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SYNTHESIS OF NANOCELLULOSE FIBERS FROM VARIOUS NATURAL RESOURCES AND RESIDUES

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ABSTRACT

Cellulose, the world's most abundant natural, renewable, biodegradable polymer is present in a wide variety of living species includingplants, animals, and some bacteria as the main structural constituent and regaining importanceas a renewable chemical resource to replace petroleum-basedmaterials. Recently, considerable interest hasbeen directed to cellulose nanofibers because of their low thermalexpansion, high aspect ratio, strengthening effect, good mechanical and optical properties whichmay find many applications in nanocomposites, paper making,coating additives, security papers, food packaging and gas barriers. These cellulose nanofibers can be extracted from various natural resources and residues using different mechanical and chemical techniques. Although the mechanical separation of fibers into smaller elementary constituents has typically required high energy input, chemical and/or enzymatic fiber pre-treatments have been developed to overcome this problem. This report provides a comprehensive review on various methods to produce cellulose nanofibers.

Keywords: Cellulose, Cellulose nanofibers, Pre-treatments, Renewable chemical resource, Residues.

I. INTRODUCTION

The emergence of nanotechnology has provided an extensive research in recent years by intersecting with various other branches of science and forming impact on all forms of life [1].Nanotechnology is a field of science which deals with production, manipulation and use of materials ranging in nanometers. In nanotechnology, nanoparticles research is an important aspect due to its innumerable applications [2]. It has rapidly become an interdisciplinary field, and one of its exciting research areas is the isolation of nanocellulose from bioresources. Nanomaterials from cellulose and lignocelluloses play a large role in the nanotechnology field. Nanocellulose is expected to have great potential because cellulose materials are the most abundant biological raw materials and can self-assemble into well-defined architectures at multiple scales, from nano to micro size. Furthermore, cellulose is not only renewable but also a multifunctional raw material and is expected to be able to replace many non-renewable materials [3].

The development of cellulose nanofibers (CNFs) has attracted significant interest in the last few decades, due to the unique characteristics they endow such high surface area-to-volume ratio, high Young's modulus, high tensile strength and low coefficient of thermal expansion [4-6].CNFs have shown great potential in several applicationsincludingbiomedical,bioimaging,nanocomposite, gas barrier films and optically transparent functional materials [7-11].

Two general classes of cellulose nanomaterials (CNs) that can be extracted from different resources such as plant, animal, or mineral plants are cellulose nanocrystals (CNCs) and cellulose nanofibrils (CNFs). Cellulose nanocrystals can be referred as cellulose nanowhiskers (CNW) or nanocrystalline cellulose (NCC) [12, 13] while cellulose nanofibrils can be referred as nanofibrillated cellulose (NFC), or microfibrillated cellulose (MFC) depending on their size and extraction method [14].

The aim of this paper is to describe the various techniques to isolate cellulose material and to extract cellulose nanofibers from different cellulosic sources i.e. natural resources and residues. However, to put this topic in context, nanocellulose isolation from bacterial cellulose and sea animals is also discussed.

II. NATURAL RESOURCES

A natural resource is anything that people can use which comes from nature. Examples include air, water, plantsetc. From these resources natural fibers are produced by plants, animals and minerals [15]. It is important to clarify that here the focus will be on natural plant-derived fibers [16]. They are also referred to as cellulosic fibers, related to the main chemical component cellulose, or as lignocellulosic fibers, since the fibers usually often also contain a natural polyphenolic polymer, lignin, in their structure [17]. The worldwide availability of natural fibers and other abundantly accessible agro waste is responsible for the new interest in research in sustainable technology. Compared to inorganic fillers, the main advantages of lignocellulosics are listed below:

- Renewable nature.
- Wide variety of fillers available throughout the world.
- Nonfood agricultural based economy.
- Low energy consumption.
- Low cost.
- Low density.
- High specific strength and modulus.
- High sound attenuation of lignocellulosic based composites.
- Comparatively easy processability.

Pectin, proteins and extractive scan are also be found in lower quantities. However, a few natural fibers such as cotton, bacteria and algae can be free of lignin and/or hemicelluloses.The chemical composition and cell structure of natural fibers are quite complicated. Each fiber is essentially a composite in which rigid cellulose microfibrils are embedded in a soft matrix mainly composed of lignin and hemicellulose [18]. The chemical composition of natural fibers varies according to their origin. Since in the current work the Attention will be focused on the isolation of nanocellulose from natural cellulosic fibers, it is important to understand the organization and structure of cellulose within these fibers.

