2009.
- [17]Peng, B. L., Dhar, N., Liu, H. L., and Tam, K. C.,“Chemistry and Applications of Nanocrystalline Cellulose and Its Derivative: A Nanotechnology Perspective”.*The Canadian Journal of Chemical Engineering*, Vol 9, pp 1-12. 2011.
- [18] Michael Ioelovich, “Study of Cellulose Interaction with Concentrated Solutions of Sulfuric Acid”*ISRN Chemical Engineering*,pp 1-7, 2012.
- [19]Bondeson, D., Mathew, A.,&Oksman, K. “Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis.”*Cellulose*, 13, pp 171-180. 2006.
- [20] Sugiyama, J.,Vuong, R.,& Chanzi, H., “Electron diffraction study on the two crystalline phases occurring in native cellulose from an algal cell wall.” *Macromolecules*, 24, pp4168-4175. 1991.
- [21] Zhang, J., Elder, T. J., Pu, Y.,Ragauskas, A. J., “Facile synthesis of spherical cellulose nanoparticles.” *Carbohydrate Polymers*.69, pp 607-611, 2007.
- [22] Beck-Candanedo, S.,Roman, M., and Gray, D. G. “Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions”*Biomacromolecules*.6(2), pp1048-1054, 2005.
- [23] Araki, J., Wada, M., Kuga, S.,& Okano, T.,“Flow Properties of Microcrystalline Cellulose Suspension Prepared by Acid Treatment of Native Cellulose.”*Colloids Surf*.142(1), pp75–82. 1998.
- [24] Saiani, A., Miller, A. F., & Donald, A. M., “Imaging of anisotropic cellulose suspensions using environmental scanning electron microscopy.” *Biomacromolecules*, 4, pp 510–517. 2003.

- [25] Pranger, L. & Tannenbaum, R., "Biobased Nanocomposites, Prepared by In Situ Polymerization of Furfuryl Alcohol with Cellulose Whiskers or Montmorillonite Clay." *Macromolecules*, 41(22), pp8682–8687. 2008.
- [26] Terech, P., Chazeau, L., & Cavaille, J. Y., "A Small-Angle Scattering Study of Cellulose Whiskers in Aqueous Suspensions." *Macromolecules*, 32(6), pp1872–1875. 1999.
- [27] De Souza Lima, M. M. & Borsali, R., "Static and Dynamic Light Scattering from Polyelectrolyte Microcrystal Cellulose." *Langmuir*, 18(4), pp992–996. 2002.

CHAPTER 2
LITERATURE REVIEW

2.1 Cellulose and Its Sources

Cellulose, the most abundant renewable and biodegradable polymer, is the promising feedstock for the production of chemicals for their applications in various industries. Annual production of cellulose in nature is estimated to be 10^{11} – 10^{12} ton in two forms, partially in a pure form, for example seed hairs of the cotton plant, but mostly as hemicelluloses in cell wall of woody plants [1]. The versatility of cellulose has been reevaluated as a useful structural and functional material. The environmental benefits of cellulosic materials have become even more apparent [2]. Cellulose is revered as a construction material, mainly in the form of intact wood but also in the form of natural textile fibers like cotton or flax, or in the form of paper and board. The value of cellulose is also recognized as a versatile starting material for subsequent chemical transformation in production of artificial cellulose based threads and films as well as of a variety of cellulose derivatives for their utilization in several industries such as food, printing, cosmetic, oil well drilling, textile, pharmaceutical, etc. and domestic life.

Anselme Payen discovered and isolated cellulose from green plants in 1838 and suggested that cell walls of almost any plant are constructed of the same substance [3]. However, it was only in the 20th century that the structure of cellulose was resolved [4,5]. Main sources for cellulose isolation are plant-based materials such as wood, cotton, and straw. In plants cellulose is constituent of the cell wall and it has a reinforcing role [6]. Cellulose can be derived from a variety of sources such as woods, annual plants, microbes, and animals. These include seed fiber (cotton), wood fibers (hardwoods and softwoods), bast fibers (flax, hemp, jute, ramie), grasses (bagasse, bamboo), algae (*Valoniaventricosa*), and bacteria (*Acetobacter xylinum*) [7]. *A. xylinum* can synthesize extracellular pellicles of cellulose from glucose. Some simple marine animals such as tunicates deposit cellulose in their cell walls [8]. Besides cellulose, these materials also contain hemicelluloses, lignin, and a comparable small amount of lignin. Wood and cotton are the rawmaterials for commercial production of cellulose. Cellulose serves as a structural material within the complex architecture of the plant cell walls with variation in its content. In wood, it constitutes about 40–50%; in leaf fibers: sisal fibers (55–73%), in bast fibers: flax 70–75%, hemp 75–80%, jute 60–65%, ramie 70–75%, kenaf 47–57%, in canes: bamboo 40–55%, bagasse 33–45%, and in cereal straw: barley 48%, oat 44–53%, rice 43–49%, rye 50–54%, wheat 49–54%. Cotton seed hairs, the purest source, contain 90–99% of cellulose [9-10]. In our

country cotton linter obtained from garments wastage, spoilage and waste paper from press and paper mill can also be a great source of cellulose if we utilize it in a proper industrial way.



Fig.2.1. Cotton linter

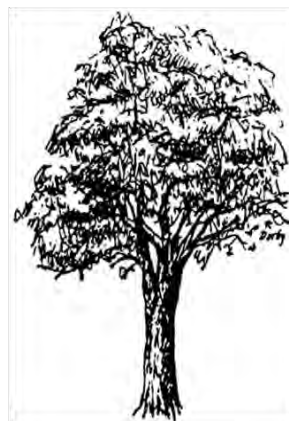
Cotton seed hairs is the purest source, contain 90–99% of cellulose.



Fig. 2.2. Cotton seed hairs

Forest is a big resource on earth. Of the wood composition approximately 40-50% is cellulose.

Wood can be divided in to hard wood and soft wood. Hard wood has lower cellulose content compared to soft wood (Fig:2.3) and the cellulose composition of spring wood is lower than the summer wood. The cellulose content of the juvenile wood is lower than the mature wood.



Hardwood

softwood

Fig. 2.3. hardwood&softwood

2.2 Structure and basic information of cellulose

Cellulose is a polysaccharide produced by linking additional sugars in exactly the same way. The length of the chain varies greatly from its sources, e.g. a few hundred sugar units in wood pulp and over 6000 for cotton. The degree of polymerization (DP) is used to describe the average number of the monomer units in a cellulose chain. DP is dependent upon the origin of the cellulose material. The length of the cellulose chains (degree of polymerization, DP) varies greatly depending on the material source and could be in the range of 300-10000 [11], although 20-30 AGUs give the material properties of cellulose [12]. It is widely known that polysaccharides are produced by plants. These are a linear polymer with very long macromolecular chains of one repeating unit, cellobiose. Cellulose is the most common biopolymer and the common organic compound on Earth and about 33 percent of all plant matter is cellulose. The total cellulose content in cotton is 90 percent and in wood it is 50 percent. Cellulose is a long chain of linked sugar molecules that gives wood its remarkable strength. It is the main component of plant cell walls, and the basic building block for many textiles and for paper. Cotton is the purest natural form of cellulose. In the laboratory, ashless filter paper is a source of nearly pure cellulose.

Cellulose is a natural polymer, a long chain made by the linking of smaller molecules. Regardless of its source, cellulose can be characterized as a high molecular weight homopolymer of β -1,4-linked anhydro-D-glucose units in which every unit is corkscrewed 180° with respect to its neighbors, and the repeat segment is frequently taken to be a dimer of glucose, known as cellobiose (Fig. 2.4). The hydroxyl group at the C2 can form hydrogen bonds with the preceding ring oxygen. The hydrogen bonds prevent the free rotation of the rings and as a consequence form stable chain structure (Fig. 2.5) [13]. The hydrogen bonding network is one of the reasons that cellulose is insoluble in common solvents [14].

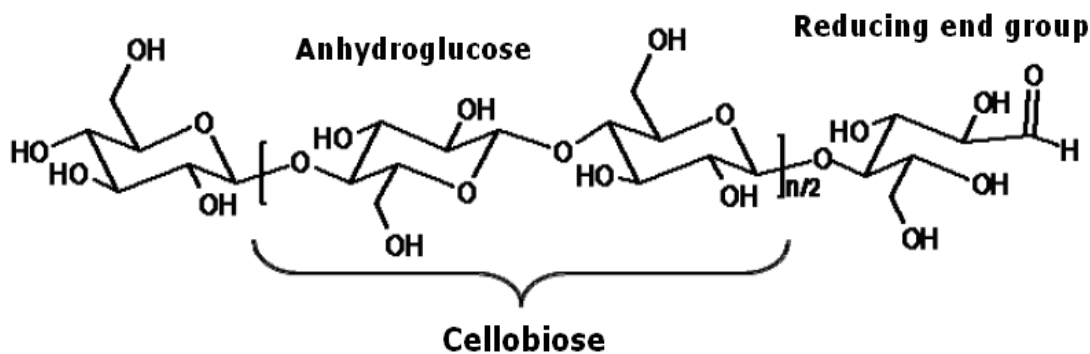


Fig. 2.4. Molecular structure of cellulose showing the cellobiose repeat unit

The cellulose chain bristles with polar -OH groups. These groups form many hydrogen bonds with OH groups on adjacent chains, bundling the chains together. The chains also pack regularly in places to form hard, stable crystalline regions that give the bundled chains even more stability and strength.

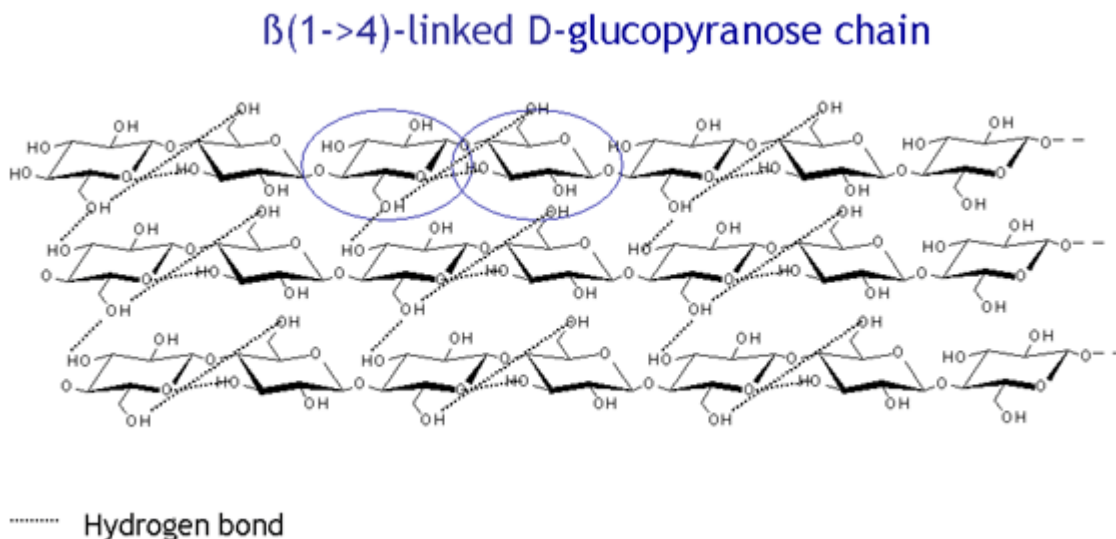


Fig. 2.5. Stable chain structure of cellulose produced by Hydrogen bonding network.

Each cellulose chain possesses a directional chemical asymmetry with respect to the termini of its molecular axis: one end is a chemically reducing functionality (Fig: 2.1) (i.e., a hemiacetal unit) and the other has a pendant hydroxyl group, the nominal nonreducing end. The number of glucose units or the degree of polymerization (DP) is up to 10 000, but shorter cellulose chains can occur and are mainly localized in the primary cell walls. All -D-glucopyranose rings adopt a

4C1 chair conformation, and as a consequence, the hydroxyl groups are positioned in the ring (equatorial) plane, while the hydrogen atoms are in the vertical position (axial). This structure is stabilized by an intramolecular hydrogen bond network extending from the O (3')-H hydroxyl to the O (5) ring oxygen of the next unit across the glycosidic linkage and from the O(2)-H hydroxyl to the O(6') hydroxyl of the next residue (Fig.2.5).

In nature, cellulose does not occur as an isolated individual molecule, but it is found as assemblies of individual cellulose chain-forming fibers. This is because cellulose is synthesized as individual molecules, which undergo spinning in a hierarchical order at the site of biosynthesis. Typically, approximately 36 individual cellulose molecules assemble are brought together into larger units known as elementary fibrils (protofibrils), which pack into larger units called microfibrils, and these are in turn assembled into the familiar cellulose fibers. However, celluloses from different sources may occur in different packing as dictated by the biosynthesis conditions. In the wood, the smallest unit of the fibrillar structure is the elementary fibril, which is aggregated into larger fibrils which are embedded in a matrix of hemicelluloses and lignin. The figure below show how the fiber is composed of fibrils and the microfibrils [15]. (Fig. 2.6)

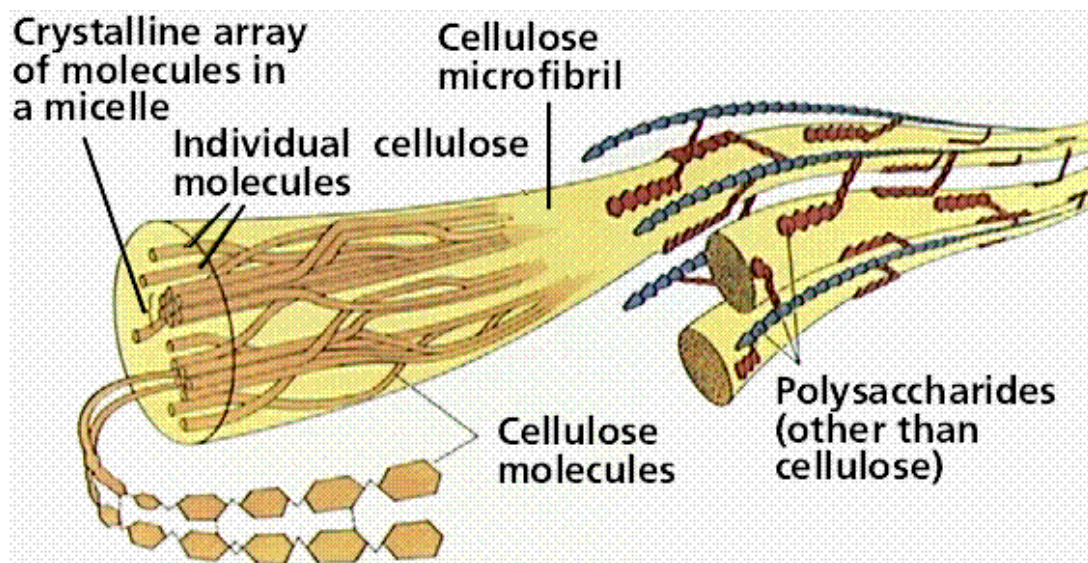


Fig. 2.6. The hierarchical structure of cellulose fibers

The cell wall of wood fibers consists of repeated crystalline structures resulting from the aggregation of cellulose chains (microfibrils). These microfibrils are surrounded by an amorphous matrix of hemicelluloses and lignin; a complex polymer (Fig: 2.7).

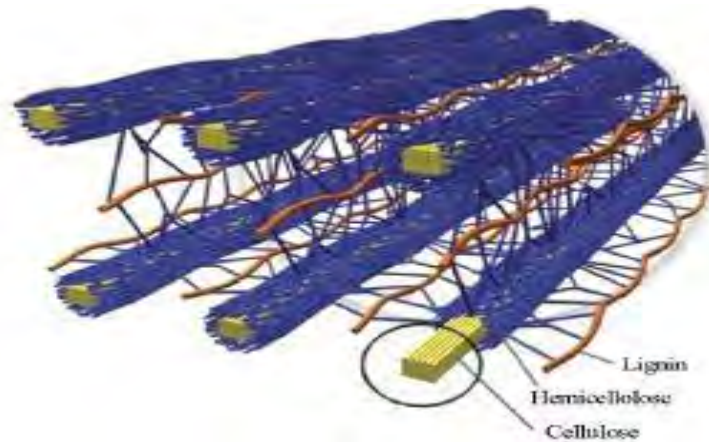


Fig. 2.7. Microfibrils; surrounded by an amorphous matrix of hemicelluloses and lignin

During the process of wood biosynthesis, the cellulose chains are synthesized in a parallel fashion, which leads to hydrogen bonding between the neighboring chains. In native cellulose 30-40 glucan chains are assembled and merged into a single microfibril, denoted as elementary fibril. These microfibrils are not completely crystalline, but they show less ordered, amorphous regions, creating an irregular pattern of amorphous and crystalline domains. These elementary fibrils have been shown to be 2.5-4 nm in diameter and up to a few micrometers in length. The elementary fibrils are then aggregated to form bundles with diameters in a range of 10-20 nm and further microscopic cellulose fibers. The scheme of cellulose hierarchical organization is shown in Figure 2.8.

In wood cellulose, the microfibrils are surrounded by an amorphous matrix of lignin and hemicellulose. In contrast to cellulose, hemicellulose is a complex, branched and heterogeneous polymeric network, based on pentoses such as xylose and arabinose, hexoses such as glucose, mannose and galactose, and sugar acids. It has a lower molecular weight than cellulose and its role is to connect lignin and cellulose fibers. Lignins are water insoluble amorphous polymers of phenylpropane units, which are removed during the pulp preparation. The lignin matrix is crosslinked with the cellulose fibrils by hemicellulose. Lignin holds together cellulose and hemicellulose fibers and gives support, resistance and impermeability to the plant.

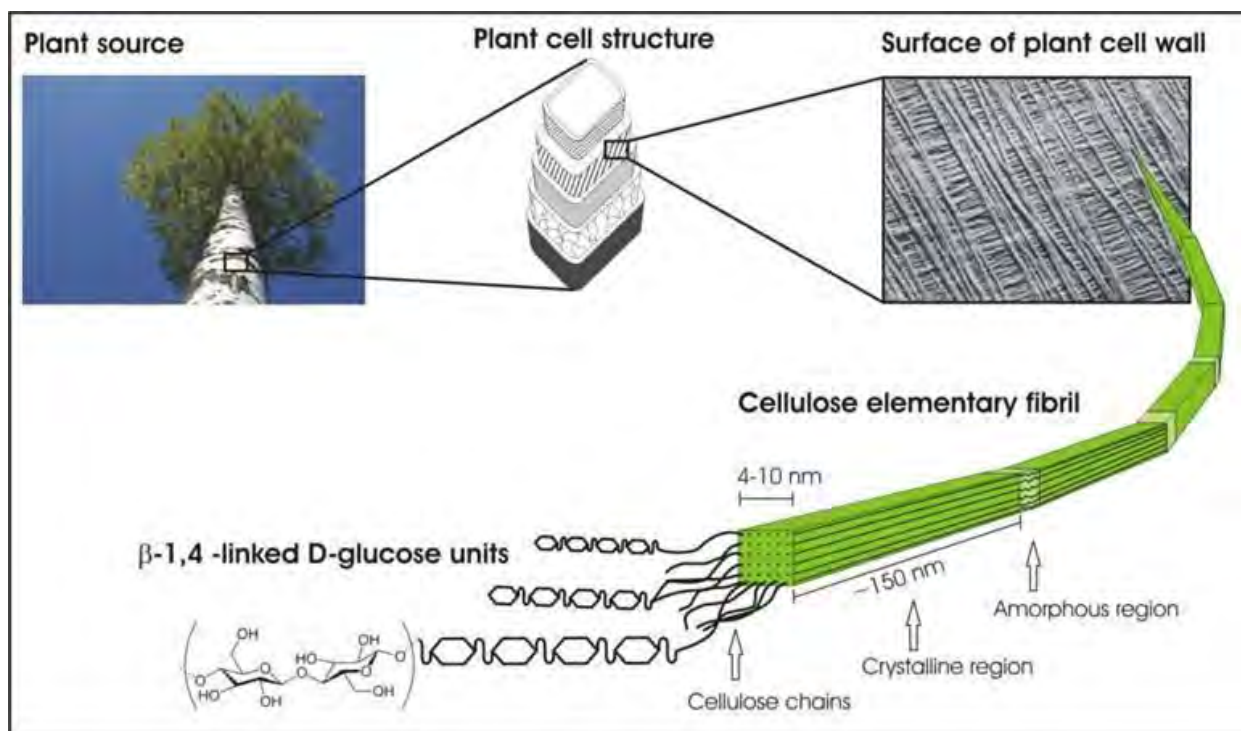


Fig. 2.8. Schematic drawing of cellulose organization in cell walls of plants showing its hierarchical structure. The existence of amorphous and crystalline regions is shown in lateral fiber structure.

2.2.1 Crystalline structure of cellulose

In cellulose, each glucose unit possesses three hydroxylic groups, two primary groups at the positions C2 and C3, and one secondary at the position C6. These hydroxylic groups are able to establish intra and intermolecular hydrogen bonds, thereby forming crystalline structures. The hydrogen-bonding network and molecular orientation in cellulose can vary widely, which can give rise to cellulose polymorphs or allomorphs, depending on the respective source, method of extraction, or treatment [16]. Infra-red spectroscopy and x-ray diffraction studies of cellulose organization in plants have shown that the main portion of cellulose is constituted by crystallites with interspersed amorphous regions of low degree of order [17]. Based on the molecular orientation and hydrogen bonding pattern, four different polymorphs of cellulose (and their allomorphs) have been identified: I, II, III and IV [18, 19]. Forms I and II are the most studied ones and the difference in their structure is shown in the Figure 2.9.

The dominant hydrogen bond for cellulose I is the O6-H---O3, whereas for cellulose II it is the O6-H---O2. Native cellulose, namely cellulose I, is the crystalline cellulose. The term regenerated cellulose, also called cellulose II, is used to refer to cellulose precipitated out of solutions, generally alkali solutions [17]. These represent the two main polymorphs of cellulose. The current knowledge on the crystallography and biosynthesis of cellulose strongly suggests that the chains in cellulose I are organized in parallel direction [20], whereas the crystalline structure of cellulose II is described as antiparallel [17]. Cellulose I is not the most stable form of cellulose. An additional hydrogen bond per glucose residue in cellulose II makes this allomorph the most thermodynamically stable form [21]. Native cellulose from plant sources occurs in form I with two allomorphs I α and I β [22], and their ratio depends on the material source. I α is a metastable form and it consists of triclinic unit cells, while I β allomorph (which is predominant in higher plants) exhibits a monoclinic type of unit cells. Cellulose II is rarely found in the nature, but it can be obtained from cellulose I by regeneration or mercerization processes. Regeneration includes solubilization of cellulose I in a solvent, while mercerization involves only swelling of cellulose in sodium hydroxide. Both processes end by a reprecipitation step, in which the more thermodynamically stable cellulose II form is obtained. Cellulose forms III and IV are formed from cellulose I and II via different chemical procedures [23-26].