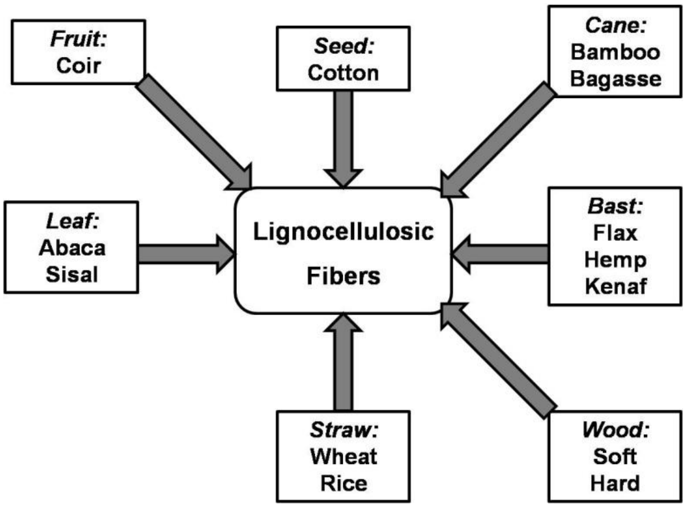

Fig. 1. Classifications of Lignocellulosic fibers.

III. CELLULOSE

Cellulose is the most abundant natural hydrophilic biopolymer composed of β-1, 4-linked anhydro-D-glucose units and having hydroxyl (-OH) groups that enable cellulose to establish strong hydrogen bonds. Major sources of cellulose are wood, cotton, hemp, flax, sisal, sugarcane bagasse (Pandanus tectorius), Phormium tenax leaf fibres, rice husk and jute etc. [13]. Cellulose is a semi-crystalline polymer while hemicellulose and lignin are amorphous polymers [20]. Plant cellulose comprises of hierarchical composite structure of nano-scale networked fibrils. Cellulose is increasingly being used for the preparation of composites with other biopolymers[21-25].

By far, the most commercially exploited natural resource containing cellulose is wood. Non-wood plant fibers such as cellulose source possessing great potential for cellulose derivatives. Other plants also contain a large amount of cellulose, including bio residue from industries and agricultural waste.Furthermore, there are non-plant sources of cellulose, for instance, cellulose produced by bacteria and tunicates. Many properties of cellulose depend on its chain length or degree ofpolymerization and the numberof glucose units that make up one polymer molecule. Individual microfibrils have a diameter rangingfrom 2 to 20 nm [27].Therefore, their isolation can be considered extensively for various high-performance applications.

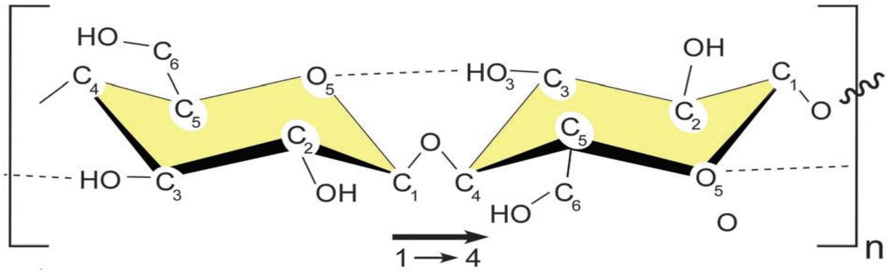

Fig. 2. Schematic of single cellulose chain repeat unit, showing the directionality of the 1-4 linkage and intrachain hydrogen bonding (dotted line). Reproduced from [26].

IV. AN OVERVIEW OF CELLULOSIC NANOMATERIALS

By either mechanical or chemical process we can obtain a wide variety of production of nanocellulose. This both methods require material purification before isolation of nanocellulose. In the next sections, the isolation methods and sources are broadly discussed.

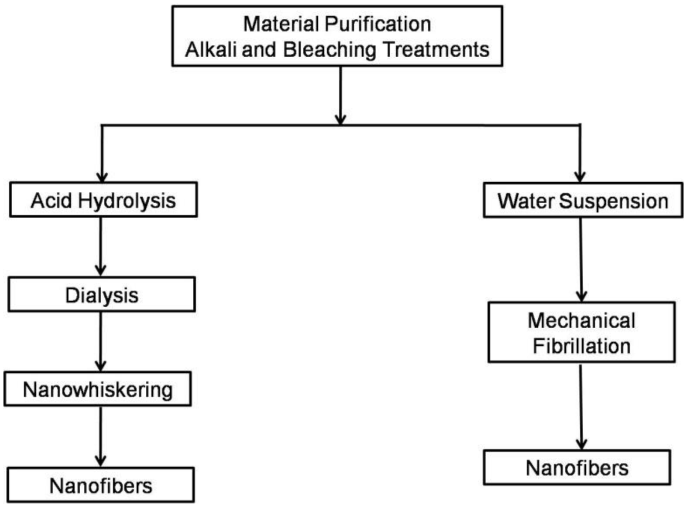

Fig. 3. Schematic of nanocellulose production routes.

4.1 Cellulose Nanofibers/Microfibrillated cellulose(CNF)

These nanofibers, mostly known as *cellulose microfibrils* by the wood science community, are found embedded in a matrix of hemicelluloses and lignin in the cell wall. In the crystalline domains, the cellulose chains are arranged in a way such that each longmolecule isconnected by hydrogen bonds to the neighboring chains forming a highly ordered crystalline form. Every molecule of these chains is made of glucose rings joined together without foldings, just as the benzene rings are joined in aramid. Even the density and the modulus of the two materials are very similar [28]. The cellulose microfibril possesses a Young’s modulus close to that of a perfect cellulose crystal,138 GPa[29], and considering that the strength of a single Kraft pulp fiber can reach a tensile strength of 1.7 GPa, the estimated tensile strength lays well beyond 2GPa.

The isolation of CNFs can beperformed by a wide variety of mechanical techniques such as refining, grinding, high pressure homogenization, cryocrushing, etc. Production of CNFs from wood pulp using homogenization was first reported in 1983[30, 31]. Thereafter, numerous investigations in this area were done [32-35]. In addition, different pretreatments can be utilized before mechanical processes in order to reduce energy consumption as well as to make the surface hydrophobic.The raw materials play a considerable role in energyconsumption during the production process, they showless impact on the characteristics of CNFs. The latter iscontrary to what happens to CNCs. In combination with a suitable matrix polymer, CNFnetworks show considerable potential as an effective reinforcement for high-quality specialty applications ofbio-based composites. Recently, because of its eminent properties such as the high strength, flexibility and aspect ratio, several groups of researchers have focused on the preparation of CNFs.

4.2. Cellulose nanocrystals (CNCs)

CNCs are needle-like cellulose particles having at least one dimension equal or lessthan 100 nm with highly crystalline nature. Various extraction processes have been used for the production of CNCs but acid-hydrolysis (H_2SO_4) is the most well-known, efficient, and widely used extraction method [5]. It has been observed that the performance of CNCs as a nano-reinforcing agent influenced with the variation of morphology and properties of these nanoparticles which depend mainly on original source of cellulose and extraction methods [4, 36 and 37].

V. SYNTHESIS TECHNIQUES OF CELLULOSE NANOFIBERS

Since there are two major structures of nanocellulose, namely cellulose nanofibers (CNFs) and cellulose nanocrystals (CNC's) which have essentially different extraction procedures, CNFs can be isolated using mechanical process such as high pressure homogenization, grinding and refining [43], whereas CNCs have been extensively isolated by using acid hydrolysis treatments [5].

5.1 Mechanical Process

5.1.1. High-Pressure Homogenization

The first mechanical treatment, which was applied by Turbaket al., in 1985, was the Gaulin homogenizer, which is still oftenused to manufacture all kinds of microfibrillated cellulose [44, 40 and 45]. A recent alternative to the Gaulin homogenizer is the microfluidizer. This equipment is increasingly being used, since it makes it possible to obtain more uniformly sized fibers.However, the application of a mechanical treatment with chambers of different sizes remains a necessary step to increase the degree of fibrillation.

The working principle of a homogenizeris that cellulose fibers are pressed through a valve at highpressure and exposed to a pressure drop to atmosphericconditions when leaving the valve, resulting in high shear forceson the fiber surface. In the case of hardwood cellulose fibers, the homogenizer was often clogged, and it was therefore necessary to remove all particles larger than 250 μm by passing the cellulose suspension through a sieve beforehomogenization. Clogging is probably due to the large particle size of the wall fragments from the vessel elements present in the hardwood fibers. Softwood cellulose suspensions could be passed directly throughthe homogenizer without clogging, and no sieving step was necessary.