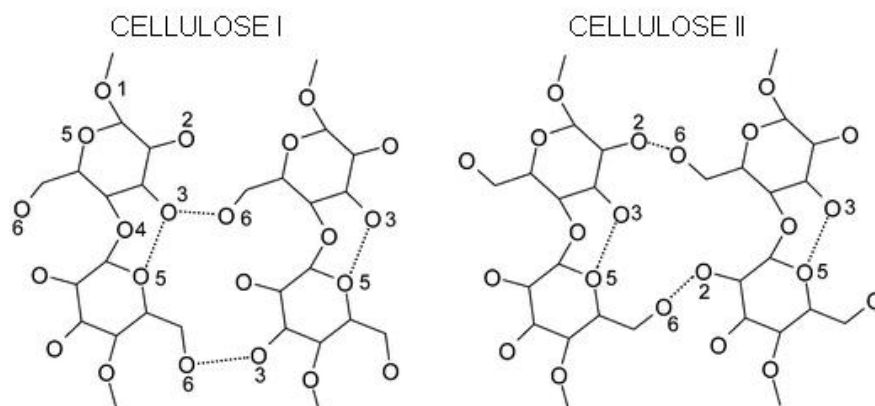


Fig. 2.9. Major supramolecular difference between cellulose I and cellulose II

The different crystalline form of cellulose; cellulose I (I α , I β) and the cellulose II, can be transformed into each other by chemical and thermal process. From earlier studies, the crystalline structure has been revealed by ^{13}C NMR spectroscopy and X-ray fiber diffraction analysis. Native cellulose consists of a mixture of two crystalline forms I α and I β lattice

(Fig.2.10). I β is mainly found in cotton and ramie, in this form two polysaccharide chains are arranged in a monoclinic unit cell. The I α is predominant in algae and bacteria. The I α has triclinic unit cell structure. The polysaccharide chain of them are the same although with a hydrogen bonding pattern that is different compared to I β , the I α can transfer into the I β , however, it is an irreversible process because the I β is more stable. The relative ratio of the two forms of lattice is dependent on the origin; as an example, the tunicate only consists of the I β .

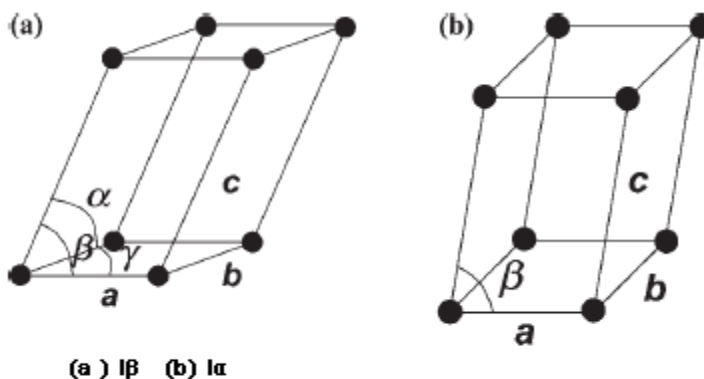


Fig. 2.10. Crystalline forms I α and I β lattice

The dimension of the nano crystals vary from species to species. The nanocrystals from the algae and bacteria [27,28] are up to several micrometers while the length of the wood nanocrystals is shorter [29]. The width of algal cellulose nanocrystals [30,31] is similar to those of cotton whereas the crystallites from wood are smaller. [29,32]

Dimensions of cellulose nanocrystals from various sources are below-

Cellulose	Type length	Cross section
Tunicate	Tunicate 100 nm – several μ m	10-20 nm
Bacterial	100 nm - several μ m	5-10 nm by 30-50 nm
Algal (Valonia)	>1000 nm	10 to 20 nm
Cotton	200-350 nm	5nm
Wood	100-300 nm	3-5 nm diameter

Table1. Dimensions of cellulose nanocrystals from various sources

The dimensions and shape of the isolated nanocrystals` are determined not only by the origin but also by the hydrolysis condition (e.g. acid, the reaction time, concentration, and temperature). The acid will break the cellulose chains, and hydrolyze the glycosidic bonds in the amorphous part and as a result separate the crystallite domains.

2.3 Reactivity and properties of cellulose

The chemical character and reactivity of cellulose is determined by the presence of three equatorially positioned OH groups in the AGU, one primary and two secondary groups [33]. In addition, the β -glycosidic linkages of cellulose are susceptible to hydrolytic attack [33]. The hydroxyl groups do not only play a role in the typical reactions of primary and secondary alcohols that are carried out on cellulose, but also play an important role in the solubility of cellulose. Cellulose is insoluble in common organic solvents and in water [33]. This is due to the fact that the hydroxyl groups are responsible for the extensive hydrogen bonding network forming both, intra- and intermolecular hydrogen bonding [34]. In order to dissolve cellulose, the prevailing hydrogen bonding network must be broken.

There are two possible mechanisms by which the OH groups in the cellulose molecule form hydrogen bonds. One is by the interaction between suitably positioned OH groups in the same molecule (intramolecular). These are located between C2-OH and C6-OH groups and C3-OH with endocyclic oxygen (Fig. 2.11. i and ii). The other mechanism occurs when neighboring cellulose chains (intermolecular) interact via their C3-OH and C6-OH groups (Figure 2.6, iii). Intramolecular hydrogen bonds between the hydroxyl group at the C-3 and oxygen of the pyranose ring were first described in the 1960s by Liang and Marchessault, and Blackwell *et al.* who claimed the existence of a second ‘pair’ of intramolecular hydrogen bonds between the C-6 and C-2 of the neighboring AGUs [35].

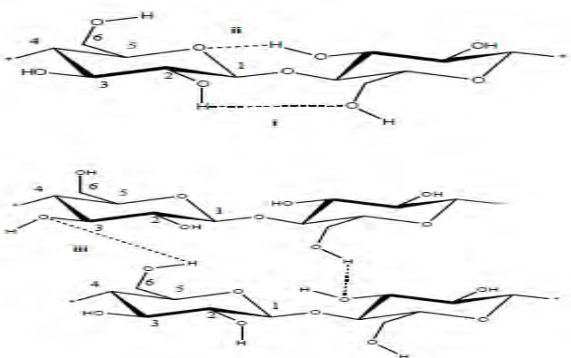


Fig. 2.11. Cellulose structures showing the intramolecular hydrogen bonding between (i) C2-OH and C6-OH (ii) C3-OH with endocyclic oxygen and (iii) the intermolecular hydrogen bonding between C3-OH and C6-OH

Cellulose is regarded as a semi-flexible

polymer. The relative stiffness and rigidity of the cellulose molecule is mainly due to the intramolecular hydrogen bonding. This property is reflected in its high viscosity in solution, a high tendency to crystallise, and its ability to form fibrillar strands. The chain stiffness property is further favoured by the β -glucosidic linkage that bestows the linear form of the chain. The chair conformation of the pyranose ring also contributes to chain stiffness. This is in contrast to the α -glucosidic bonds of starch.

Since cellulose contain both amorphous and crystalline structures, pretreatment (Fig:2.12) can separate the crystalline part from the lignocellulosic materials. An effective pretreatment should meet the following requirements [36],

- 1) Overcome lignocellulosic materials recalcitrance, deconstructing the three-dimensional structure of lignocellulose, and breaking down the semi-crystalline cellulose and hemicellulose
- 2) Afford high yields to sugars or chemicals and/or give highly digestible pretreated solid;
- 3) Avoid carbohydrates degradation and in particular preserve the utility of pentose (hemicellulose) fraction;
- 4) avoid the formation of inhibitory toxic byproducts;
- 5) Allow lignin recovery and exploitation to give valuable co-products;
- 6) Be cost-effective, involving reasonable size reactors, low wastes amount and low energetic requirements.

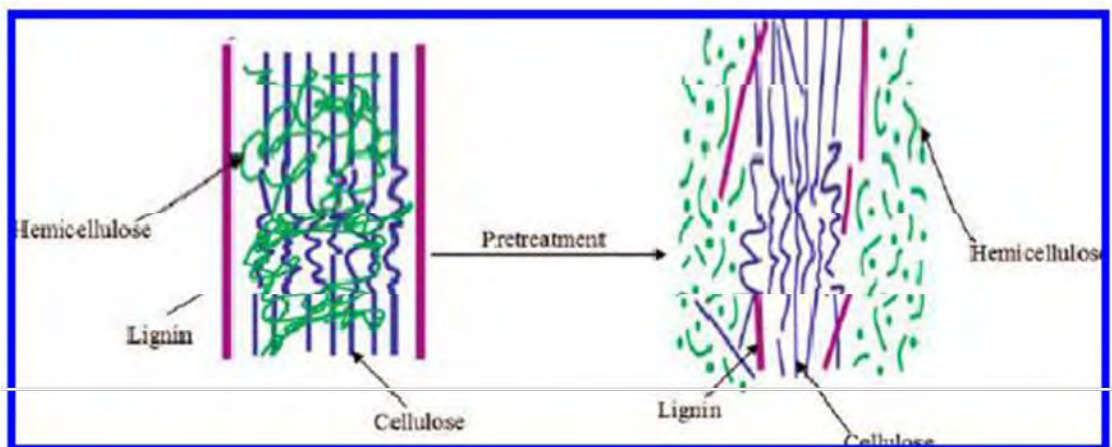


Fig. 2.12. Separation of crystalline cellulose from lignocellulosic materials

Cellulose is a relatively stable polymer [37], due to the hydrogen bond network, it does not dissolve in common aqueous solvents [38] and has not a melting point. In contrast with mineral fibers (glass, carbon fibers), the cellulose fibers have a good flexibility and elasticity, these properties allowing them to maintain a high aspect ratio in the process of manufacturing.

Cellulose nano-fibers have many advantages comparing with the inorganic fibers, some of the most relevant being the following: low density, renewable sources, biodegradability, non-food agricultural based economy, low energy consuming per product unit, low abrasively which ensures a greater longevity of the processing equipment, reduced carbon dioxide emission in the environment, high specific strength and modulus, high sound attenuation of lignocelluloses based composites, relatively reactive surface, which can be used for grafting specific groups and modest price[39-41].The main reason in using cellulose nano-fibers in composite materials is due to the potentially high stiffness of the cellulose fibers for reinforcement. This property can be achieved with the reducing amount of amorphous material by breaking the structure of the plant in individualized nano-fibers with high crystallinity. Cellulose nano-fibers and the composite materials reinforced with this kind of fillers have found many potential applications in important fields like electronic and electrical industry [42-46], constructions, biomedicine and cosmetics [41-44], paper industry [45], packaging [46], building materials, textile industry and others. The fact that almost any cellulose material could be considered as a potential source for isolation nano-cellulose structures represents another important advantage in using cellulose elements as reinforcing phase in polymeric matrix composites. Despite of these attractive characteristics,cellulose fibers have also a few disadvantages due to their polar and hydrophiliccharacter. These limitations make them poorly compatible with non-polar matrices, such as polyolefin, and induce loss of mechanical properties [47]. Cellulose nano-fibers can be submitted to specific surface modification in order to avoid these drawbacks.

2.4 Preparation of degraded low molecular crystalline cellulose

There are several methods to prepare low molecular weight micro and nano crystalline cellulose.

General methods of preparation of cellulose are:

- Chemical method
- Mechanical method
- Chemical and mechanical method
- Enzyme method

The structure of native cellulosic fibers results in two families of nanocellulosematerials. Since the cellulose microfibrils consist of both amorphous and crystallineregions, treatment of them in

strongly acidic conditions leads to an extensive hydrolysis of the amorphous fractions and formation of short rod-like cellulose crystals [48] with high crystallinity and low aspect ratio (Figure 2.4). The diameter of this crystal is typically around 2-20 nm, while they have wide length distribution of 100-600 nm. In a controlled acid hydrolysis procedure, microcrystalline cellulose and nanocrystalline cellulose can be produced from cellulose microfibrils. When the macroscopic cellulose fibers are mechanically disintegrated avoiding the strongly acidic conditions, long nanoscale partly amorphous fibrils named nanofibrillated cellulose [49-51] are produced (Figure 2.13).

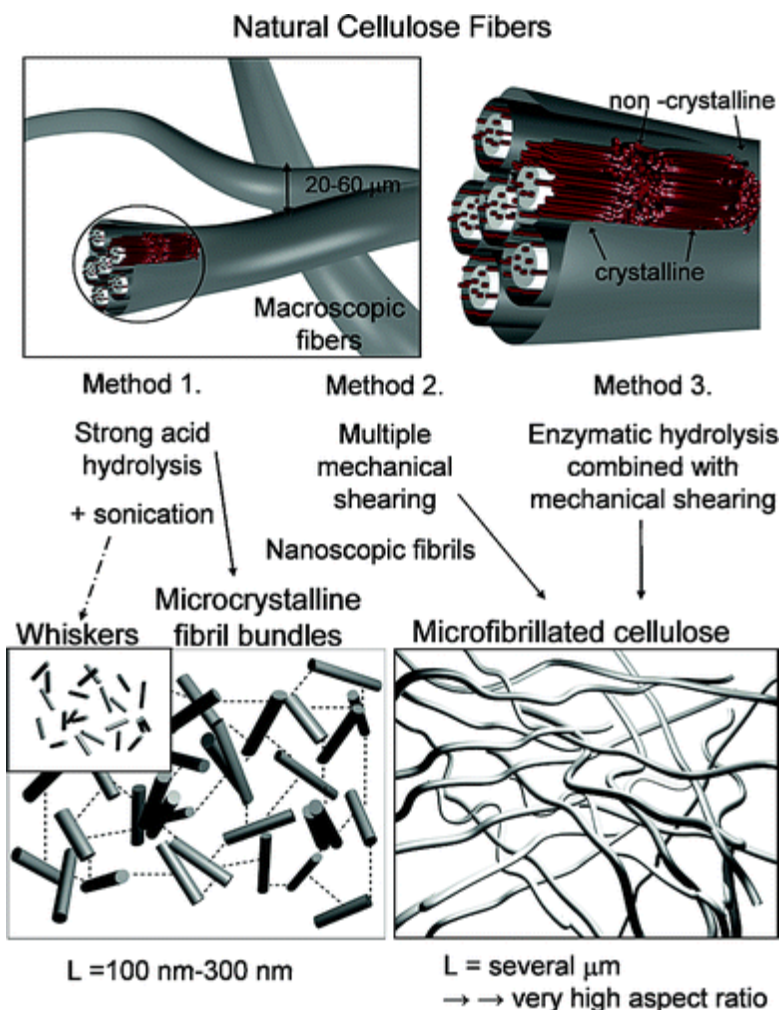


Fig. 2.13. Three methods to disintegrate macroscopic cellulose fibers into micro- or nanoscale fibers or crystals [52].

Cellulose has an extremely high degree of crystallinity and this is due to the formation of several hydrogen bonds originating from its hydroxyl groups. Its high stereo regularity is also a

contributory factor for its high crystallinity. Pure cellulose, also known as α -cellulose, is a material insoluble in 17.5 % NaOH. β -cellulose and γ -cellulose are not true cellulose. β -Cellulose is believed to be degraded. It has low degree of polymerization cellulose and is insoluble in 17.5 % NaOH; γ -Cellulose is completely soluble at any pH and is thought to be hemicelluloses such as xylans, mannans, galactans etc [53-54]. Pretreatment is required to alter the structure of cellulosic materials to make cellulose more accessible to reactants and is a necessary element in bioconversion of lignocellulosic materials to fuels and chemicals. Pretreatment methods are either physical or chemical, some methods incorporate both. Chemical treatments with acids or bases promote hydrolysis and improve the yield of glucose from cellulose by removing hemicellulose or lignin during pretreatment. The most commonly used acid and base are H_2SO_4 and NaOH, respectively; however, nitric, hydrochloric acid and phosphoric acid have also been tested. Acid hydrolysis releases oligomers and monosaccharides and has already been modeled as a homogenous reaction in which acid catalyzes the breakdown of hemicellulose to xylose followed by breakdown of xylose to furfural.

The main process for the isolation of micro and nano crystalline cellulose from cellulose fibers is based on acid hydrolysis. Disordered or paracrystalline regions of cellulose are preferentially hydrolyzed, whereas crystalline regions that have a higher resistance to acid attack remain intact [55]. Thus, following an acid treatment that hydrolyzes the cellulose (leading to removal of the microfibrils at the defects), cellulose rod-like nanocrystals are produced. The actual occurrence of the acid cleavage event is attributed to differences in the kinetics of hydrolysis between amorphous and crystalline domains [56]. This hypothesis was based on the reasonable assumption that disordered or para-crystalline domains are regularly distributed along the microfibrils and therefore they are more susceptible to acid attack (in contrast to crystalline regions that are more impervious to attack). Also, homogeneous crystallites were supposed to be generated after acid hydrolysis. These assumptions were actually confirmed by X-ray crystal diffraction [57], electron microscopy with iodine-staining [58], small-angle X-ray diffraction [59], and neutron diffraction analyses [57]. Typical procedures currently employed for the production of MCC and NCC consist of subjecting pure cellulosic material to strong acid hydrolysis under strictly controlled conditions of temperature agitation, and time. The nature of

the acid and the acid-to-cellulosic fibers ratio are also important parameters that affect the preparation.

Sulfuric and hydrochloric acids have been extensively used for the preparation of crystalline cellulose, but phosphoric [60] and hydrobromic acids have also been reported for such purposes. The formation of MCC depends upon the source and hydrolysis condition, controlled hydrolysis with hydrochloric acid produce microcrystal as powder form [61]. Whereas the stable suspension of cellulose nanocrystals can be obtained by sulfuric acid hydrolysis.

If the crystalline celluloses are prepared by hydrolysis in hydrochloric acid, their ability to disperse is limited and their aqueous suspensions tend to flocculate [62]. On the other hand, when sulfuric acid is used as a hydrolyzing agent, it reacts with the surface hydroxyl groups of cellulose to yield charged surface sulfate esters that promote dispersion of the nanocrystal in water [63]. However, the introduction of charged sulfate groups compromises the thermostability of the nanocrystals [64]. With respect to the morphology of the particles, a combination of both sulfuric and hydrochloric acids during hydrolysis steps appears to generate spherical nanocrystal instead of rod-like nanocrystals when carried out under ultrasonic treatment [65]. These spherical nanocrystals demonstrated better thermal stability mainly because they possess fewer sulfate groups on their surfaces.

2.5 Crystallinity, micro & nanocrystallinity

The term crystallinity has a somewhat ambiguous use in polymer chemistry. A synthetic polymer may be described as crystalline if it contains regions of three-dimensional ordering on atomic rather than macromolecular length scales. It usually arises from intramolecular folding and/or stacking of adjacent chains. Synthetic polymers may consist of both crystalline and amorphous regions. The degree of crystallinity can express in terms of a weight fraction or volume fraction of crystalline material. Few synthetic polymers are entirely crystalline [66]. The crystallinity of polymers is characterized by their degree of crystallinity, ranging from zero for a completely non-crystalline polymer to one for a theoretical completely crystalline polymer. Increasing degree of crystallinity tends to make a polymer more rigid. It can also increase the brittleness of polymeric materials. Polymers with a degree of crystallinity approaching zero or one will tend to

be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline/glassy regions.

In mineralogy and crystallography, a crystal structure is a unique arrangement of atoms or molecules in a crystalline liquid or solid. A crystal structure describes a highly-ordered structure, occurring due to the intrinsic nature of molecules to form symmetric patterns. A crystal structure can be thought of as an infinitely repeating array of 3D 'boxes', known as unit cells. The unit cell is calculated from the simplest possible representation of molecules, known as the asymmetric unit. The asymmetric unit is translated to the unit cell through symmetry operations, and the resultant crystal lattice is constructed through repetition of the unit cell infinitely in 3-dimensions. Patterns are located upon the points of a lattice, which is an array of points repeating periodically in three dimensions. The lengths of the edges of a unit cell and the angles between them are called the lattice parameters.

Although a broad definition, nanomaterials are those which have structured components with at least one dimension less than 100 nm. Materials that have one dimension in the nanoscale (and are extended in the other two dimensions) are **layers**, such as a thin films or surface coatings. Some of the features on computer chips come in this category. Materials that are nanoscale in two dimensions (and extended in one dimension) include nanowires and nanotubes. Materials that are nanoscale in three dimensions are **particles**, for example precipitates, colloids and quantum dots (tiny particles of semiconductor materials). Nanocrystalline materials, made up of nanometre-sized grains, also fall into this category. A **microcrystalline** material is a crystallized substance or rock that contains small crystals visible only through microscopic examination. A **nanocrystalline** (NC) material is a polycrystalline material with a crystallite size of only a few nanometers. These materials fill the gap between amorphous materials without any long range order and conventional coarse-grained materials. Definitions vary, but nanocrystalline material is commonly defined as a crystallite (grain) size below 100 nm. Grain sizes from 100–500 nm is typically considered "**ultrafine**" grains. The grain size of a nanocrystal sample can be estimated using x-ray diffraction. In materials with very small grain sizes, the diffraction peaks will be broadened. This broadening can be related to a crystallite size using the Scherrer equation (applicable up to ~50 nm), a Williamson-Hall plot, or more sophisticated methods such as the Warren-Averbach method or computer modeling of the diffraction pattern. The crystallite size can be measured directly using transmission electron microscopy.

2.6 MCC

Microcrystalline cellulose is white, odorless, tasteless, neutral, nonreactive free flowing versatile excipient. It is purified, partially depolymerized cellulose. Its physical chemical and rheological properties make it a filler & binder of choice in a variety of pharmaceutical and industrial operation. Due to its non-irritating inert and nontoxic properties, it has been used as many topical preparations. It is stable over a wide range of temperature.

Microcrystalline cellulose (such as Avicel) has a degree of polymerization (DP) value of less than 400 [67]. Since the cellulose contain both amorphous and crystalline structures, the highly crystalline cellulose can be prepared from selective methods based on the source of the cellulose. Among them MCC is derived by severe acid hydrolysis to remove the amorphous cellulose portions, yielding particles consisting of bundle-like needle-like microcrystals. It can be prepared by treating different native cellulose sources such as wood pulp, bamboo, viscous rayon and cotton with mineral acids [68,69]. The native cellulose has both amorphous and crystalline regions. The amorphous regions are interacted first with solvents and chemical reagents, because of their loose structures. The removal of the amorphous regions with an acid treatment of cellulose is the most commonly used method for the production of MCC. The acid hydrolysis breaks the β -(1 \rightarrow 4) glycoside bond, thus decreasing the DP of the resulting MCC [56].

Commercially available MCC is derived from both gymnosperms (generally conifers) and other softwoods, and from hardwood dicotyledons. These woods differ considerably in chemical composition (proportions of cellulose, hemicelluloses and lignin) and structural organization which affect the composition of the α -cellulose extracted and the composition and crystallinity of MCC finally produced [70]. Besides the wood pulp as a source of cellulose and its derivatives, the purified cotton linters obtained from *Gossypium* species are also a common source.

There are two types of MCC, powder MCC and colloidal MCC. Powder MCC is made by spray-drying of aqueous MCC suspension and has its average particle size ranging from about 20-90 μm . Colloidal MCC is MCC colloids in water with the colloidal size of $<0.2\mu\text{m}$ in diameter [71]. MCC has excellent mechanical properties and can potentially be used as reinforcing fillers in polymer composites [72]. MCC as a reinforcing filler in polymer composites offers several advantages over glass fibers and other inorganic fillers: renewability, nonfood sources, low energy required for its production, low cost, low density, and high specific strength and modulus [73]. Like other inorganic fillers such as glass fibers, MCC fillers have hydrophilic surfaces and

are not very compatible with hydrophobic plastics. Coupling agents or compatibilizers are often required for improving the bonding between MCC and the plastic matrix. Moreover, the processing temperature of MCC-filled composites is restricted to about 200 °C because MCC starts to degrade near 230 °C, whereas glass-fiber-reinforced composites can have a much higher processing temperature [74].

2.6.1 Properties of MCC

General properties of MCC are: excellent compressibility, rapid disintegration, free flowing, freedom from chemical reaction with all other ingredients, good moisture stability, excellent in absorbing water oil and solvents, excellent initial color and long-term stability, excellent microbiological qualities. MCC is very much hygroscopic and stable substance. Large quantities should be stored in a cool dry airtight container.

The gel network formed by colloidal MCC offers the following properties:

Thixotropy - gels made with MCC readily break down with shear; when the shear is removed, the gel will reform over time with minimal loss to viscosity.

Foam Stability - MCC is a premier foam stabilizer. The microcrystalline network thickens the water phase between air cells and acts as a physical barrier to maintain the air cells in suspension. Although MCC does not have significant film forming properties, it does work to increase the film strength.

Stabilized Emulsions - MCC forms a colloidal network of particles when properly dispersed in water. This colloidal network sets up at the oil-water interface to physically prevent the oil globules from coalescing. The MCC acts to stabilize the emulsion as well as thicken the water phase to improve cling properties.

Heat Stability - temperature changes have little or no effect on the functionality and viscosity of MCC dispersions. This property is extremely important in the preparation of heat stable products, particularly when acids are present. MCC will hold up during heat processing, including baking, retorting, UHT processing and microwave heating with minimal loss in viscosity.

Shorten Texture - MCC can be used to modify textures- it can shorten textures or add body without creating a gummy or pasty texture. In food systems, this quality results in a cleaner mouth feel and excellent flavor release.

Suspend Particles - the stability and thixotropic rheology of MCC makes it a useful suspension aid. In an aqueous system, the 3-dimensional matrix sets-up at low-use levels to effectively suspend particulates.

Replace Fats and Oils - MCC can be used to replace some or all of the oil in emulsion type products. The MCC mimics many of the rheological properties associated with full oil emulsions.

Control Ice Crystal Growth - the 3-dimensional matrix created with dispersed colloidal MCC and the surface area of the microcrystals create a stabilizing system that maintains a homogeneous state during freeze/thaw cycles. MCC helps prevent moisture migration and inhibits the aggregation of protein and other solids. The 3-dimensional network formed with MCC is extremely effective in maintaining the three-phase system of water/fat/air.

Extend Starches - using a ratio of 4 parts starch/1 part MCC allows processors to reduce the amount of starch thickener required by as much as 25%. The MCC will also improve heat and shear stability over prolonged process cycles.

Opacity - insoluble cellulose crystallites act as opacifiers and can add whiteness to products.

2.6.2 Application of MCC

Microcrystalline Cellulose (MCC) is a kind of purified and partially depolymerized cellulose, white, odorless, tasteless and in the shape of crystalline powder made up of porous particles. It is commercially available material used for applications in the pharmaceutical (tablet binder-, one brand name is Avicel) and food industries, and is prepared by acid hydrolysis of wood fiber, back-neutralization with alkali, and spray-dried. The resulting particles are porous, about 10–50 μm in diameter, have a high cellulose content, a higher crystallinity, and are composed of aggregate bundles of multi-sized cellulose microfibrils that are strongly hydrogen bonded to each other [75]. Usually the MCC aggregates are broken up into smaller micron-sized rod-like particles (1–10 μm in length) prior to use in composites.

Microcrystalline Cellulose is widely used in the pharmaceutical, cosmetics, food and other industries. Different particle sizes and moisture contents have different characteristics and applications.

The Application of MCCs are below-

1. In the Pharmaceutical Industry

It is often used as adsorbents, suspending agents, diluents and disintegrating agents. Microcrystalline Cellulose is widely used in the pharmaceutical preparation, mainly as diluents and adhesives in oral tablets and capsules. It can be used for wet granulation as well as direct compression by dry method. It has some lubrication and disintegration action so is very useful in tablet preparation.

MCC is one of the most used filler-binders in direct tablet compression. Its popularity in direct compression is due to its excellent binding properties when use as a dry binder. It also works as a disintegrant and lubricant and has a high dilution potential in direct compression formulations. In addition to its use in direct compression formulations, MCC is used as a diluent in tablets prepared by wet granulation as well as a filler for capsules and spheres [76]. MCC can be used to dry or absorb active ingredients that are viscous or oily to produce relatively free-flowing forms. The newer technology for manufacturing capsule dosage forms has created another area for the application of MCC. As a binder, MCC is especially useful in formulations which are compressed before insertion into the hard gelatin capsule.

Microcrystalline cellulose is a product designed primarily for pharmaceutical solid dosage formulation. The suitability of MCC for tableting operations is proven by the numbers and variety of functions it can perform

<u>Direct Compression</u>	<u>Wet Granulation</u>
Binder, Lubricant, Disintegrant, filler, flow aid.	Binder, Permits fast addition of granulation fluid, Rapid wicking action.

Table 2. Function of MCC

2. In the Food Industry

In the food industry, Microcrystalline Cellulose can be used as an important base in functional foods and is an ideal health food additive.

- 1) It can maintain emulsification and foam stability.
- 2) It can maintain high temperature stability.
- 3) It can improve the liquid stability.
- 4) It can act as nutritional supplements and thickeners.

5) It has many other uses.

Microcrystalline Cellulose is widely used in the oral preparations and food, a relatively non-toxic and non-irritating substance. It cannot be absorbed orally, with almost no potential toxicity. Heavy use may cause mild diarrhea. It has no difficulty as an excipient of pharmaceutical formulation.

Besides tableting binder MCC is used as binder of many other cosmetics, food and industrial ingredients. MCC has versatile application as:

- Coating
- binder
- Carrier
- Cellulose Component
- Functional fillers
- Anti-caking agent
- Micro Dispersant
- Quick Drying or absorbing agent
- Non-Nutritive Bulking
- Emulsion Stabilizer
- Hydration aid
- Disintegrate
- Texture Modification
- Heat Stabilizer

2.7 NCC

Nanocrystalline cellulose (NCC) is an emerging renewable nanomaterial that holds promise in many different applications, such as in personal care, chemicals, foods, pharmaceuticals, etc. NCCs are rigid rod-like crystals with diameter in the range of 10–20nm and lengths of a few hundred nanometers were obtained by using a 63-65 (w/w)% sulfuric acid concentration for approximately 2 h and which can be prepared from a variety of sources, e.g., cotton linter [77] microcrystalline cellulose [78], bacterial cellulose [80], algal cellulose (valonia) [81], hemp [82], tunicin [83], cotton [84], ramie, sisal [85], sugar beet [86], and wood [79]. By appropriate modification of NCC, various functional nanomaterials with outstanding properties, or

significantly improved physical, chemical, biological, as well as electronic properties can be developed. The nanoparticles are stabilized in aqueous suspension by negative charges on the surface, which are produced during the acid hydrolysis process. NCC suspensions can form a chiral nematic ordered phase beyond a critical concentration, i.e. NCC suspensions transform from an isotropic to an anisotropic chiral nematic liquid crystalline phase. Due to its nanoscale dimension and intrinsic physicochemical properties, NCC is a promising renewable biomaterial that can be used as a reinforcing component in high performance nanocomposites. Many new nanocomposite materials with attractive properties were obtained by the physical incorporation of NCC into a natural or synthetic polymeric matrix. Simple chemical modification on NCC surface can improve its dispersability in different solvents and expand its utilisation in nano-related applications, such as drug delivery, protein immobilisation, and inorganic reaction template. This review paper provides an overview on this emerging nanomaterial, focusing on the surface modification, properties and applications of NCC. One of the program's most exciting research avenues involves developing new materials from cellulose, the main component of the cell walls of trees and other plants. In its almost-pure form, cellulose has a tiny crystalline molecular structure. Known as nanocrystalline cellulose, or NCC, this substance has intriguing properties and uses.

2.7.1 Properties of NCC

The basic properties of NCC are:

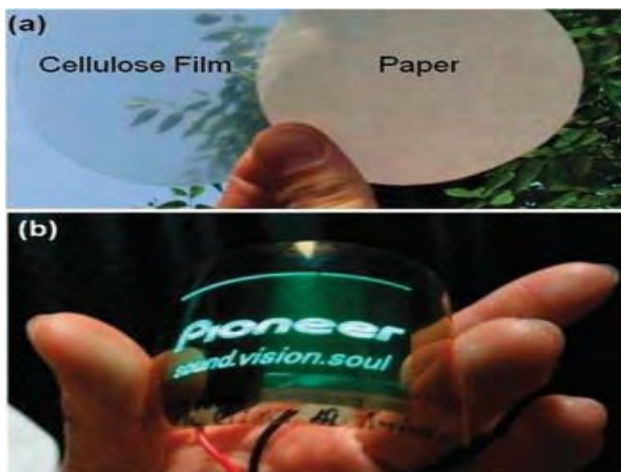
- The relative low density (1.6 gm/Cm³)
- Uniform size distribution
- High surface area(~ 250 m²/g)
- High aspect ratios (typically > 30-100 μm)
- Thermal properties(thermal degradation temperature, T_d= 200- 300⁰c)
- Mechanical properties with elastic modulus and tensile strength higher than Kevlar makes NCC a very attractive material.)
- At high concentrations, birefringent and has liquid crystalline properties due to ordering.
- High optical transparency
- Reinforcing agent

- High moisture absorption capacity
- High functionality
- The surface atoms specify the properties
- Super insulation properties of nanocomposites polymer

2.7.2 Application of NCC

NCC increases the strength and stiffness of materials it's added to. Just a small amount can increase resistance to stress threefold, making it attractive as a high-performance reinforcing material.

NCC can also alter the surface of material like paper, changing its permeability, strength, flexibility and optical properties. Adding a little NCC to paper noticeably boosts its gloss. NCC also improves tensile strength, stiffness, surface smoothness and bulk, paving the way for new



types of paper with novel applications and for paints, varnishes and advanced high-strength materials.

Fig. 2.14. Applications of cellulose nanoparticles. (a) Transparent paper for packaging [87] and (b) luminescence of an organic light-emitting diode deposited onto a flexible, low-CTE and optically

transparent wood-cellulose nanocomposite [88].

Films made of NCC appear iridescent, making them an ideal decorative treatment for papers. Optical films enhanced with NCC are well suited for use in specialty packaging, biosensors and security devices; they could even help prevent counterfeiting. In addition, because NCC is affected by magnetic and electrical fields, it could prove useful as a filler in magnetic paper, electronic memory cards and readers, and other electronic products.

The properties of nanocellulose (e.g. mechanical properties, film-forming properties, viscosity etc.) makes it an interesting material for many applications and the potential for a multibillion-dollar industry [89].

Paper and paperboard

There is potential of nanocellulose applications in the area of paper and paperboard manufacture. Nanocelluloses are expected to enhance the fiber-fiber bond strength and, hence, have a strong reinforcement effect on paper materials. Nanocellulose may be useful as a barrier in grease-proof type of papers and as a wet-end additive to enhance retention, dry and wet strength in commodity type of paper and board products [90].

Composite

As described above the properties of the nanocellulose makes an interesting material for reinforcing plastics. Nanocellulose has been reported to improve the mechanical properties of, for example, thermosetting resins, starch-based matrixes, soy protein, rubber latex, poly (lactide). The composite applications may be for use as coatings and films, paints, foams, packaging.

Food

Nanocellulose can be used as a low-calorie replacement for today's carbohydrate additives used as thickeners, flavor carriers and suspension stabilizers in a wide variety of food products and is useful for producing fillings, crushes, chips, wafers, soups, gravies, puddings etc. The food applications were early recognized as a highly interesting application field for nanocellulose due to the rheological behavior of the nanocellulose gel.

Hygiene and absorbent products

Different applications in this field include

- Super water absorbent (e.g. for incontinence pads material)
- Nanocellulose used together with super absorbent polymers
- Use of nanocellulose in tissue, non-woven products or absorbent structures
- Use as antimicrobial films

Emulsion and dispersion

Apart from the numerous applications in the area of food additives, the general area of emulsion and dispersion applications in other fields has also received some attention [91]. Oil in water applications was early recognized. The area of non-settling suspensions for pumping sand, coal as well as paints and drilling mud was also explored by the early investigators.

Oil recovery

Hydrocarbon fracturing of oil-bearing formations is a potentially interesting and large-scale application. Nanocellulose has been suggested for use in oil recovery applications as a fracturing fluid. Drilling mud based on nanocellulose have also been suggested.

Medical, cosmetic and pharmaceutical

The use of nanocellulose in cosmetics and pharmaceuticals was also early recognized. A wide range of high-end applications have been suggested

- Freeze-dried nanocellulose aerogels used in sanitary napkins, tampons, diapers or as wound dressing
- The use of nanocellulose as a composite coating agent in cosmetics e.g. for hair, eyelashes, eyebrows or nails
- A dry solid nanocellulose composition in the form of tablets for treating intestinal disorders
- Nanocellulose films for screening of biological compounds and nucleic acids encoding a biological compound
- Filter medium partly based on nanocellulose for leukocyte free blood transfusion
- A Bucco dental formulation, comprising nanocellulose and a polyhydroxylated organic compound
- Powdered nanocellulose has also been suggested as an excipient in pharmaceutical compositions
- nanocellulose in compositions of a photoreactive noxious substance purging agent
- Elastic cryo-structured gels for potential biomedical and biotechnological application.
- Matrix for 3D cellculture.

Other applications

- Activate the dissolution of cellulose in different solvents
- Regenerated cellulose products, such as fibers films, cellulose derivatives
- Tobacco filter additive
- Organometallic modified nanocellulose in battery separators
- Reinforcement of conductive materials
- Loud-speaker membranes

- High-flux membranes
- Flexible electronic displays
- Computer components
- Capacitors
- Lightweight body armor and ballistic glass
- Corrosion inhibitors

2.8 Reference

- [1] Klemm, D., Phillip, B., Heinze, T., Heinze, U., Wagenknecht, W., "Comprehensive cellulose chemistry, Functionalization of Cellulose." *Wiley-VCH*; vol 2. 1998.
- [2] Hon, D.N.S., "Cellulose and its derivatives." In: Dumitriu S (ed) *Polysaccharides in medicinal applications. Marcel Dekker*, New York. 1996a.
- [3] Payne, A., "Memoire sur la composition du tissu propre des plantes et du ligneux" (Memoir on the composition of the tissue of plants and of woody material)," *Comptes rendus*, vol. 7, pp. 1052-1056, 1838.
- [4] Dore, W.H., Sponsler, O. L., "The structure of ramie cellulose as derived from x-ray data." *Colloid symposium monograph*, 4: p. 174. 1926.
- [5] Naworth, W.A., Hirst, E. L., Thomas, H. A., "The Existence of the Cellobiose Residue in Cellulose." *Nature*, 126(3177): p. 438. 1930.
- [6] Klemm, D., Heinze, T., Wagenknecht, W., Phillip, B., Heinze, U., "Comprehensive Cellulose Chemistry." *Weinheim, Wiley-VCH*. Vol. 1. p 282. Germany, 1998.
- [7] Nevell, T.P., Zeronian, S.H., "Cellulose chemistry and its applications." *Polymer Int.*, Ellis Horwood, Chichester, 1985.
- [8] Coffey, D.G., Bell, D.A., Henderson, A., "Food polysaccharides and their application." *Marcel Dekker*, New York, 1995.
- [9] Hon, D.N.S., "Chemical modification of lignocellulosic material." *Marcel Dekker*, New York. 1996b.
- [10] Han, J.S., Rowell, J.S., "Chemical composition of fibers." In: Rowell, R.M., Young, R.A., Rowell, J., (eds) *Paper and composites from agrobased resources*. CRC, London. 1996.
- [11] Klemm, D., Heublein, B., Fink, H.P., Bohn, A., "Cellulose: Fascinating Biopolymer and Sustainable Raw Material." *Angewandte Chemie International Edition*, 44(22): p. 3358-3393. 2005.
- [12] Kobayashi, S., Sakamoto, J., Kimura, S., "In vitro synthesis of cellulose and related polysaccharides". *Progress in Polymer Science*, 26(9): p. 1525-1560. 2001.
- [13] Whistler, R. L., BeMiller, J. M., "Cellulosic in Carbohydrate Chemistry for Food Scientists." *American Association of Cereal Chemists*, vol. 7, pp. 155. Inc.: Minnesota 1997.

- [14] D. G.; Bell, D. A., Henderson, A. “Cellulose and Cellulose Derivatives in Food Polysaccharides and their Applications.” *Coffey*, pp. 124. New York 1995.
- [15] Purves, William K.; Orians, Gordon H.; Heller, H. C Raig, “Life: The Science of Biology.” *Sinauer Associates Inc Hardcover*, 4th Edition. 1994.
- [16] Atalla, R. H. “Struct., Funct., Biosynth. Plant Cell Walls.” *Proc. Annu. Symp. Bot.*, 7th, 381. 1984.
- [17] Daniel, J. R. “Cellulose structure and properties. In Encyclopedia of Polymer Science and Engineering.” Kroschwitz, J.I., Ed.; *Wiley-Interscience Publication John Wiley & Sons*, 3, pp 86-123. New York, NY, USA, 1985.
- [18] Horii, F., Hirai, A., Kitamaru, R., “Solid-state high-resolution ¹³C-NMR studies of regenerated cellulose samples with different crystallinities”. *Polymer Bulletin*, 8(2): pp163-170. 1982.
- [19] Dudley, R.L., Fyfe, C. A., Stephenson, P. J., Deslandes, Y., Hamer, G. K., Marchessault, R. H., “High-resolution carbon-13 CP/MAS NMR spectra of solid cellulose oligomers and the structure of cellulose II.” *Journal of the American Chemical Society*, 105(8): pp 2469-2472. 1983.
- [20] Dinand, E., Vignon, M., Chanzy, H., & Heux, L., “Mercerization of primary wall cellulose and its implication for the conversion of cellulose I→cellulose II.” *Cellulose*, 9, pp 7-18. 2002.
- [21] Saxena, I. M., Brown, R. M., “Cellulose biosynthesis: current views and evolving concepts.” *Ann. Bot.*, 96:9-21. 2005.
- [22] VanderHart, D.L., Atalla, R. H., “Studies of microstructure in native celluloses using solid-state carbon-13 NMR.” *Macromolecules*, 17(8): pp 1465-1472. 1984.
- [23] O'Sullivan, A., “Cellulose: the structure slowly unravels.” *Cellulose*, 4(3): pp 173-207. 1997.
- [24] Sarko, A., Southwick, J., Hayashi, J., “Packing Analysis of Carbohydrates and Polysaccharides. 7. Crystal Structure of Cellulose III and Its Relationship to Other Cellulose Polymorphs.” *Macromolecules*, 9(5): p. 857-863. 1976.
- [25] Gardiner, E.S., Sarko, A., “Packing analysis of carbohydrates and polysaccharides. 16. The crystal structures of celluloses IV_I and IV_{II}.” *Canadian Journal of Chemistry*, 63(1): pp 173-180, 10.1139/v85-027. 1985.
- [26] Arthur J. Stipanovic, Anatole Sarko, “Packing Analysis of Carbohydrates and Polysaccharides. 6. Molecular and Crystal Structure of Regenerated Cellulose II.” *Macromolecules*, 1976, 9 (5), pp 851–857. 1976.

- [27] Tokoh, C.; Takabe, K.; Fujita, M.; Saiki, H. , “Cellulose synthesized by *Acetobacter xylinum* in the presence of acetyl glucomannan.” *Cellulose*, vol. 5, pp. 249-261. 1998.
- [28] Grunert, M.; Winter, W. T. J. “Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals.” *Polym. EnViron*, vol. 10, pp. 27-30. 2002.
- [29] Fengel, D; Wegnener, G., Walter de Gruyter, “Wood.Chemistry, Ultrastructure, Reactions.” *J. Polym. Sci. B Polym. Lett. Ed.*23(11), John Wiley & Sons, Ltd New York. 1985.
- [30] Revol, J.-F., “On the Cross-Sectional Shape of Cellulose Crystallites in *Valoniaventricosa*,” *Carbohydrate Polymer*. vol. 2, pp.123-134. 1982.
- [31] Hanley, S. J., Giasson, J., Revol, J.-F., Gray, D. G., “Atomic force Microscopy of cellulose Microfibrils; comparison with Transmission Electron Microscopy.” *Polymer* vol. 33, pp. 4639-4642. 1992.
- [32] Araki, J., Wada, M., Kuga, S., Okano, T., Surf, A., “Flow properties of microcrystalline cellulose suspension prepared by acid treatment of native cellulose in Colloids.” vol. 142, pp. 75-82. 1998.
- [33] Klemm, D., Philipp, B., Heinze, T., Heinze, U., & Wagenknecht, W. “Comprehensive Cellulose Chemistry.” Volume 1, Fundamentals and Analytical Methods, *Wiley-VCH, Weinheim*. 1998.
- [34] Krässig, H., “Cellulose, Polymer Monographs.” Volume 11, *Gordon and Breach Science Publishers*, pp 6-42. Amsterdam, 1996.
- [35] Machessault, R., & Liang, C.Y, “Infrared spectra of crystalline polysaccharides. III. Mercerized cellulose.” *J. Polym. Sci.*, 43, pp 71-84, 1960.
- [36] Alvira, P., Tomas-P, Ballesteros M., Negro MJ., “Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review.” *Bioresour. Technol.* vol. 101, 4851–4861. 2010.
- [37] Whistler, R. L.; BeMiller, J. M., “Cellulosic in Carbohydrate Chemistry for Food Scientists.” *American Association of Cereal Chemists, Inc.:* vol. 7, pp. 155. Minnesota 1997.
- [38] Coffey, D. G.; Bell, D. A., Henderson, A., “Cellulose and Cellulose Derivatives in Food Polysaccharides and their Applications.” *Marcel Dekker*, p124. New York 1995.
- [39] A. K. Bledzki, S. Reihmane, and J. Gassan, “Properties and modification methods for vegetable fibers for natural fiber composites,” *Journal of Applied Polymer Science*, vol. 59, no. 8, pp. 1329–1336, 1996.

- [40] P. R. Hornsby, E. Hinrichsen, and K. Tarverdi, "Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibres: part II analysis of composite microstructure and mechanical properties," *Journal of Materials Science*, vol. 32, no. 4, pp. 1009–1015, 1997.
- [41] K. Oksman, L. Wallstrom, L. A. Berglund, and R. D. T. Filho, "Morphology and mechanical properties of unidirectional sisal-epoxy composites," *Journal of Applied Polymer Science*, vol. 84, no. 13, pp. 2358–2365, 2002.
- [42] R. Jonas and L. F. Farah, "Production and application of microbial cellulose," *Polymer Degradation and Stability*, vol. 59, no. 1–3, pp. 101–106, 1998.
- [43] J. Shah and R. M. Brown Jr., "Towards electronic paper displays made from microbial cellulose," *Applied Microbiology and Biotechnology*, vol. 66, no. 4, pp. 352–355, 2005.
- [44] H. Yano, J. Sugiyama, A. N. Nakagaito et al., "Optically transparent composites reinforced with networks of bacterial nanofibers," *Advanced Materials*, vol. 17, no. 2, pp. 153–155, 2005.
- [45] C. Legnani, H. S. Barud, W. G. Quirino et al., "Transparent nanocomposite bacterial cellulose used as flexible substrate for OLED," in Proceedings of the 11th International Conference on *Advanced Materials*, Rio de Janeiro, Brazil, September 2009.
- [46] B. R. Evans, H. M. O'Neill, V. P. Malyvanh, I. Lee, and J. Woodward, "Palladium-bacterial cellulose membranes for fuel cells," *Biosensors and Bioelectronics*, vol. 18, no. 7, pp. 917–923, 2003.
- [47] Adriana N. Frone, Denis M. Panaitescu, Dan Donescu, "composite material upon moisture adsorption." *U.P.B. Sci. Bull.*, Series B, Vol. 73, Iss. 2, 2011
- [48] Iwamoto, S., Nakagaito, A. N., Yano, H., "Nano-fibrillation of pulp fibers for the processing of transparent nanocomposites." *Applied Physics A: Materials Science & Processing*, 89(2): p. 461-466. 2007.
- [49] Khanari, K., Syverud, K., Chinga-Carrasco, G., Paso, K., Stenius, P., "Structure of nanofibrillated cellulose layers at the o/w interface." *Journal of Colloid and Interface Science*, 356(1): p. 58-62. 2011.
- [50] Zimmermann, T., Bordeanu, N., Strub, E., "Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential." *Carbohydrate Polymers*, 79(4): p. 1086-1093. 2010.

- [51]Borges, A.C., Eyholzer, C., Duc, F., Bourban, P.E., Tingaut, P., Zimmermann, T., Pioletti, D.P., Manson, J.A.E., “Nanofibrillated cellulose composite hydrogel for the replacement of the nucleus pulposus.” *Acta Biomaterialia*, 7(9): p. 3412-3421. 2011.
- [52]Paakko, M., Ankerfors, M., Kosonen, H., Nykanen, A., Ahola, S., Osterberg, M., Ruokolainen, J., Laine, J., Larsson, P. T., Ikkala, O., Lindstrom, T., “Enzymatic hydrolysis combined with mechanical shearing and high-pressure homogenization for nanoscale cellulose fibrils and strong gels.” *Biomacromolecules*,8(6): p. 1934-1941. 2007.
- [53] Chauhan, Y. P., Sapkal, R. S., Sapkal V. S., and Zamre, G. S., “Microcrystalline cellulose from cotton rags(waste from garment and hosiery industries)” *Int. J. Chem. Sci.:* 7(2), 681-688, 2009.
- [54] V. R. Gowarikar, N. V. Viswanathan and SreedharJaydev, Polymer Science, *New Age International (P) Limited*, New Delhi, 1986.
- [55] Angles, M. N., & Dufresne, A., “Plasticized Starch/Tunicin Whiskers Nanocomposite Materials. 2. Mechanical Behavior.” *Macromolecules*,34(9), 2921. 2001.
- [56]Håkansson, H., Ahlgren, P., “Acid hydrolysis of some industrial pulps: effect of hydrolysis conditions and raw material” *Cellulose*, 12,177.2005.
- [57] Nishiyama, Y., Kim, U. J., Kim, D. Y., Katsumata, K. S., May, R. P., &Langan, P., “Periodic disorder along ramie cellulose microfibrils.” *Biomacromolecules*, 4, p1013. 2003.
- [58] Schurz, J., John, K., “Long periods in native and regeneratedcelluloses.” *Cellul. Chem.Technol.*, 9, pp 493-501. 1975.
- [59] Yachi, T. Hayashi, J., Takai, M., & Shimizu, Y. J., “Supermolecular structure of cellulose: stepwise decrease in LODP and particle size of cellulose hydrolyzed after chemical treatment.” *Appl. Polym. Sci.: Appl. Polym. Symp.*,37, 325-343. 1983.
- [60] Koshizawa, T.Kami Pa Gikyoshi, “Degradation of wood cellulose and cotton linters in phosphoric acid.”14, pp 455-458, 1960.
- [61] Abd-Allah MA.Nada,MohammedY.El-Kady , Essams.Abd El-Sayed, and Fatma M.Amine., “preparation and characterization of Microcrystallinecellulose.” *BioResources*4(4),1359-1371. .2009.
- [62] Araki, J., Wada, M., Kuga, S., Okano, T., “Flow properties of microcrystalline cellulose suspension prepared.” *Colloids Surf. Physicochem. Eng. Aspects*142, 75–82. 1998.

- [63]Revol, J. F., Bradford, H., Giasson, J., Marchessault, R. H., & Gray, D. G., "Helicoidal self-ordering of cellulose microfibrils in aqueous suspension." *Int. J. Biol. Macromol*,14(3), 170. 1992.
- [64] Roman, M., & Winter, W. T., "Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose." *Biomacromolecules*, vol.5, p 1671. 2004.
- [65] Wang, N., & Ding, E., Cheng, R., "Preparation and liquid crystalline properties of spherical cellulose nanocrystals." *Langmuir*,24, 5. 2008.
- [66] Venien, A, Levieux, D. "Differentiation of bovine from porcine gelatins using polyclonal anti-peptide antibodies in indirect and competitive indirect ELISA" *Pharmaceut Biomed*, 39,418–24, 2005.
- [67]Klemm, D., Heublein, B., Fink, H. P., & Bohn, A., "Cellulose: Fascinating Biopolymer and Sustainable Raw Material." *Cellulose*, 44, pp 3358-3393. 2005.
- [68] Battista, O.A., & Smith, P.A., "MICROCRYSTALLINE CELLULOSE" *J. Ind. Eng. Chem.*, 54, pp 20-29. 1962.
- [69] Sun, Y., Lin, L., Deng, H., Li, J., He, B., Sun, R., & Ouyang, P., "Structural changes of bamboo cellulose in formic acid," *BioResources*, 3, 297-315. 2008.
- [70]Landin M, Martinez-Pacheco R, Gomez-Amoza JL, Souto C, Concheiro, A. and Rowe, R.C., "Effect of batch variation and source of pulp on the properties of microcrystalline cellulose." *Int. J. Pharm.* 91, 133-141. 1993.
- [71] Gan, L.X., Whistler, R.L., "Formylation of primary hydroxyl groups in sugars" *Carbohydr Res*, vol. 206, 65-69. 1990.
- [72]Qiu, W., Zhang, F., Endo, T., & Hirotsu, T., "Preparation and characteristics of composites of high-crystalline cellulose with polypropylene: Effects of maleated polypropylene and cellulose content." *Journal of Applied Polymer Science*, 87, 337-345. 2003.
- [73] Azizi Samir, M.A.S., Alloin, F., & Dufresne, A., "Review of Recent Research into Cellulosic Whiskers, Their Properties and Their Application in Nanocomposite Field." *Biomacromolecules*, 6(2), 612-626. 2005.
- [74]Ardizzone, S., Dioguardi, F.S., Mussini, T., Mussini, P.R., Rondinini, S., Vercelli, B., & Vertova, A., "Microcrystalline cellulose powders: structure, surface features and water sorption capability." *Cellulose*, vol. 6(1), 57-69. 1999.

- [75] Levis S. R., and Deasy P. B., "Production and evaluation of size reduced grades of microcrystalline cellulose." *Int. J. Pharm.*, Vol.213(1-2), pp13–24. 2001.
- [76] Bolhuis, G.K. and Chowhan, Z.T. "Materials for Direct compaction." In: Alderborn, G. and Nystrom C. (Ed) *Pharmaceutical Powder Compaction Technology*, pp 419-500, *Marcel Dekker, Inc.*, New York, 1996.
- [77] Yiyang Yue, "A comparative study of cellulose I and II fibers and Nanocrystals." B.S., August 2011, Heilongjiang Institute of Science and Technology, 2007.
- [78] Dong, X. M., Revol, J.F., & Gray, D., "Effect of microcrystalline preparation." *Cellulose*, 5, 19-32. 1998.
- [79] Beck-Candanedo, S., Roman, M., & Gray, D. "Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions." *Biomacromolecules*, 6, 1048-1054. 2005.
- [80] Hirai, A., Inui, O., Horii, F., & Tsuji, M., "Phase separation behavior in aqueous suspensions of bacterial cellulose nanocrystals prepared by sulfuric acid treatment." *Langmuir*, 25, 497-502. 2009.
- [81] Sugiyama, J., Chanzi, H., & Revol, J.F. "On the polarity of cellulose in the cell wall of Valonia." *Planta*, 193, 260-265. 1994.
- [82] Cao, X., Chen, Y., Chang, P. R., Stumborg, M., & Huneault, M. A., "Green Composites Reinforced with Hemp Nanocrystals in Plasticized Starch." *J. Appl. Polym. Sci.*, 109, 3804-3810. 2008.
- [83] Bonini, C., Heux, L., Cavaille, J.Y., Lindner, P., Dewhurst, C., & Terech, P., "Rodlike Cellulose Whiskers Coated with Surfactant: A Small-Angle Neutron Scattering Characterization." *Langmuir*, 18, pp3311-3314. 2002.
- [84] Thielemans, W., Warbey, C. R., & Walsh, D. A., "Permselective nanostructured membranes based on cellulose nanowhiskers." *Green Chem*, 11, 531-537. 2009.
- [85] Garcia de Rodriguez, N. L., Thielemans, W., Dufresne, A., "Sisal cellulose whiskers reinforced polyvinyl acetate nanocomposites." *Cellulose*, 13, 261-270. 2006.
- [86] Azizi Samir, M.A.S., Alloin, F., Paillet, M., Dufresne, A., "Tangling Effect in Fibrillated Cellulose Reinforced Nanocomposites." *Macromolecules*, 37(11), 4313-4316. 2004.
- [87] Nogi, M., Iwamoto, S., Nakagaito A. N., and Yano, H., "Optically Transparent Nanofiber Paper." *Adv. Mater.* 21, pp1595-1598. 2009.

- [88] Okahisa, Y., Yoshida, A., Miyaguchi, S., and Yano, H., "Optically transparent wood cellulose nano composite as a base substrate for flexible light-emitting displays." *Compos. Sci. Technol.*, 69, 1958–1961. 2009.
- [89] Brown, Elvie E., Hu, Dehong, Abu Lail, Nehal; Zhang, Xiao. "Potential of Nanocrystalline Cellulose Fibrin Nanocomposites for Artificial Vascular Graft Applications." *Biomacromolecules*, 14 (4):1063. 2013.
- [90] Syverud, K.; Stenius, P. "Strength and barrier properties of MFC films". *Cellulose*. 16: 75–85. 2008.
- [91] Khanari, K., Syverud, K., Stenius, P., "Emulsions stabilized by microfibrillated cellulose: the effect of hydrophobization, concentration and o/w ratio". *Dispersion Science and Technology*. 32 (3): 447–452. 2011.

CHAPTER 3
EXPERIMENTAL
& CHARACTERISATION
TECHNIQUE

3.1 Materials

1. Two types of cotton cloths [local voile cotton cloth (B), Textile cotton cloth(T)]
2. commercial wood pulp
3. Filter paper
4. commercial Microcrystalline cellulose
5. H₂SO₄, HCl, Paraffin oil, Sodium hypochlorite, NaOH
6. Magnet bar
7. phosphoric acid
8. AgNO₃
9. Barium chloride

All the chemicals were analytical grade and were used directly without further purification.

3.2 Apparatus and Instruments

1. Round bottom flask condenser
2. Thermometer
3. Hot plate stirrer
4. Centrifuge machine
5. Digital balance
6. Controlled heating vacuum oven
7. Vacuum desiccators
8. Vacuum pump
9. Ultrasonic bath
10. Oil bath
11. Sample vial
12. X-ray Diffractometer
13. Scanning Electron microscopy
14. Fourier Transform Infrared Spectroscopy (FTIR)
15. Thermogravimetric analyzer

3.3 Preparation of MCC

In the present work MCC was prepared from two types of cotton cloths voile cloth designated as (type-B), textile cotton cloth designated as (type-T) and wood pulp as (type-W). The preparation method was adopted by optimizing the type of acid, concentration of acid, hydrolysis time and temperature. The cotton based cloths were collected from local shop and from hosiery industry. The commercial wood pulp was collected from a paper industry. The MCC was prepared by following techniques.

Pretreatment of the sample

Cellulosic materials were cut in to small pieces by scissors then washed and bleached by NaOCl(7%) to remove the dirt and colors. After bleaching the cellulosic materials were subjected to treatment with 4% NaOH.

Hydrolysis

The cleaned bleached cotton (type-B, type-T) cloth and wood pulp (type-W) were hydrolyzed with 2N-10N hydrochloric acid for about 1 hour after pretreatment 4% NaOH. The hydrolysis proceeds with and without pretreatment of NaOH. The hydrolysis also proceeds in different time and temperature condition in round bottom flask with condenser [Fig: 3.2]. The round bottom flask was placed in oil bath to maintain the constant reaction temperature. A magnetic stirrer is used to continuously stir the acid-cellulose solution.

The ratio between lignocellulosic materials and acid was 1:50. After completing hydrolysis the reaction was stopped by instantly adding ice and then the solution was diluted 10 times. The acid of the solution was removed by repeated addition of distilled water. The water portion is separated by centrifugation & filtration. For better microcrystal, the solution was dispersed by using ultrasonic bath for 5-10 minutes. MCC was then collected by centrifugation and filtration. The MCC was dried below 80°C.

The prepared different MCC sample was subjected to analytical techniques FESEM, FTIR, XRD, TGA to find the optimum reaction condition. Commercial MCC was also analyzed to compare with prepared samples. Fig. 3.1. Illustrate overall preparation procedure of MCC.

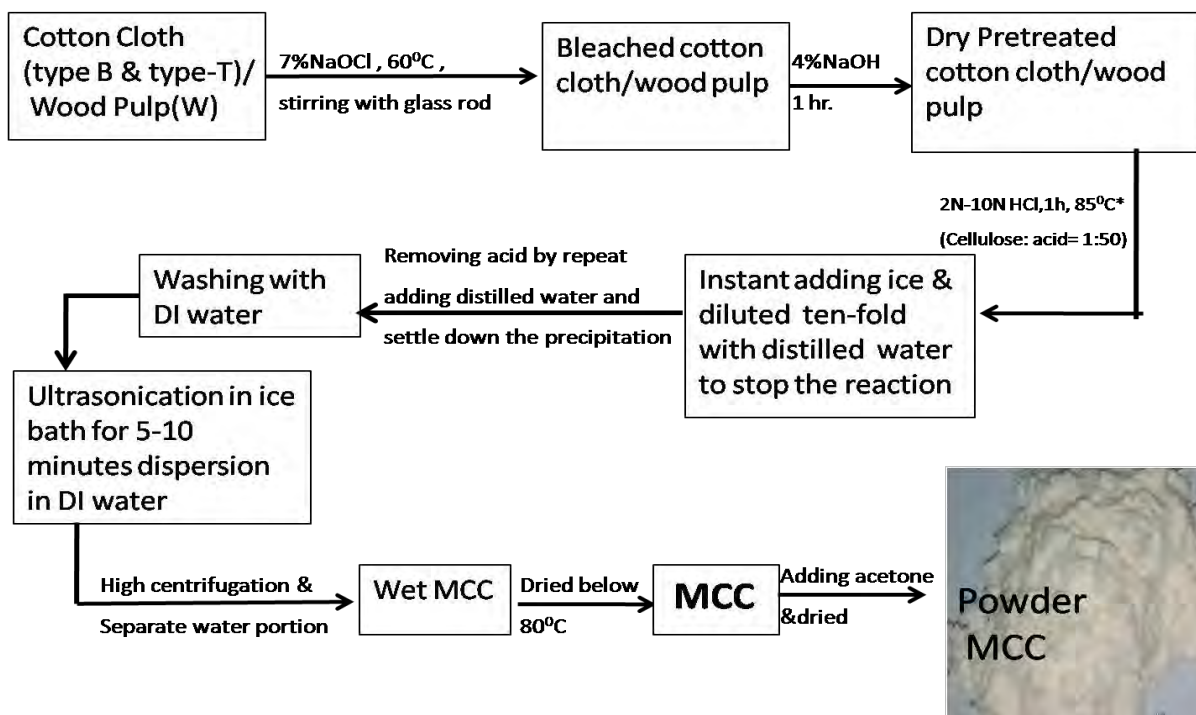


Fig. 3.1. Flow chart of Preparation procedure of MCC

The sample collected from cellulosic materials named 1st (B) & 2nd(T) type cotton cloth, wood pulp are mention as B-Series, T-Series, W-Series. Another series is experimented from 2nd(T) type cloth named S-Series is done at different condition (without pretreatment with NaOH).

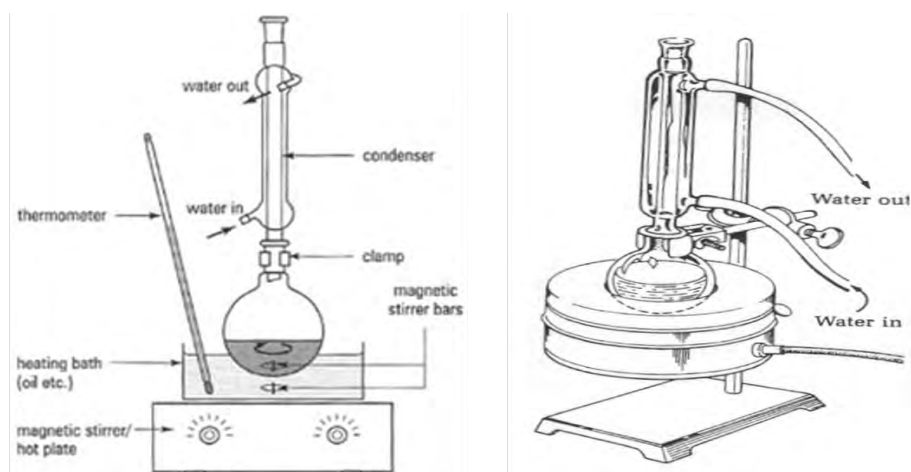


Fig. 3.2. Round bottom flask condenser

The collected analytical sample history is below

Different type of prepared MCC with a short description (Analytical sample history)

M=Commercial MCC

B₁, B₂, B₃, B₄ =voile cloth is washed then hydrolyzed with 2.5N, 5N, 7.5N, 10N HCl in 85 ⁰ C
S₁, S₂, S₃, S₄ =Textile cloth is bleached with NaOCl, then hydrolyzed with 2.5N, 7.5N, 10N HCl about 1 hr. in 85 ⁰ C
T₁, T₂, T₃, T₄ =Textile cloth is bleached with NaOCl, then treated with 4% NaOH about 1 hr. in 80 ⁰ C then hydrolyzed with 2.5N, 5N, 7.5N, 10N HCl about 1hr in 85 ⁰ C
W₁, W₂, W₃, W₄ = Wood pulp is bleached with NaOCl, then treated with 4% NaOH about 1 hr. in 80 ⁰ C then hydrolyzed with 2.5N, 5N, 7.5N, 10N HCl about 1hr in 85 ⁰ C

Table 3. Analytical sample history

3.4 Preparation of NCC

Although several preparation techniques of NCC were established, based on the physical appearance of the prepared NCC gel and its film transparency optimum hydrolysis conditions were selected for the preparation of NCC by this study. The procedure was as follows: A 500 mL round bottom flask containing 10g of bleached cotton cloths were placed in an oil bath at a 60⁰C temperature. Simultaneously, 200 mL 65 % (w/w) H₂SO₄ (cellulose-to-acid weight ratio of 1 to 20) was adjusted to the desired temperature. When the two substances reached working temperature, H₂SO₄ was mixed with the cellulose, and the mixture was hydrolyzed at 60 °C temperature for 60 minutes with continuous stirring with a magnetic stirrer. The ultrasonication was applied during (every 30 minutes). Immediately following hydrolysis, the suspension was diluted ten times to stop the reaction and allowed to settle for several hours until the suspensions were layered, and the clear top layer was decanted off, and then repeatedly washed with distilled water until they were not layered. The suspension was then transferred into centrifuge tubes and

repeated centrifugation was performed at 4,000 rpm for 10 minutes to remove excess acid and water-soluble fragments. The fine cellulose particles became dispersed in the aqueous solution approximately at pH 4. The turbid supernatant containing the polydisperse cellulose particles was then collected for further centrifugation at 4000 rpm for 45 minutes to separate the NCC suspension. The suspension was then washed with deionized water. The process was repeated four to five times for each sample to reduce the acid content. Afterward, the resulting suspension was placed in regenerated cellulose dialysis tubes having a molecular weight cutoff of 12,000–14,000 and dialyzed against deionized (DI) water for several days until the water pH remained constant. The purified NCC suspension was kept in a refrigerator at 5°C. Some fraction of dialyzed NCC was dried in freeze dryer for the preparation of powdered sample.

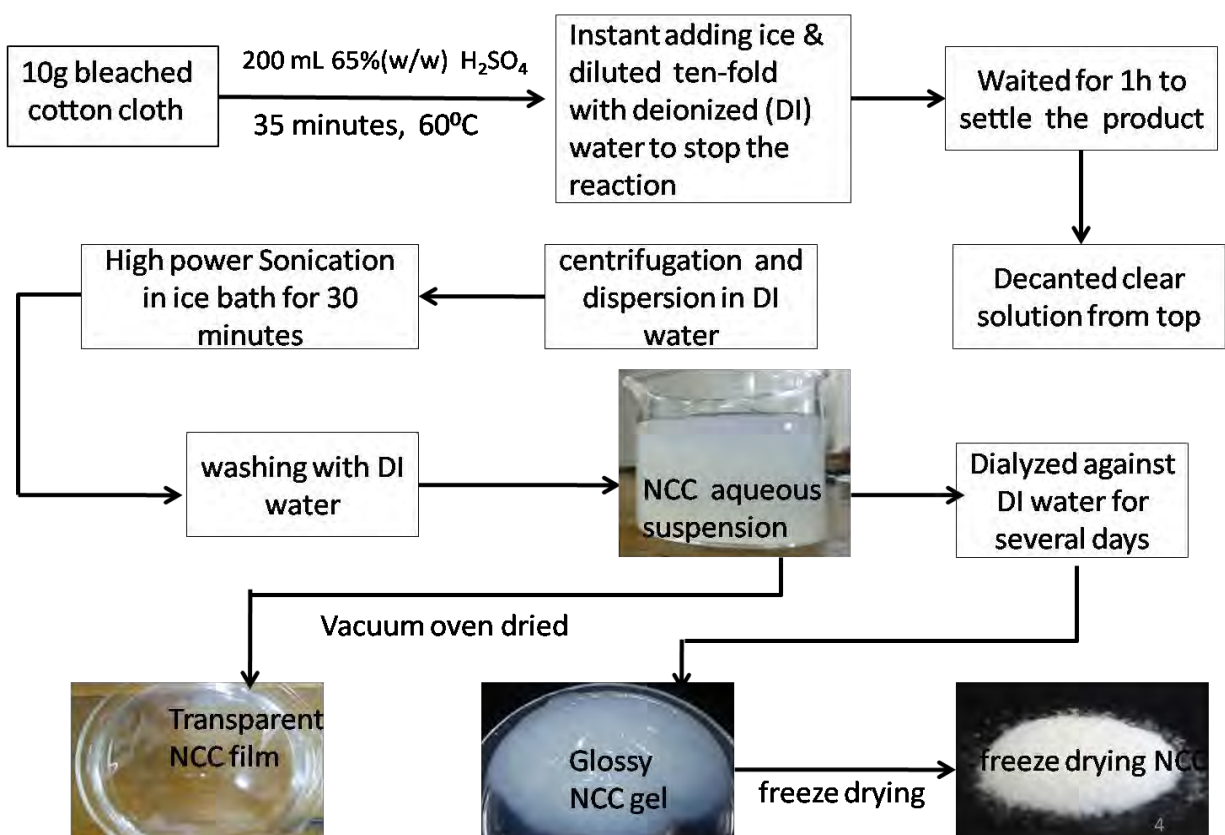


Fig. 3.3. Flow chart of preparation of NCC

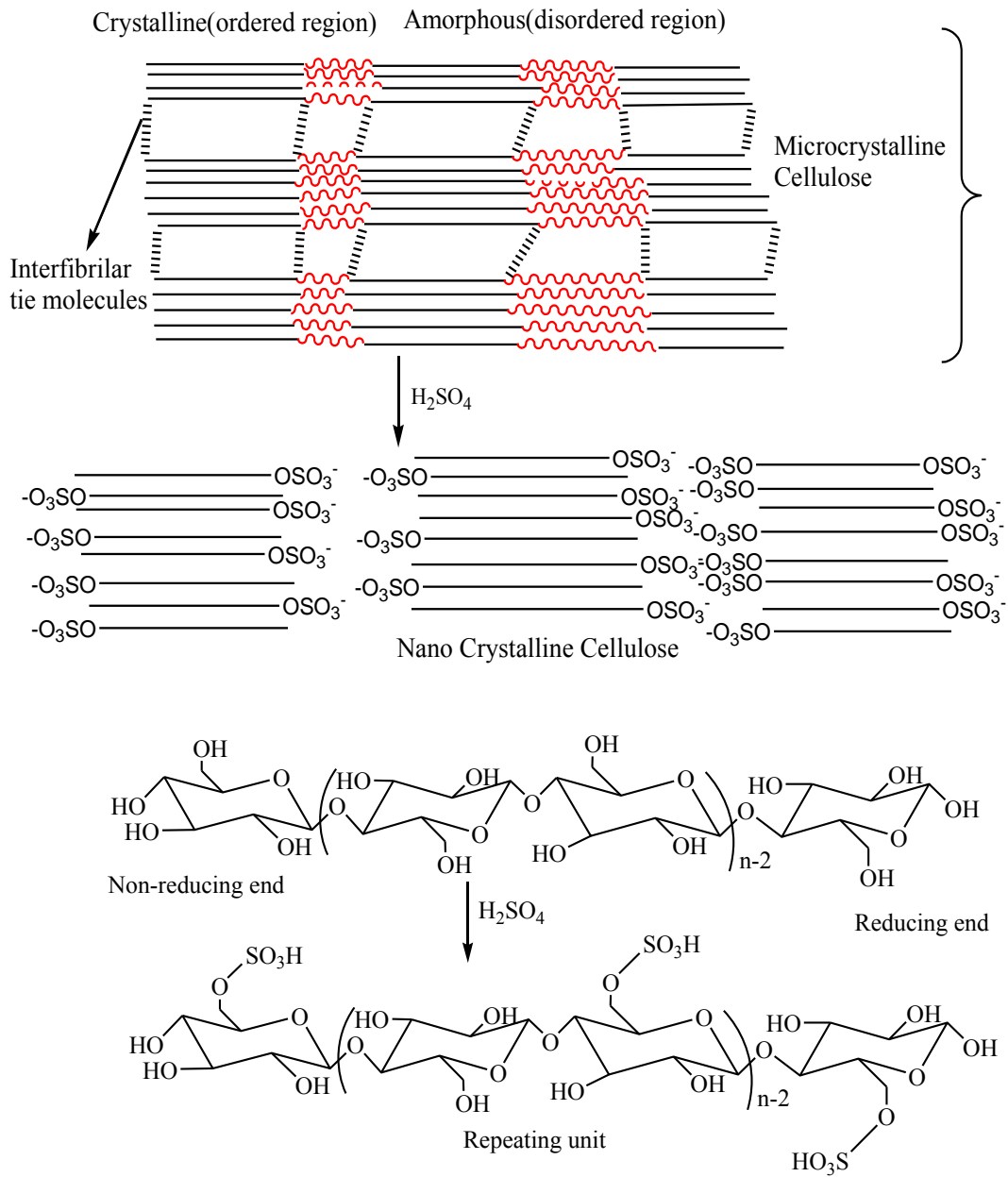


Fig. 3.4. Hydrolysis of cotton cloth with H_2SO_4

3.5. Characterization

3.5.1 X-ray diffraction (XRD)

It is well known that the mechanical properties of cellulose products were strongly dependent on the crystallinity and crystal structure. To determine the crystal structure and crystallinity, XRD patterns of the MCC and NCC were measured by automated powder X-ray diffractometer. Before testing, samples were dried in a vacuum oven at 50 °C for 24 h to remove moisture. The powder samples were pressed in a square aluminum sample holder (40mm X 40mm) with a 1 mm deep rectangular hole (20mm x 15mm) and pressed against an optical smooth glass plate. The upper surface of the sample was labeled in the plane with its sample holder. The sample holder was then placed in the diffractometer. The WXR D data were generated by a diffractometer with Cu-K α radiation ($\lambda = 1.542 \text{ \AA}$) at 40 kV and 30 mA over the range $2\theta = 10^\circ\text{--}50^\circ$, a size step of 0.02° , and a time step of 2.0 s, (1.0 h per scan).

The degree of crystallization was determined using the method of X-ray Crystallinity index. The formula below was used in calculating degree of crystallization.

$$\text{Crystallinity index} = \frac{I_{\text{cry}} - I_{\text{am}}}{I_{\text{cry}}} \text{-----} 3.3$$

Where I_{cry} represents the diffraction intensity of crystallization at the 200 peak and I_{am} represents the diffraction intensity of amorphous region.

3.5.2 Scanning electron microscopy

Morphological analysis was performed using Field Emission Scanning Electron Microscopy (FESEM). The samples were sprayed in the carbon strip for analysis, in case of NCC a drop of dilute suspension was deposited on small piece of carbon strip and allowed to dry at vacuum drier at 40°C. The sample surface was coated with a thin layer of gold to provide electrical conductivity. The sample was then placed in the main SEM chamber to view its surface.

3.5.3 Fourier transform infrared (FTIR) measurement

In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular finger prints of the sample. This makes infrared spectroscopy useful for several types of analysis like identifying

unknown materials, determining the quality or consistency of a sample, and determining the number of components in a mixture. Materials can be identified from their functional groups, chemical bonds etc. which can be detected through their characteristic infrared absorption frequencies or wave lengths. FTIR studies were conducted using Shimadzu IR spectrometer. Sample with KBr with a 1:100 “samples-to-KBr” ratio was maintained to prepare disk. The sample disks were then scanned in the wave number range of 4000 to 400 cm^{-1} with an average of 30 scans per measurement. The resolution of the spectrometer was 4 cm^{-1} .

The prepared MCC and NCC were dried in a vacuum oven at 50°C for 24 hours and then cooled to room temperature for Fourier transform infrared (FTIR) analysis.

3.5.5 Thermogravimetric analysis

The thermal stability of MCC, NCC were studied by a thermo-gravimetric analyzer (TGA) in a nitrogen atmosphere. Approximately 5 mg oven dried film samples in a platinum pan were heated from 30 to 600°C at a heating rate of 10°C/min under a nitrogen flow of 60 mL min^{-1} . Before the data acquisition segment, the sample was equilibrated at 25°C for 5 min to obtain an isothermal condition. The weight-loss rate was obtained from derivative thermo-gravimetric (DTG) data.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Acid hydrolysis of cellulosic materials

Since the cellulose contains both amorphous and crystalline structures, the highly crystalline cellulose can be prepared from selective methods based on the source of the cellulose. Among them MCC&NCC is derived by severe acid hydrolysis to remove the amorphous cellulose portions, yielding particles consisting of bundle-like and needle-like micro and nanocrystals respectively. A number of different factors affecting the acidic hydrolysis of cellulose were examined. A complete set of investigated parameters include: reaction time and temperature, acid concentration, source of cellulose, ratio of cellulose to acid, and the effect of applied external energy (ultrasonic). The main focus was to optimize the conditions needed for production of white powder form MCC & transparent gel of NCC from raw cotton cloth and wood pulp.

Due to the cellulose's strong ability to form hydrogen bonds, the product tended to agglomerate to form larger particles after reaction. The ultrasonic energy was applied after the reaction to stop down the aggregation to increase the crystallinity of microcrystal & transparency of nanocrystals. In this study, ultrasonic energy was vigorously applied in the production of NCC to get better transparent nanocrystals. While the application of ultrasonic energy after hydrolysis has been previously documented [1], but the mechanism of ultrasonic effect has not been clearly understood till today. The aggregate formation manifested itself especially in the absence of surface charges when the repulsion forces between the individual nanocrystals were minimized. One solution for decreasing the aggregation issue is to introduce negative charges on the surface of NCCs. Sulfuric acid is known to introduce negative charges on the surface of the NCCs via an esterification reaction with the sulfate anions [2-4].

It has been proved that the complete hydrolysis of cellulose under strong acid and high temperature (~100°C) results in glucose or even carbonization [5]. While under relatively mild conditions in the present study, the chemical degradation mechanism can be acid-catalyzed cleavage of β -1-4-glycosidic bond [6]. In the present study, different concentration of hydrochloric acid & sulfuric acid was used to the preparation of MCC and NCC.

The degradation of cellulosic materials could proceed in three steps, outline shown in Fig.4.1. Firstly, the glycosidic oxygen linking two sugar units is rapidly protonated under acidic

condition, forming a conjugate acid. Then the cleavage of the C–O bond and breakdown of the conjugate acid to the positively charged ion take place. After a rapid addition of water, the resulted segments and a proton are liberated. Assuming that the cleavage of the C–O bond takes place more rapidly at the end than in the middle of the polysaccharide chain, more monosaccharides and lower yields of MCC & NCC are resulted.

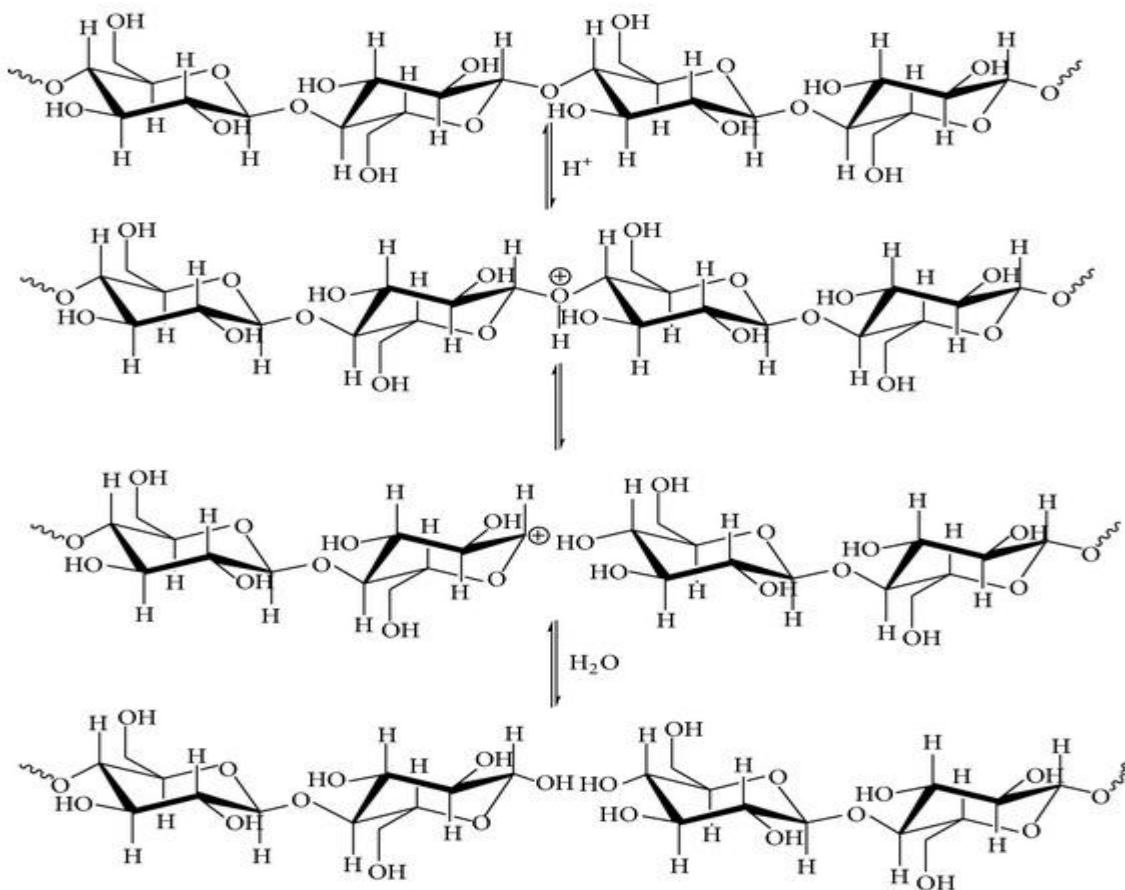


Fig.4.1. Mechanism of acid-catalyzed hydrolysis of cellulose by cleavage of β-1-4- glycosidic bond

The plant cell wall (the stuff wood is made of) is a mixture of many different substances, especially polysaccharides and lignin. All of these compounds are stable in NaOH. However, they can be extracted from the wood under different conditions.

To make cellulose more accessible to reactants during bioconversion of lignocellulosic materials pretreatment is required. Since lignin and other complex polymer is soluble in NaOH at any pH

it can easily remove during pretreatment. In this study, lignocellulosic materials were treated with sodiumhydroxide to remove hemicelluloses, xyline, lignin[7] and other polysaccharides. Cellulose does not react directly with NaOH. When lignocellulosic materials with the contamination of hemicelluloses, xylinie, lignin and other polysaccharides; is treated with sodiumhydroxide, it is expected that it could dissolve loosely bound protein and lignin. Since it is extremely corrosive and dangerous at such a high concentration, 4% NaOH is used in the study.

4.2 Physical appearance of the prepared MCC

Fig.4.2 shows prepared MCC at different conditions. Based on the physical appearance whether it was fibrous or powder from comparing with commercial MCC hydrolysis conditions were selected for the preparation of MCC. The characteristic properties of the samples were further justified by different techniques to get optimum condition. From the physical appearance, it was assuming that B₃, S₃, T₂ & W₂ sample were almost similar physical appearance as white powder as commercial MCC (M) with similar fineness. S₃, S₄ were approximately similar appearance and T₂, T₃ were approximately similar appearance.

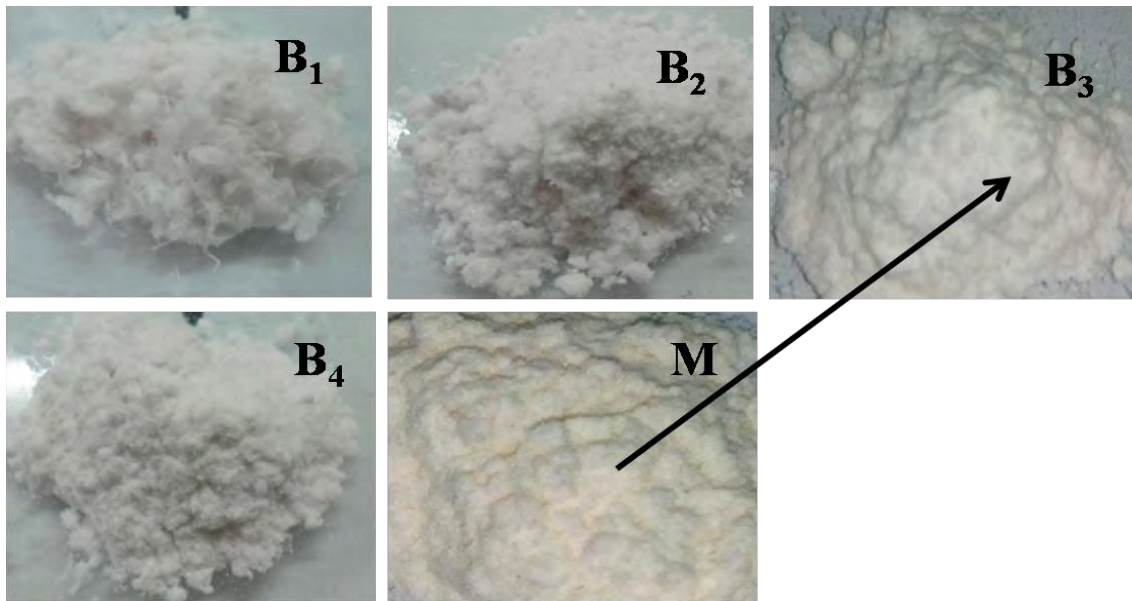


Fig. 4.2(a). Physical appearance of MCC of the samples type-B series comparing with commercial MCC(M)

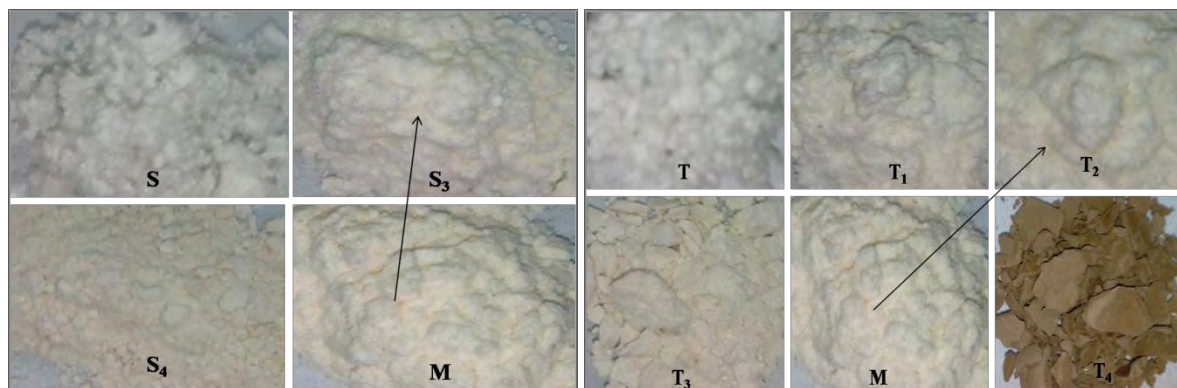


Fig. 4.2(b). Physical appearance of MCC of the sample type-S & type-T series comparing with commercial MCC(M)

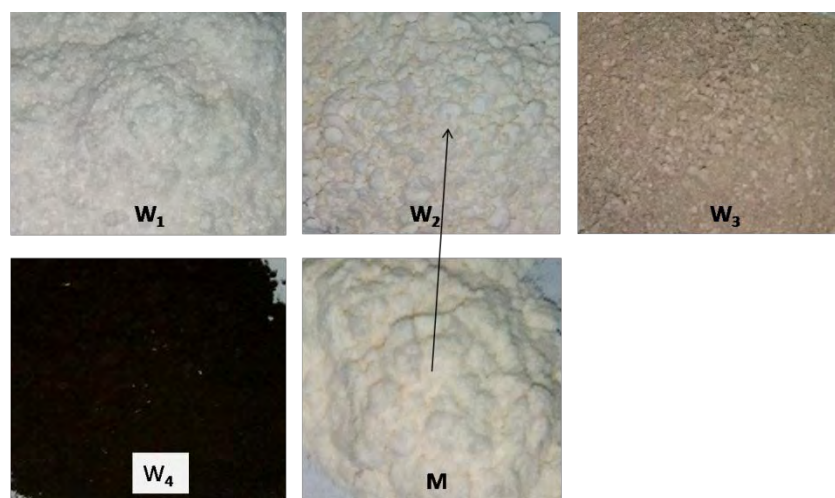


Fig. 4.2(c). Physical appearance of MCC of the samples type-W series comparing with commercial MCC (M)

From the physical appearance, it can be concluded that the formation of MCC depends upon the source and hydrolysis condition. For example, in this study T-type cloth (textile cotton cloth) needs 7.5N HCl (S₃) acid to form white powder MCC, while after treating with 4% NaOH it needs 5N HCl (T₂). It forms brownish powdered cellulose at the 10N HCl (T₄). Thus, the formation of MCC depends upon hydrolysis condition. Again T-type cloth (textile cloth) needs 7.5N HCl to form almost similar physical appearance to the commercial MCC, while at the same condition wood pulp produce brownish powdered MCC. At 10N HCl wood pulp produce almost black powder, which indicate carbonization occurred here. On the other hand, voile cloth needs 7.5N

HCl to produce almost same appearance of commercial MCC. At 10N HCl hydrolysis it also forms white powder MCC. i.e. the formation of MCC depends upon the source of the cellulose.

4.3 Characterization of prepared MCC through HCl hydrolysis by FESEM image

From the physical appearance, it was assuming that from type-B, sample B₃ form powder MCC leaving the fibrous appearance which was similar in appearance as the commercial MCC sample M. From type-T, T₂ is approximately similar as the commercial MCC sample M. From type-W, W₂ is approximately similar as the commercial MCC sample M. Sample B₃, T₂ and W₂ were subjected to FESEM image to justify whether the sample was in micro dimension or not.

The FESEM image of commercial MCC (M) is below-

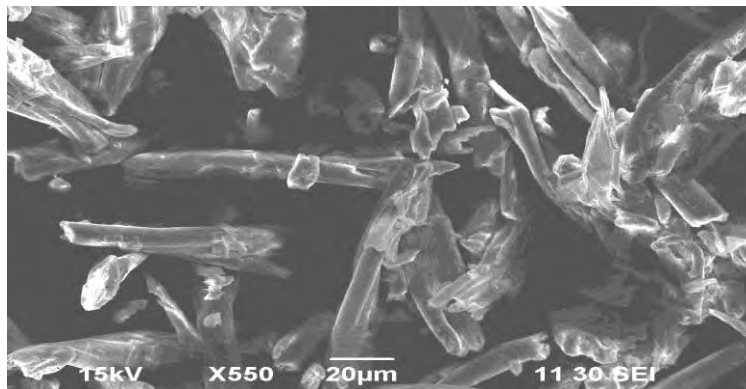


Fig. 4.3. FESEM image of commercial MCC (sample M)

The comparative FESEM image of B₃, W₂, T₂ with Commercial MCC (M) are below-

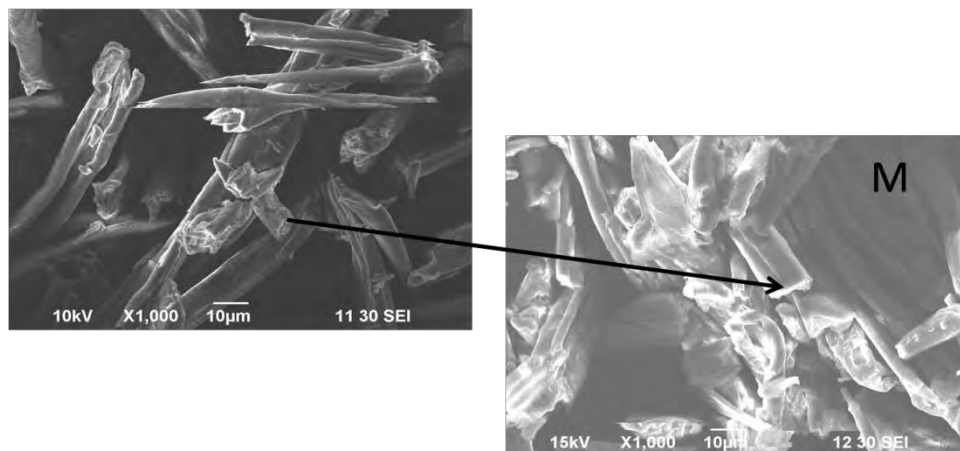


Fig. 4.3(a). FESEM –image of sample B₃ comparison with commercial MCC.

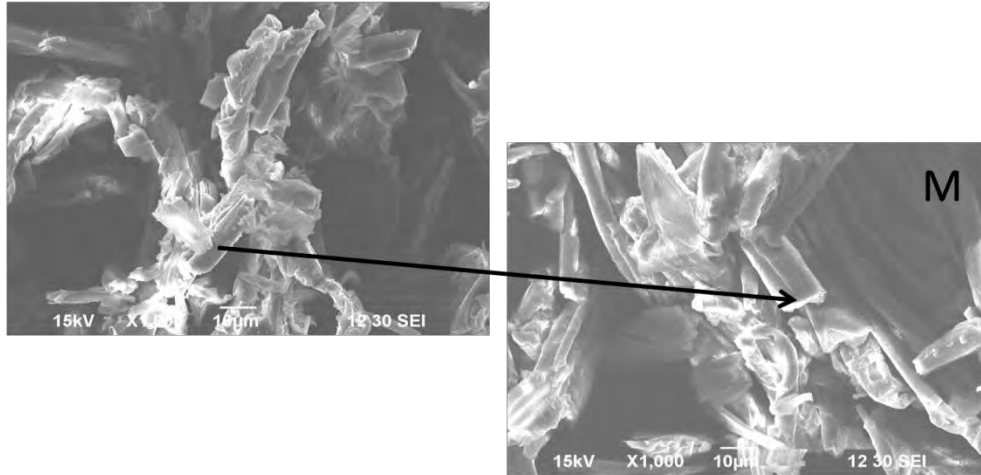


Fig. 4.3(b).FESEM –image of sample T₂ comparison with commercial MCC.

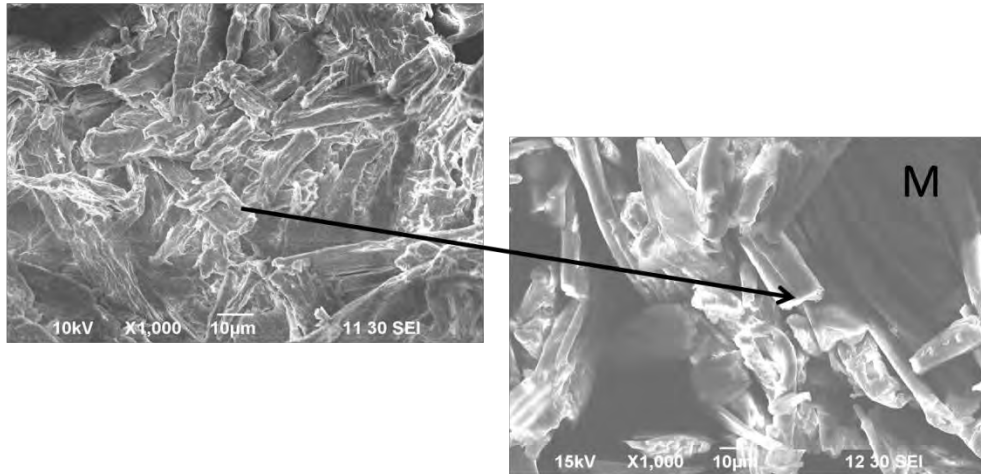


Fig: 4.3(c). FESEM –image of sample W₂ comparison with commercial MCC.

Microcrystalline material is crystallized substance that contains small crystal visible only through microscopic examination. From the above FESEM images we saw the average diameter was about 10 µm and length was about 50 µm, while the diameter of commercial MCC was 10 µm and length was about 20 µm, So, from the FESEM images it can be concluded that all the prepared MCCs have in micro-scale dimension with some morphological differences as like as commercial grade MCC. From the above discussion, it can be claimed that the experimental lignocellulosic materials are successfully converted into microcrystalline cellulose.

4.4 Characterization of prepared MCC by FTIR Spectral analysis

FTIR Spectroscopic studies were carried out in order to get some qualitative information on the prepared samples. The molecular structure of different samples was characterized by FTIR spectroscopy in the region of 4000-400 cm^{-1} .

Figure: 4.4.1. Illustrates the FTIR spectra of commercial MCC. The absorbance at 3343, 2908, 1641, 1364, 1146 and 1053 cm^{-1} are associated with native cellulose. A strong band at 3343 cm^{-1} is attributed to the stretching of hydroxyl groups. The absorption at 2908 cm^{-1} originates from the C-H stretching. Band 1641 cm^{-1} arises from the H-O-H bending of the absorbed water. The peak at 1364 cm^{-1} corresponds to the O-H bending and that at 1146 cm^{-1} is attributed to the C-O antisymmetric bridge stretching. A strong band at 1053 cm^{-1} is due to the C-O-C pyranose ring skeletal vibration. Small absorbances at 1323 cm^{-1} and 1427 cm^{-1} corresponding to the C-O stretching of the syringyl ring and aromatic skeletal vibrations [8], which indicate the present of lignin at amorphous region in low concentration. In addition, the absence of a peak at 1210 cm^{-1} indicates the absence of polysaccharides [9]. The observed absorbance peaks indicate the typical structure of cellulose.

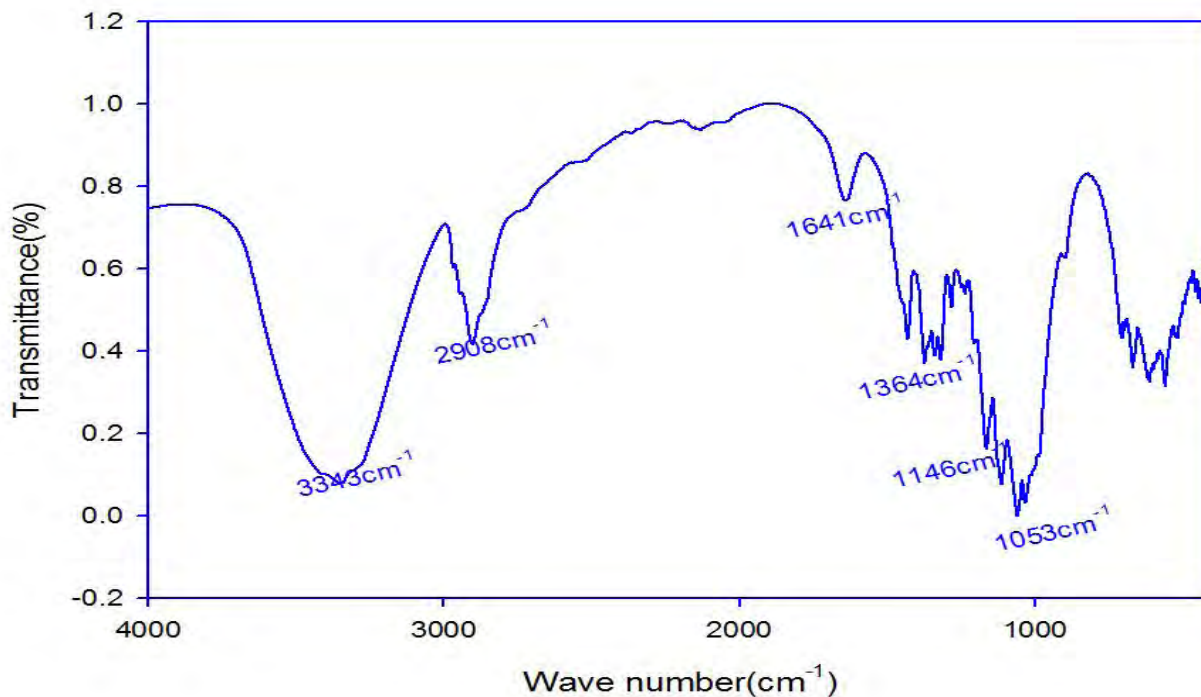


Fig: 4.4. FTIR spectra of commercial MCC

FTIR analysis for B-Series

The FTIR spectrum of MCC obtained from cotton cloth in different concentration are shown in the Fig.4.4(a) The FTIR spectrum of prepared sample showed very similar characteristic absorption peak with that of commercial MCC. Therefore, the prepared MCC sample from voile cotton cloth has same chemical characteristics as like as that of commercial MCC.

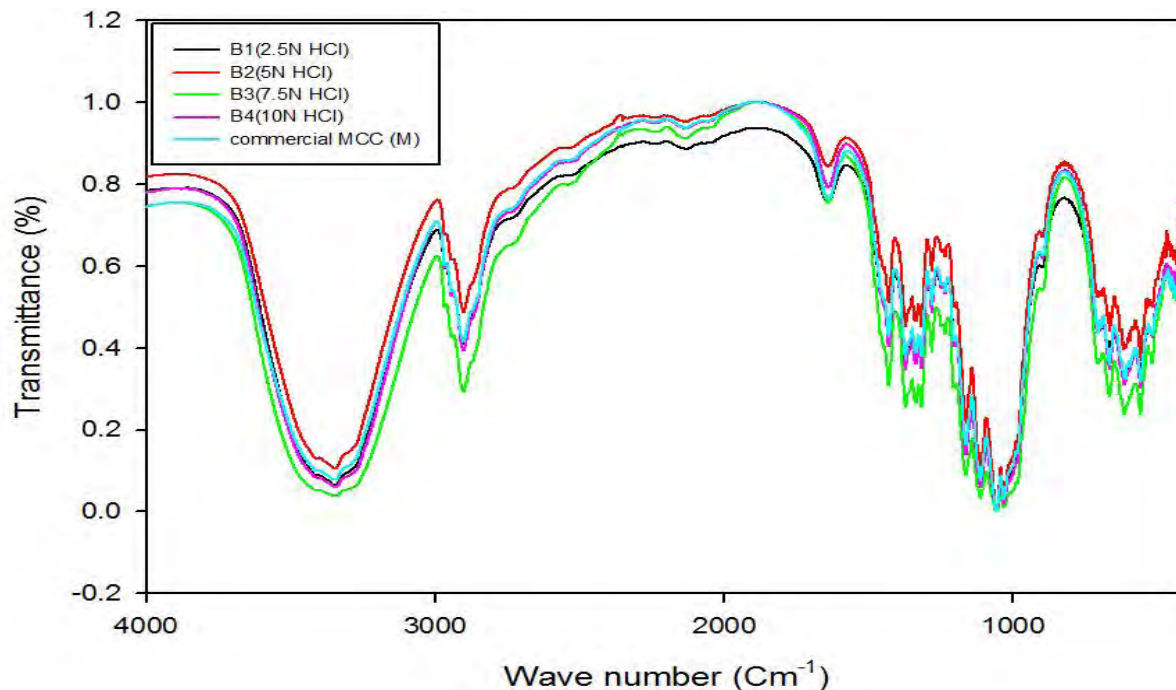


Fig: 4.4(a).Comparison spectra of commercial MCC(M) VS B-Series

FTIR analysis for T-Series

The FTIR spectrum of MCC obtained from Textile cottoncloth in different concentration are shown in the Fig.4.4 (b).The FTIR spectrum of prepared sample showed very similar absorption peak with that of commercial MCC. Therefore, the prepared MCC sample from textile cotton cloth has same chemical characteristics as like as that of commercial MCC. The slight change of -OH band at wave number 3354cm^{-1} (T₂) to low wave number 3344cm^{-1} (T₃) may indicate the change of crystallinity index.

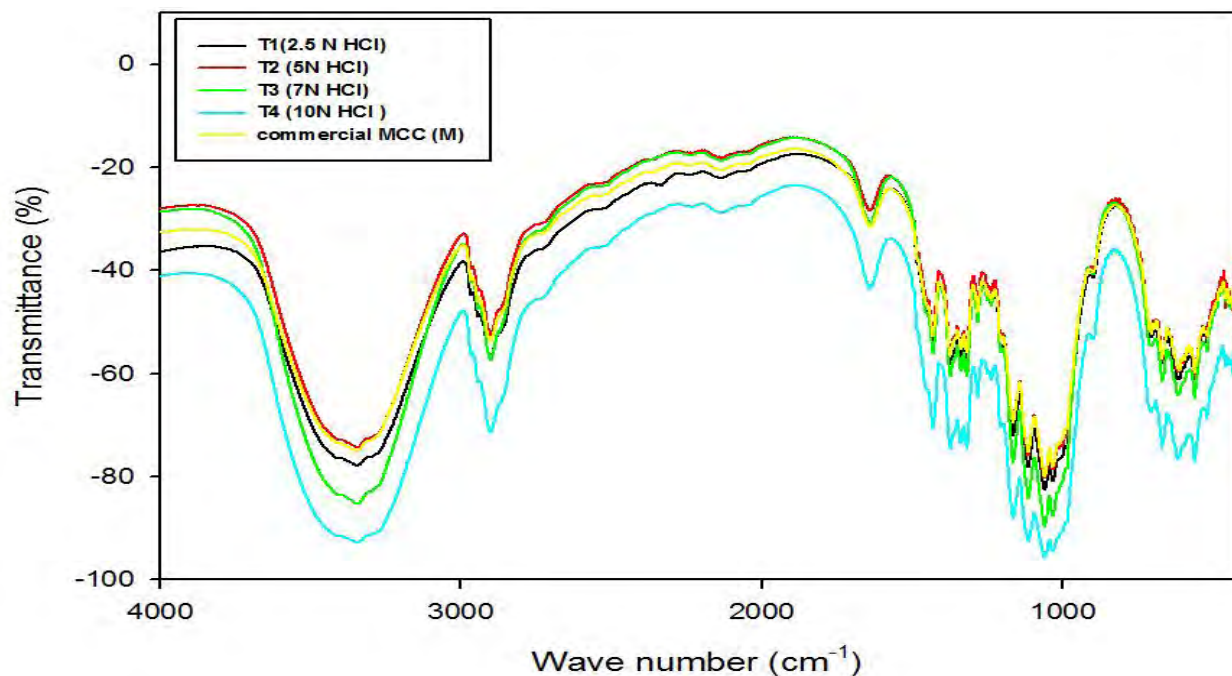


Fig. 4.4(b).Comparison FTIR graph of T-Series with commercial MCC.

FTIR analysis for W-Series

The FTIR spectrum of MCC obtained from wood pulp in different concentration are shown in the Fig.4.4(c).This result indicates all the prepared MCC from wood pulp have very similar chemical nature as that of commercial MCC.

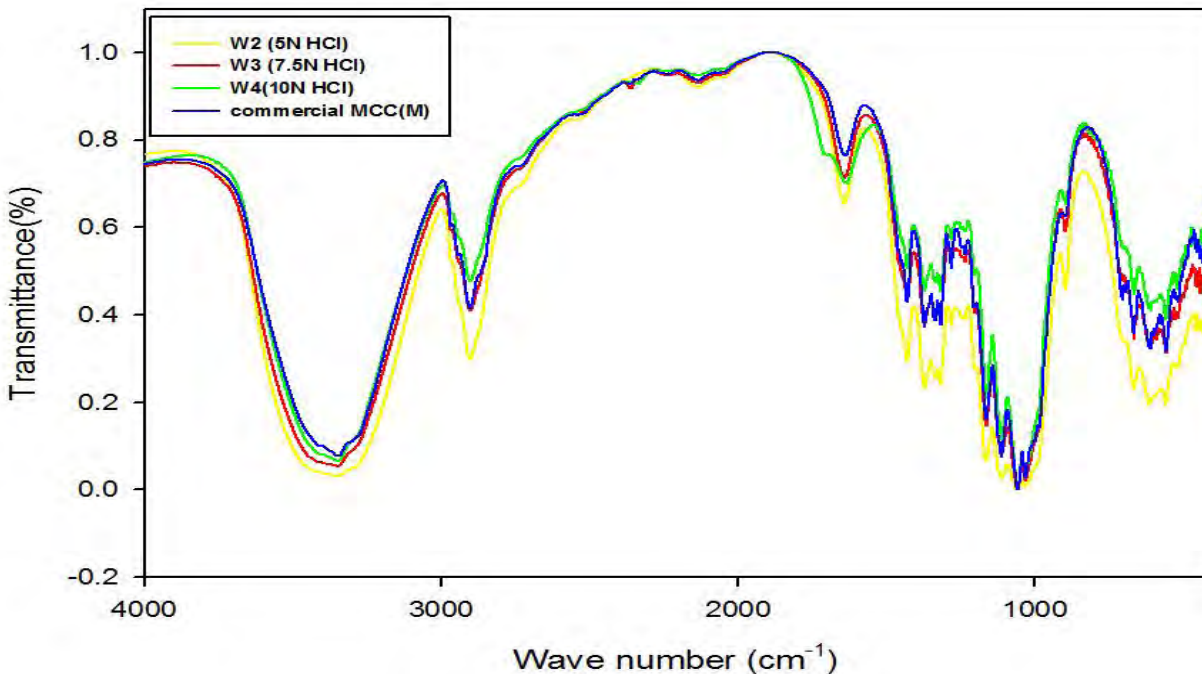


Fig: 4.4(c).Comparison FTIR graph of W-Series with commercial MCC.

4.5 X-ray diffraction (XRD) Analysis

From the crystallographic planes, all the prepared and commercial MCC indicate the typical structure of cellulose. The crystallographic planes were labeled according to the native cellulose structure, as described by Wada et al. [10]. After deconvolution, all diffractograms show the 14.5° – 15.3° 2θ reflection assigned to the (1–10) crystallographic plane, the 15.7° – 16.30° 2θ reflection assigned to the (110) crystallographic plane, the 18.30° – 18.40° 2θ reflection assigned to the amorphous phase and the 21.90° – 22.20° 2θ reflection assigned to the (200) crystallographic plane of cellulose I [10,11]. The XRD profiles of commercial MCC and prepared MCC from textile cotton cloth are presented in Fig.4.5 (a). All the samples exhibited a peak around $2\theta = 15.1^{\circ}$, 16.5° and 22.5° and 34.6° which are supposed to represent the typical cellulose structure. The cellulose crystals exhibit characteristic assignments of 1–10, 110, 200, and 004 planes, respectively [12-13] (Fig.4.5).

The X-ray diffractometer was used to investigate the crystalline structure of the samples. From the observation, it was clear that the X-ray diffraction patterns of prepared samples and commercial MCC are similar. The prepared MCC from cotton cloth have similar characteristic peaks at the same position. The only difference that is discernible is slight change in their peak

intensities, representing some changes in the crystallinity due to the change of the concentration of acid during chemical treatment and hydrolysis of cellulose.

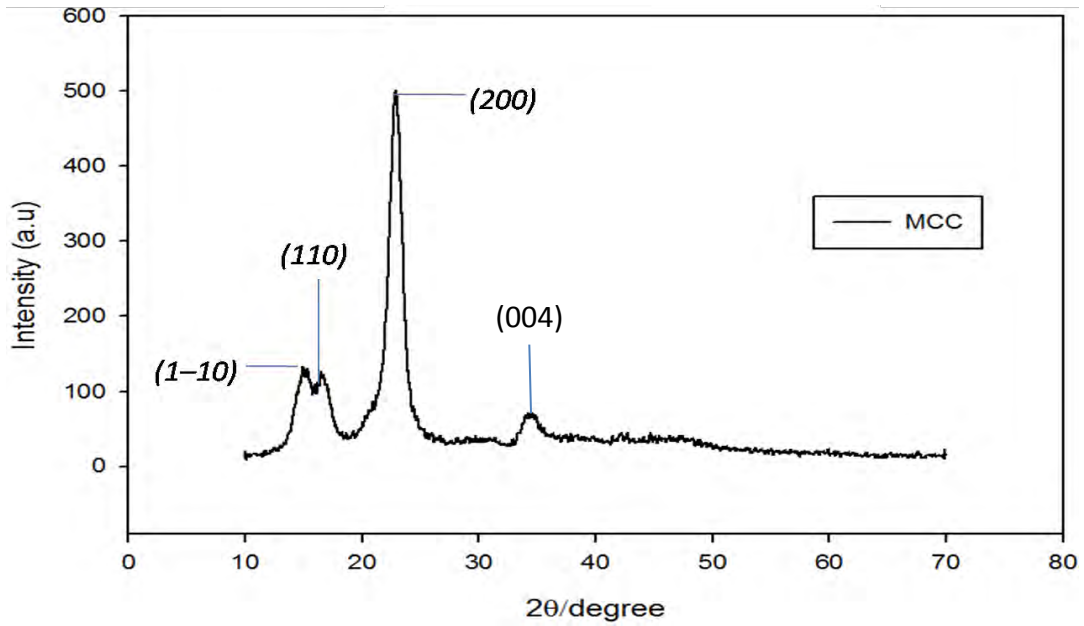


Fig. 4.5. Crystallographic plane of commercial MCC.

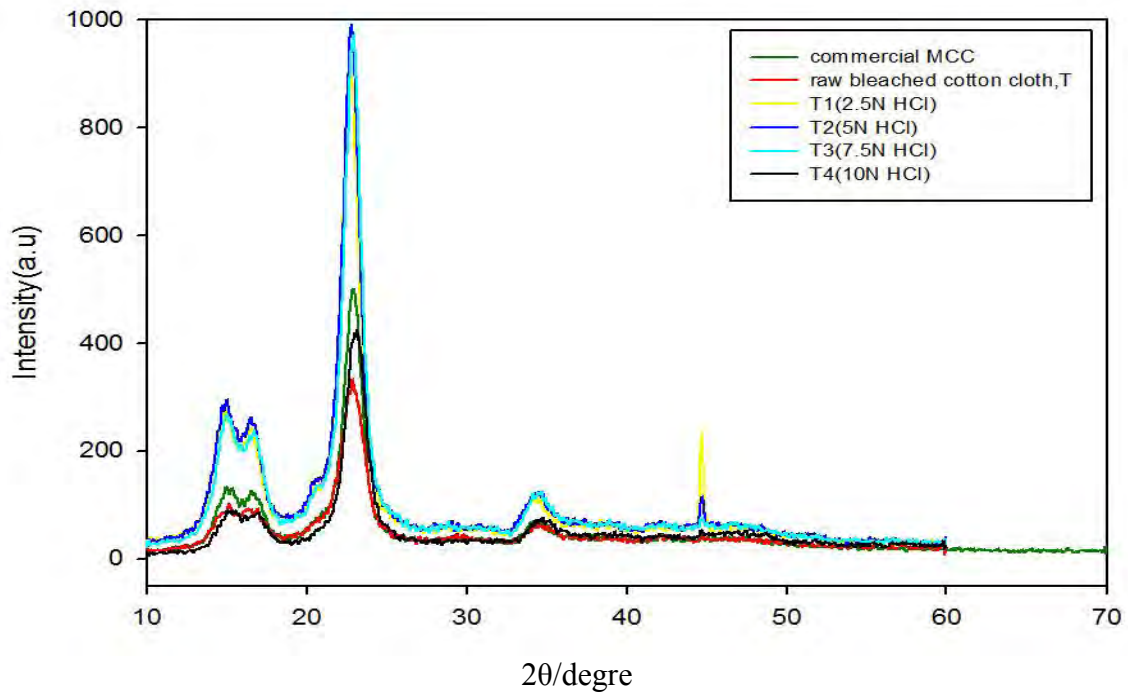


Fig. 4.5(a). XRD- graph of T-Series comparison with commercial MCC.

The crystallinity index of the samples was calculated according to amorphous subtraction method. The crystallinity of cellulose is defined as [14],

$$\text{Crystallinity} = \frac{I_{\text{cry}} - I_{\text{am}}}{I_{\text{cry}}} \times 100 (\%) \text{-----} \quad (4.1)$$

It was the empirical method proposed by Segal *et al. in 1959* [11,15].

Here, I_{cry} is the intensity of the 200 planes reflection, typically located around $2\theta = 22.5^\circ$; I_{am} is the intensity at $2\theta = 18^\circ$, corresponding to the minimum in a diffractogram [15].

Fig:4.5(b). shows the height of crystalline and amorphous region to calculation of crystallinity of commercial MCC.

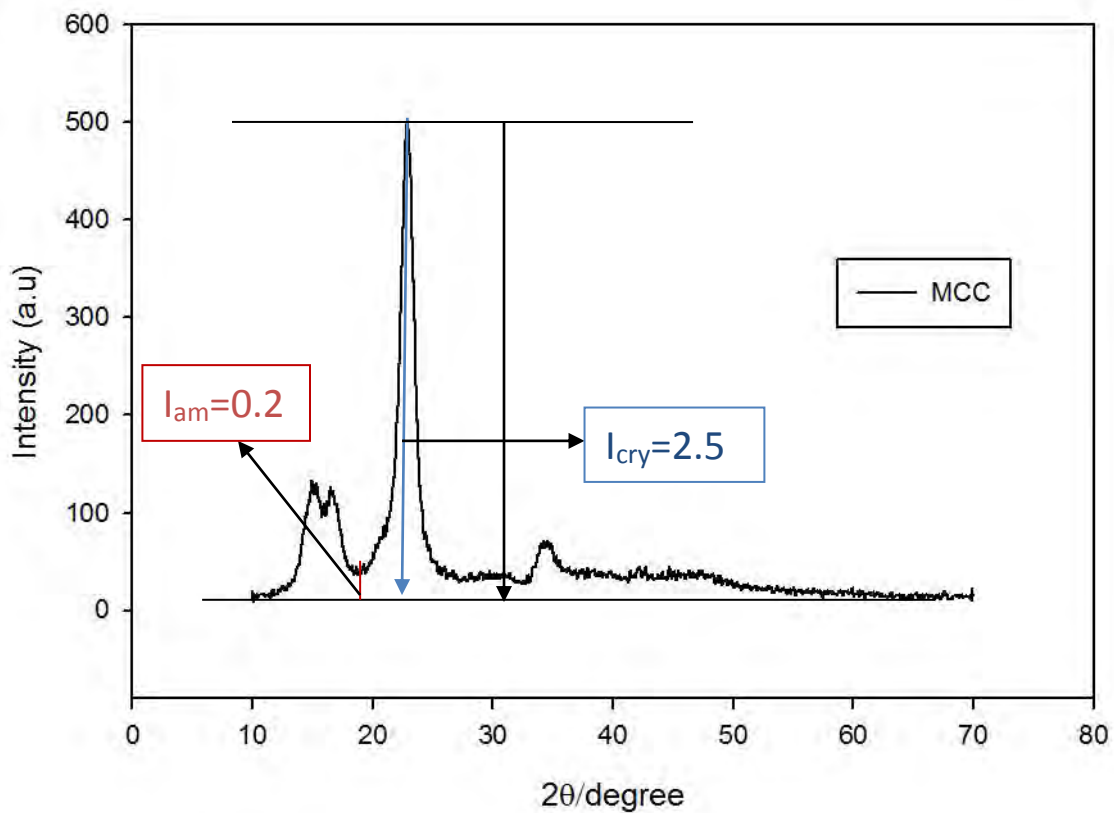


Fig. 4.5(b).Height of crystalline and amorphous region to calculation of crystallinity of commercial MCC

Putting the value of I_{cry} & I_{am} in Eq. (4.1) we get the crystallinity of commercial microcrystalline cellulose as,

$$\text{Crystallinity} = \frac{2.5-0.2}{2.5} \times 100 = 92\%$$

Similarly using Eq. (4.1), the Crystallinity of the samples; T, T₁, T₂, T₃, T₄ from textile cotton cloth (treating with NaOH) are 87%, 89%, 93%, 95%, 92%. This result follows the experiments performed by Nada et al. (2009) who showed that hydrolyzed cellulose had much higher crystallinity than unhydrolyzed cellulose, and the crystallinity increases with the increase of the acid concentration. [16]

The crystallinity of the sample S₃ (bleached textile cotton cloth without treating with NaOH) is 94%. That means there is some effect of NaOH treatment on textile cloth. i.e. there is very few lignin portion in the local voile cloth.

Sample	Crystallinity (%)
Commercial microcrystalline cellulose (M)	92
T (Bleached raw textile cotton cloth without hydrolysis)	87
T ₁ (Bleached raw textile cotton cloth treating with NaOH then hydrolysis with 2.5N HCl)	89
T ₂ (Bleached raw textile cotton cloth treating with NaOH then hydrolysis with 5N HCl)	93
T ₃ (Bleached raw textile cotton cloth treating with NaOH then hydrolysis with 7.5N HCl)	95
S ₃ (Bleached raw textile cotton cloth without treating with NaOH then hydrolysis with 7.5N HCl)	94
T ₄ (Bleached raw textile cotton cloth treating with NaOH then hydrolysis with 10N HCl)	92

Table 4. Crystallinity of the prepared sample collected from textile cotton cloth series (T-series)

In the experiment, it was seen that the crystallinity increases with the acid concentration, but hydrolysis with at 10N Hydrochloric acid the crystallinity decreases. It may be due to the

carbonization occurring or may be the burning of the sample. From the agreement with the physical appearance, T₄ sample was brownish color.

4.6 Thermo-degradation behavior of MCC

Thermal analysis techniques such as thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) were widely used to measure the thermal stability and pyrolysis behavior of polymers in different conditions. TG curves show the changes in weight during heating. The results of the thermogravimetric (TG) analysis of commercial MCC (M), prepared MCC are shown in Fig. 4.7. All samples showed a slight weight loss at low temperatures (< 150⁰C), corresponding to evaporation of absorbed water. However, the degradation behavior was different in the high temperature range. All samples showed one major pyrolysis process, and associated weight loss in the temperature range from 220 to 380⁰ C was observed but the maximum weight loss occurred at different temperature from one another which might be due to the crystallinity changes. The weight loss occurred at 297-355⁰C of commercial MCC was 2.40%, The weight loss occurred at 303-376⁰C of sample B₃ was 7.92 %, The weight loss occurred at 300-364⁰C of sample T₃ was 5.27 %. At high temperatures, the repolymerization pathway of cellulose yields tar (levoglucosan), which further decomposes with the formation of char and this mostly occurs in crystalline regions. Generally, cellulose thermal degradation involves dehydration, depolymerization and decomposition of glycosyl-units and then formation of a charred residue.

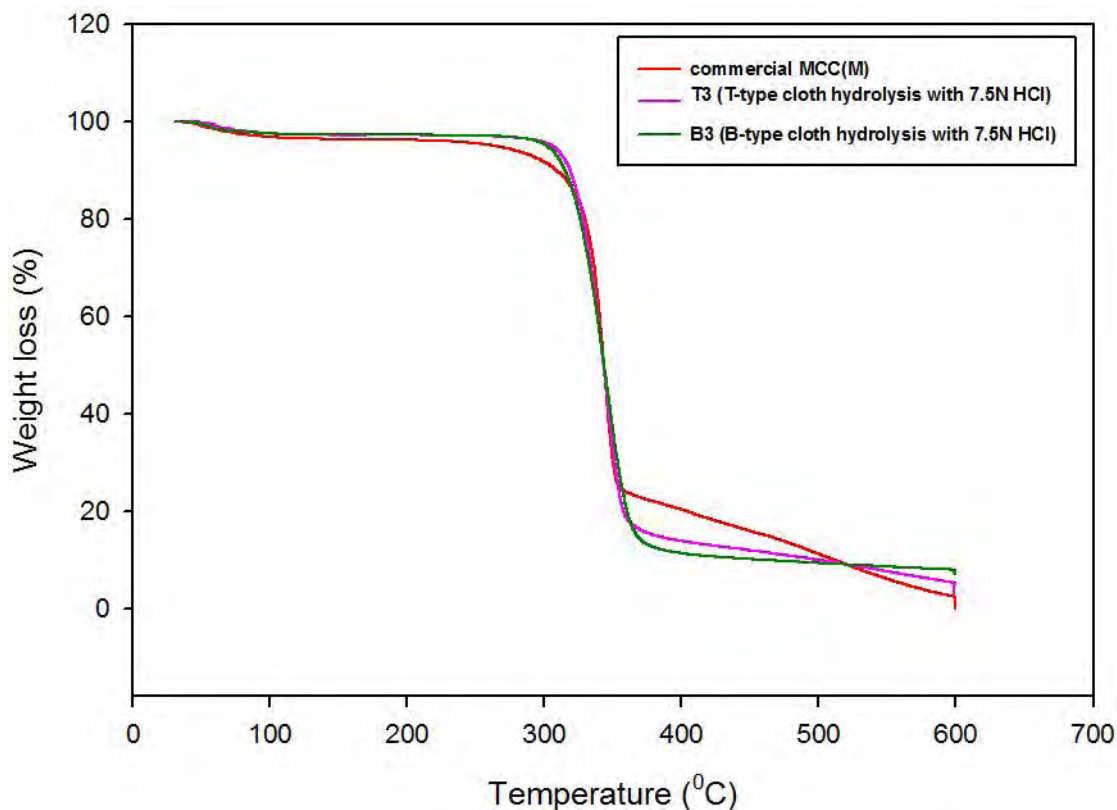


Fig. 4.6.TGA graph of commercial MCC and prepared MCC.

The loss in weight was increased with rising acid concentration from 2.5-10N. A high increased in loss of weight was obtained by increasing the acid concentrations from 5N-10N HCl acid. B₃ (303-760⁰c) is more stable than T₃(300-365⁰c). i.e, T₃ is more crystalline than B₃. The weight loss occurred at 297-355⁰c of commercial MCC. The crystallinity sequence M>T₃>B₃. From the above observation, it can be say that, the stability ranges of commercial MCC and prepared MCC are approximately same. Weight loss occurred at different temperature from one another which might be due to the crystallinity changes. Therefore, Thermal degradation occurs at higher temperature within broader ranges of temperature showing higher thermal stability due to presence of amorphous region.Prepared MCC is stable over a wide range of temperature which is approximately similar the TGA of commercial MCC.

4.7 Optimization of the preparation condition of NCC

Though there are several preparation techniques of NCC. In this study,optimum hydrolysis conditions were selected for the preparation of NCC based on the physical appearance of the

prepared NCC gel and its film transparency. The preparation of NCC was optimized by the variation of acid concentration, hydrolysis time, temperature of hydrolysis and ultrasonic time and power. Fig.4.8. shows the physical appearance of prepared NCC collected from different condition.

The conditions were selected by following several set of experimental technique,

a) Variation of concentration

NCC was prepared using different concentration of sulfuric acid with cotton-to-acid weight ratio of 1 to 20 at 50 °C temperature. The prepared bleached cotton cloths were pre-mixed with the acid and the mixture was stirred vigorously for 40 minutes. Immediately following hydrolysis, the suspension was diluted ten-fold to stop the reaction. The suspension was then transferred into centrifuge bottles and was centrifuged at 4000 rpm for 10 minutes to remove excess acid and water-soluble fragments and separate the gel type ppt. from the suspension. The gel was then washed with distilled water and then mixture was centrifuged again & then collected the gel of the solution by high centrifugation.

The variation of concentration taken

were, $S_1=25\%$, $S_2=30\%$, $S_3=35\%$, $S_4=40\%$, $S_5=45\%$, $S_6=50\%$, $S_7=55\%$, $S_8=60\%$, $S_9=65\%$ (w/w)

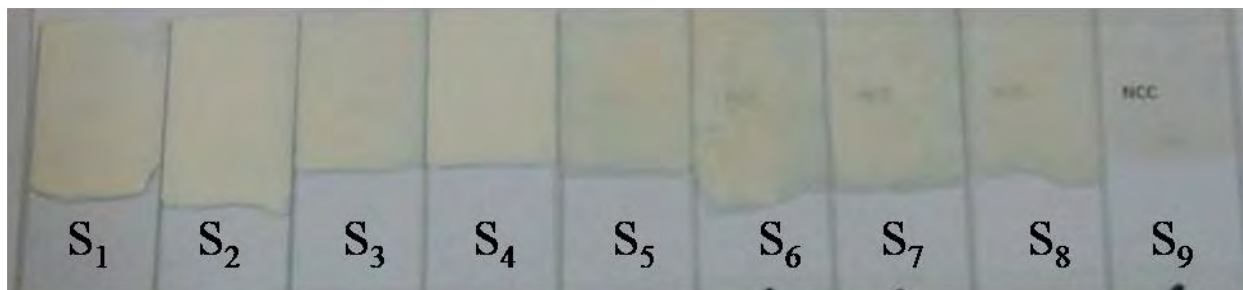


Fig: 4.7(a): Physical appearance of prepared NCC collected from different concentration

From the physical appearance of the prepared NCC gel transparency on glass slide, concentration of sulfuric acid was found $S_9=65\%$ (w/w) at 50°C temperature for 40 minutes hydrolysis.

b) Variation of temperature

NCC was prepared using 65% (w/w) aqueous solution of sulfuric acid at different temperature with cotton-to-acid weight ratio of 1 to 20 for 40 minutes hydrolysis. The variation of temperature taken per degree centigrade were $T_1=20^{\circ}\text{C}$, $T_2=25^{\circ}\text{C}$, $T_3=30^{\circ}\text{C}$, $T_4=35^{\circ}\text{C}$, $T_5=40^{\circ}\text{C}$, $T_6=45^{\circ}\text{C}$, $T_7=50^{\circ}\text{C}$, $T_8=55^{\circ}\text{C}$, $T_9=60^{\circ}\text{C}$.

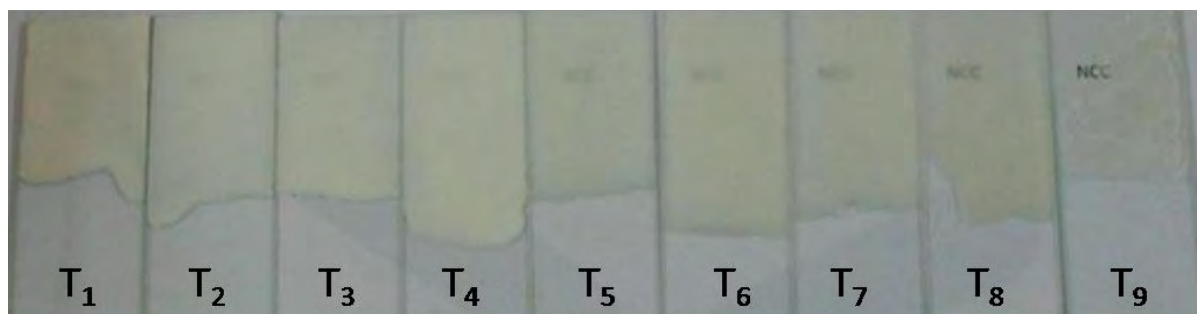


Fig: 4.7(b): Physical appearance of prepared NCC collected from temperature variation.

From the physical appearance of the prepared NCC gel on glass slide, the transparent NCC gel was formed at 60°C.

c) Variation of hydrolysis time

NCC was prepared from hydrolysis of bleached cotton cloth with 65% H₂SO₄ at 60°C with variation of time at constant acid-cotton ratio 1:20. The following time variation were t₁=25min, t₂=30min, t₃=35min, t₄=40min.

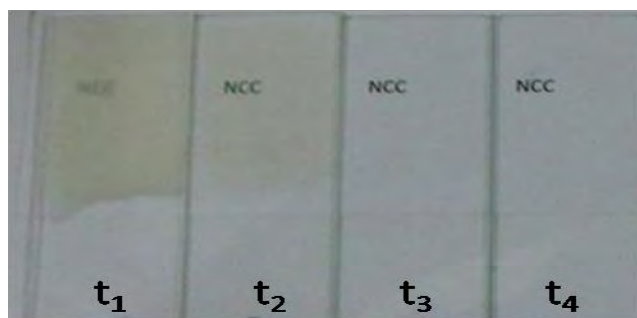


Fig: 4.7(c): Physical appearance of prepared NCC collected from time variation.

From the physical appearance of the prepared NCC gel on glass slide, the minimum time at 60°C and 65% H₂SO₄ concentration was 35 min.

So, from the above sets of experiments the optimum condition was decided as follows,

Concentration of H₂SO₄ – 65% (w/w)

Temperature- 60°C

Hydrolysis time- 35 min

4.8 Physical appearance of prepared NCC in different states

Fig.4.8. shows NCC at different state. The appearance of a stable glossy gel at is an obvious indication of the presence of NCC. The NCC powder is obtained by freeze drying exhibits white metallic luster color. Vacuum evaporation of aqueous suspensions of NCC at room temperature produces solid films with perfect optical transparency.

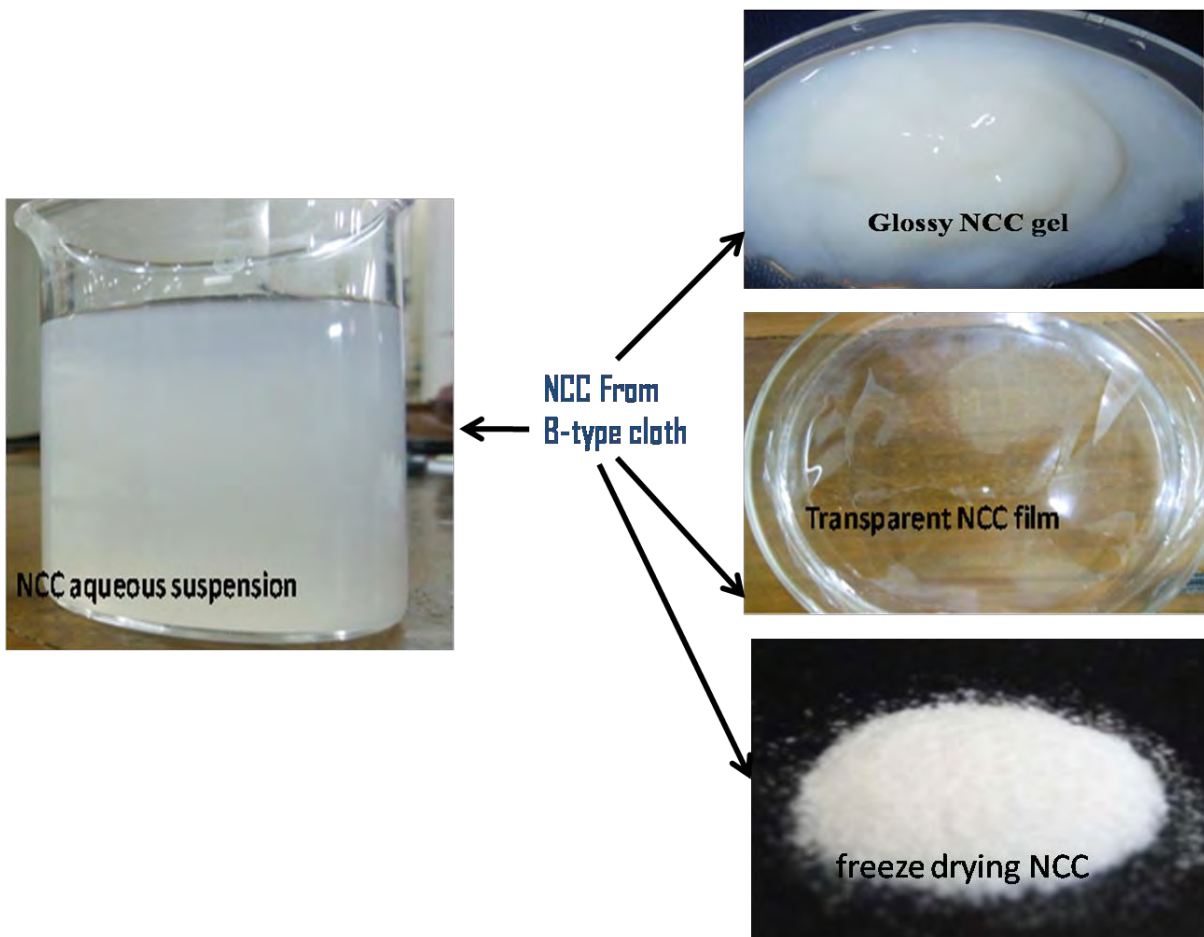


Fig.4.8. NCC at different state

4.9 Characterization of NCC prepared through H_2SO_4 hydrolysis by FESEM

A complete set of experiments were performed to examine the formation of transparent NCC without complete hydrolysis at the time of time, temperature and concentration optimization. When the concentration of H_2SO_4 was 60%, the products were white powder like commercial MCC. On the other hand, when acid concentration was 70% the product was blackish product. It might happen due to the carbonization of cellulose. These finding gave us an indication to

choose 64-65% sulfuric acid concentration for hydrolysis purpose and at this concentration the transparent gellike product formed [2]. In the same way acid to cellulose ratio, temperature of the hydrolysis and time for hydrolysis were also investigated and the results from those studies gave indication to choose the optimum condition for hydrolysis. The optimum condition of hydrolysis was carried out at 60°C temperature for 35 minutes with 65% (w/w) H₂SO₄ at the acid to cellulose ratio 20:1.

After hydrolysis, the diameter and size of fibrils of hydrolyzed cellulose was reduced to great extent due to removal of most the amorphous region of cellulosic materials leaving nano-scale cross-linked fiber like crystals. Fig. 4.9(a) shows the FESEM micrographs of a very dilute suspension of NCC, showing agglomerated 'cross-linked fiber' nanocrystals. The diameter of nanocrystals has wide range of distribution but the size of most of the 'cross-linked fiber' nanocrystals are within the range 100-300 nm in length and 10-20 nm in diameter. The compact agglomeration of CNCs shows that cellulose chains have an intermolecular hydrogen bonding and a strong hydrophilic interaction in between the cellulosic chains. From Fig. 4.9(b), the FESEM image of prepared MCC from voil cloth hydrolysis with 7.5N HCl, it can say that MCC particles were irregular shapes and their average diameter was about 10 μm and length was about 50 μm. The irregularity may be due to the presence more amorphous region in MCC compare to NCC. From the above discussion, it can be claimed that the local lignocellulosic material cotton (voile) is successfully converted into nanocrystalline cellulose.



Fig 4.9. (a) FESEM image of NCC and (b) FESEM image of MCC

4.10 Characterization of prepared NCC by FTIR

FTIR Spectroscopic studies were carried out in order to get some qualitative information on the prepared samples. The molecular structure of different samples is characterized by FTIR spectroscopy in the region of 4000-400 cm^{-1} . Figure: 4.11 illustrate the FTIR spectra of prepared NCC. The absorbance at 3343, 2911, 1647, 1320, 1166 and 1068 cm^{-1} in spectrum is associated with native cellulose. A strong band at 3,343 cm^{-1} is attributed to the stretching of hydroxyl groups. The absorption at 2,911 cm^{-1} originates from the C-H stretching. The band at 1,647 cm^{-1} arises from the H-O-H bending of the absorbed water. The peak at 1,320 cm^{-1} corresponds to the O-H bending and that at 1,166 cm^{-1} is attributed to the C-O antisymmetric bridge stretching. A strong band at 1,068 cm^{-1} is due to the C-O-C pyranose ring skeletal vibration. The small absorbance at 1320 cm^{-1} and 1427 cm^{-1} corresponding to the C-O stretching of the syringyl ring and aromatic skeletal vibrations [10], which indicate the very little present of lignin at amorphous region. In addition, the absence of a peak at 1210 cm^{-1} indicates the absence of polysaccharides [11].

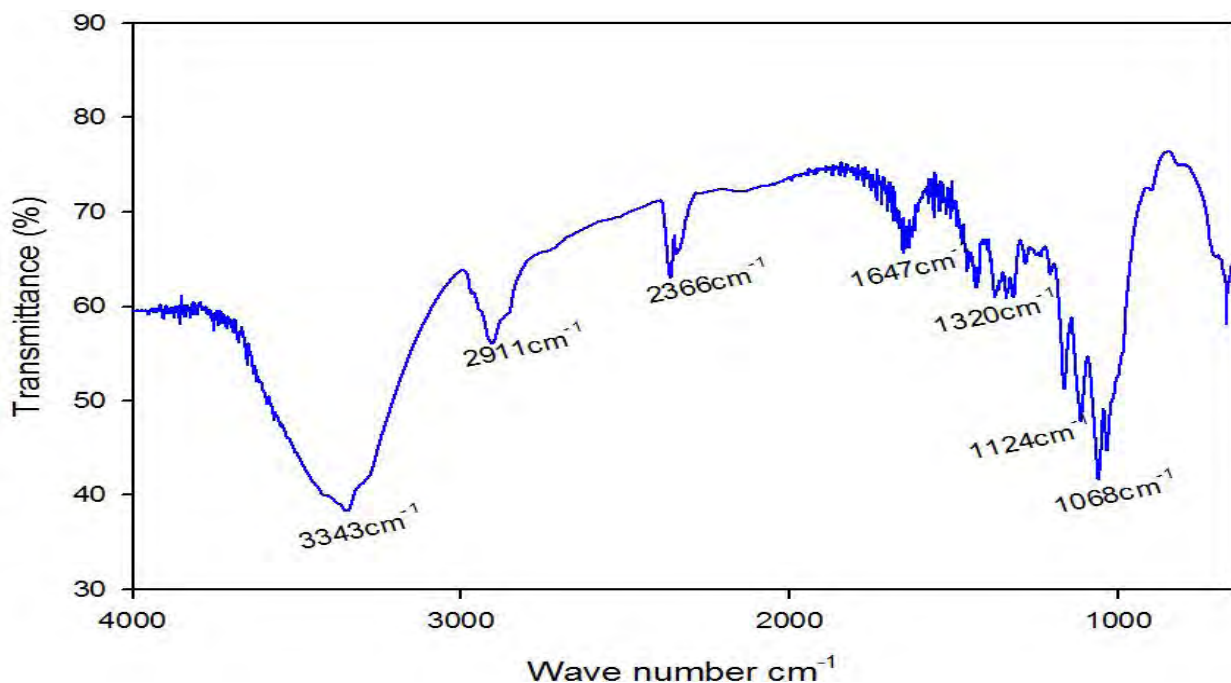


Fig. 4.10. FTIR spectrum of prepared NCC from local voile cloth.

4.11 Characterization of prepared NCC by X-ray diffraction (XRD) Analysis

An empirical method for determining the crystallinity of native cellulose was studied with an x-ray diffractometer using the focusing and transmission techniques. The influence of fluctuations in the primary radiation and in the counting and recording processes has been determined. The intensity of the 200 interference and the amorphous scatter at $2\theta = 18^\circ$, 22.5° was measured. The percent crystalline material in the total cellulose was expressed by an x-ray "crystallinity index." This was done for cotton cellulose decrystallized with aqueous solutions containing from 70% to nominally 100% ethylamine. The x-ray "crystallinity index" was correlated with acid hydrolysis crystallinity, moisture regain, density, leveling-off degree of polymerization values, and infrared absorbance values for each sample. The results indicate that the crystallinity index is a time-saving empirical measure of relative crystallinity.

The crystallinity index of the sample NCC was calculated according to amorphous subtraction method. The crystallinity of cellulose is defined as [14]

$$\text{Crystallinity} = \frac{I_{\text{cry}} - I_{\text{am}}}{I_{\text{cry}}} \times 100 (\%) \text{ -----} \quad (4.1)$$

It was the empirical method proposed by Segal *et al. in 1959* [10,15].

Here, I_{cry} is the intensity of the 200 planes reflection, typically located around $2\theta = 22.5^\circ$; I_{am} is the intensity at $2\theta = 18^\circ$, corresponding to the minimum in a diffractogram [15].

Fig:4.11. shows the height of crystalline and amorphous region total calculation of crystallinity of prepared NCC. Putting the value of I_{cry} & I_{am} in Eq. (4.1) we get the crystallinity of prepared NCC,

$$\text{Crystallinity} = \frac{2.8 - 0.2}{2.8} \times 100 = 92.85\%$$

The crystallinity is not absolute value, because the background scale of XRD-graph is not same at different analysis.

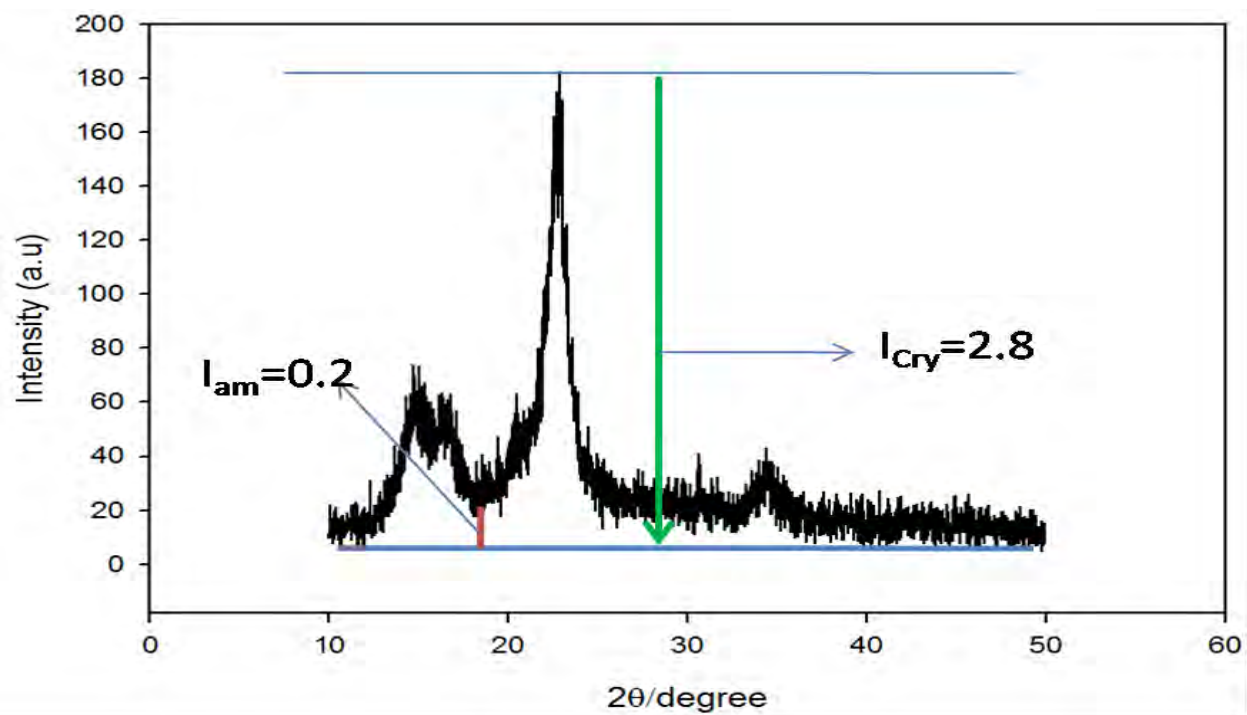


Fig. 4.11. Height of crystalline and amorphous region to calculation of crystallinity of prepared NCC

4.12 Characterization of prepared NCC by thermal stability compared with commercial MCC and prepared MCC

In Fig 4.12, the first weight loss occurred at 220-262^oC of NCC. In case of MCC, thermal degradation occurs at higher temperature within broader ranges of temperature showing higher thermal stability due to their amorphous region. On the other hand, in case of NCC, thermal degradation occurs at lower temperature within broader ranges of temperature showing lower thermal stability due to their nano-sizes and greater number of free ends in the chain of NCC, and may show drastic reduction in the molecular weight and degradation of highly sulfated amorphous regions. The weight residues for both samples are same. Here, remnant sulfate groups are responsible for the reduced thermal-stability of the nanocrystals [17] because the elimination of H₂SO₄ in sulfated anhydro-glucose units require less energy [18], therefore, sulfuric acid molecules were released at much lower temperatures during the degradation process.

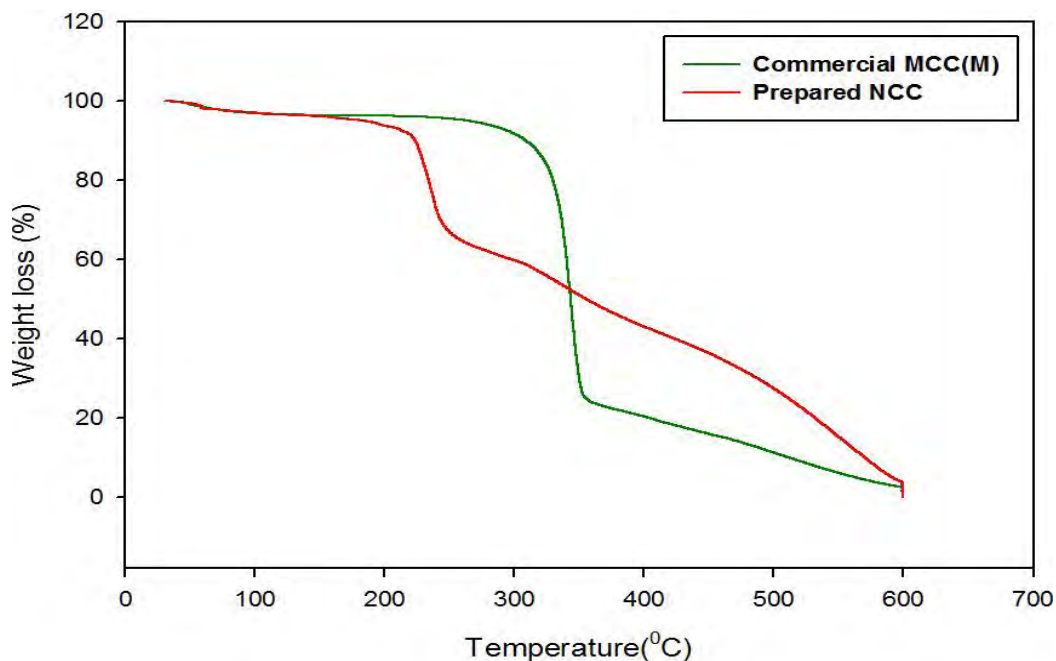


Fig.4.12. Comparison of thermogravimetry (TG) curves of commercial MCC and prepared MCC & NCC.

4.13 Transparency studies of NCC&MCC

Aqueous slurry of microcrystalline cellulose on glass slide form a nontransparent white thin layer but nanocellulose forms a transparent thin film (Fig. 4.13). Both sides were kept on a small piece of paper which was written NCC and MCC and figure bellow clearly shows NCC is transparent whereas MCC is not.

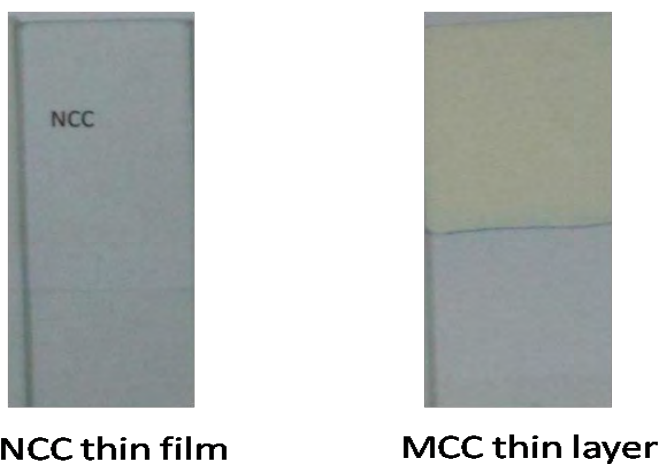


Fig. 4.13. Thin layer of NCC and MCC on glass slide

4.14. References

- [1] Bondeson, D., Mathew, A., Oksman, K., “Optimization of the isolation of nanocrystals from microcrystalline cellulose by acid hydrolysis.” *Cellulose*, 13, 171. 2006.
- [2] Beck-Candanedo, S., Roman, M., Gray, D., & Gray, G., “Effect of Reaction Conditions on the Properties and Behavior of Wood Cellulose Nanocrystal Suspensions.” *Biomacromolecules*, 6, 1048. 2005.
- [3] Araki, J., Wada, M., Kuga, S., & Okano, T., “Influence of surface charge on viscosity behavior of cellulose microcrystal suspension.” *J WoodSci*, 45(3), pp258-261. 1999.
- [4] Dong, X. M., Kimura, T., Revol, J., & Gray, D. G., “Effects of Ionic Strength on the Isotropic–Chiral Nematic Phase Transition of Suspensions of Cellulose Crystallites.” *Langmuir*, 12, 2076-2082. 1996.
- [5] Xiang, Q., Lee, Y. Y., Pettersson, P. O., & Torget, R., “Heterogeneous aspects of acid hydrolysis of alpha-cellulose.” *Applied Biochemistry and Biotechnology*, 105–108, 505–514., 2003.
- [6] Potthast, A., Rosenau, T., & Kosma, P., “Analysis of Oxidized Functionalities in Cellulose.” *Advance in Polymer Science*, 205, 1–48. 2006.
- [7] Chauhan, Y. P., Sapkal, R. S., Sapkal V. S., and Zamre. G. S., “Microcrystalline cellulose from cotton rags waste from garment and hosiery industries.” *Int. J. Chem. Sci.*: 7(2), 681-688, 2009.
- [8] Pandey, K.K., “A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy.” *J. Appl. Polym. Sci.* 1999, 71, 1969-1975.
- [9] F. Xu, R.C. Sun, Q. Lu, “Characteristics of cellulose isolated by a totally chlorine-free method from caragana korshinskii.” *J. Appl. Polym. Sci.* 101, 3251-3263. 2006.
- [10] Wada, M.; Okano, T., “Localization of I α and I β phases in algal cellulose revealed by acid treatments.” *Cellulose*, 8, 183–188. 2001.
- [11] Popescu, M.-C., Popescu, C.-M., Lisa, G.; Sakata, Y., “Evaluation of morphological and chemical aspects of different wood species by spectroscopy and thermal methods.” *J. Mol. Struct.* 988, 65–72. 2011.

- [12] Nishiyama, Y., Langan, P., & Chanzy, H., "Crystal structure and hydrogen-bonding system in cellulose I_β from synchrotron X-ray and neutron fiber diffraction." *J Am Chem Soc*, 124, 9074–9082. 2002.
- [13] Wada, M., Heux, L., & Sugiyama, "Polymorphism of cellulose I family: reinvestigation of cellulose IV." *J. Biomacromolecules*, 5, 1385-1391. 2004.
- [14] Duchemin, B., Newman, R., & Staiger, M., "Phase transformations in microcrystalline cellulose due to partial dissolution." *Cellulose*, 14, 311–320. 2007.
- [15] Gumuskaya, E., Usta, M., Kirei, H., "The effects of various pulping conditions on crystalline structure of cellulose in cotton linters." *Polym. Degrad. Stab.* 81, 559–564, 2003.
- [16] Abd-Allah, Nada, MA., Mohammed Y. El-Kady, Essams. Abd El-Sayed, and Fatma M. Amine., "Microcrystalline cellulose." *BioResources* 4(4), 1359-1371. 2009.
- [17] Dong, X. M., Revol, J. F., & Gray, D., "Effect of microcrystallite preparation conditions on the formation of colloid crystals of cellulose." *Cellulose*, 5, 19-32. 1998.
- [18] Kumar, A., Negi, Y. S., Bhardwaj, N. K., & Choudhary, V., "Synthesis and characterization of methylcellulose/PVA based porous composite." *Carbohydr. Polym.* 88, pp1364-1372. 2012.

CHAPTER 5

CONCLUSION

5. Conclusion

The white powder form microcrystalline cellulose and transparent Nanocrystalline cellulose gel were successfully prepared by hydrochloric acid hydrolysis and sulfuric acid hydrolysis, respectively, from local lignocellulosic materials.

The optimum condition for the preparation of MCC using hydrochloric acid treatment (acid to cellulose ratio: 50:1, Time -1hour) at 85°C was found as follows

Voile cloth	7.5 N
Textile cloths	
Pretreatment with NaOCl and 4% NaOH	5N
Pretreatment with NaOCl and without pretreatment with NaOH	7.5N
Wood pulp	
Pretreatment with NaOCl and 4% NaOH	5N

The optimum condition for the preparation of NCC gel using sulfuric acid (acid to cellulose ratio: 20:1) and ultrasonic treatment from **Voile cloth** was found as follows

Concentration of acid	65% (w/w)
Temperature	60°C
Hydrolysis time	35 minutes

FESEM image of MCC showed that the average diameter of microcrystals was about 10 µm and length was about 50 µm, while FESEM micrographs of NCC and showed that the diameter of nanocrystals has wide range of distribution but the size of most of the ‘cross-lined fiber’ nanocrystals lies within the range of 10-20 nm in diameter and of 100-300 nm in length.

From analysis from XRD, it was found that all the prepared sample of MCC and NCC are crystalline in nature. The thermogravimetric analysis showed the higher thermal stability of MCC as compared with NCC.