High pressure homogenization (HPH) process includes passingthe cellulose slurry at high pressure into a vessel through very smallnozzle. It can be considered as an efficient method for refining of cellulosic fibers, because of high efficiency, simplicity and noneed for organic solvents. Various mechanical pretreatments are used before HPH, the series of experiments are conducted to produce nanofibers using HPH from kenaf bast fiber, core [41].

5.1.2. Grinding process

Masukoc was the first to build and sell apparatus using this approach, which is usually called a grinder. The principle consists of the breakdown of the cell wall structure owing to the shearing forces generated by the grinding stones. The pulp is passed betweena static grind stone and a rotating grind stone revolving at about 1500 rpm. The nanofibers that compose the cell wall in a multilayer structure are thus individualized from the pulp. With a higher number of passes, no significant changes were observed in the fiber morphology. It was deduced, then, that with five passes through the grinder, the fibrillation of pulp fibers was almost complete.Unlike the homogenizer process, the grinding process apparently requires fewer passes to obtain MFC.

However, this process can degrade the pulp fibers and decrease their length, which might affect the reinforcement and physical properties of MFC.

5.1.3. Cryocrushing

Another method, which is very rarely used, was proposed by [42], who carried out a cryocrushing process to produce MFC from sugar beet pulp. Cryocrushing consists of the crushing of frozen pulp with liquid nitrogen [39]. Ice crystals within the cells are then formed, and under mechanical crushing, they slash the cellular wall and release wall fragments. By [38] obtained MFC from flax, hemp, and rutabaga fibers via cryocrushing (with diameters of 5–80 nm). From [43]they applied this process to soybean stock to produce MFC with diameters in the range 50–100 nm.

5.1.4. Refining

Refining can be used as a pretreatment before HPH. This mechanical process cancause irreversible alterations in cellulosic fibers and also increases their bonding potentials [43]. Refining and homogenization at 50 MPa were applied by [45] to fibrillate nanofibers for hardwood and softwood pulps.

5.2. Chemical Processes

5.2.1. Alkali treatment of the fiber

The alkali treatment leads to more exposureof fibers tobleaching and acid hydrolysis. The optimum caustic soda treatment is both a very effective surface modification and a low cost surface treatment for fibers [45].

5.2.2. Steam explosion of the alkali treated fiber

The term used ‘steam exploded fiber’ means the alkali treatment followed by steam exploded fiber. Steam explosion technique was applied on the mercerized fiber at a pressure of 137 Pa (20 lbs) for 1 h. Steam pre-treatment is performed by loading the lignocellulosic material directly into the steam gun and treating it with high pressure steam at temperatures within 200–250 ◦C [45].

5.2.3. Bleaching treatment

Alkali treated and steam exploded samples are then subjected to bleaching. The bleaching treatment with sodium chlorite ($NaClO_2$) solution was performed to remove the remaining lignin [45].

5.2.4. Acid treatment

The bleached sample is then subjected to mild acid treatment using optimized conditions of H_2SO_4 or HCl or oxalic acid.

VI. CONCLUSIONS

“Back to Nature” is the present day notion of the modern world. The current trend is to find out new materials based on natural substances and residues. Cellulose which has been considered as a promising material for producing nanosize reinforcement fibers for a broad range of applications are extracted using different techniques from various natural sources and bioresidues. CNFs and CNCs are produced from the available techniques like mechanical and chemical treatments. Consequently, more research targeting novel, environmentally-friendly methods of extraction, as well as an understanding of the mechanism of reactions during the formation of cellulose nanofibers, is now required.

REFERENCES

[1] Baker.s. and Satish.s,"Endophytes: Toward a vision in synthesis of nanoparticles for future therapeutic arents", *Int.J.Bio-Inorg. Hybd. Nanomat.,pp:1-11.*

[2] Kavitha.K.S, syed.B, Rakshith.D, Kavitha.H.U., Yashwantha Rao H.C., Harini.B.P. and Satish.S., " plant as green source towards synthesis of nanoparticles",*Int.Res.J.Biol.Sci.,2013,pp:2-66.*

[3] Wegner TH, Jones PE Advancing cellulose-based nanotechnology. *Cellulose, 2006 13:115–118.*

[4] Eichhorn, S. J., Dufresne, A., Aranguren, M., Marcovich, N.E., Capadona, J. R., Rowan, S. J., Weder, C., Thielemans, W., Roman, M., Renneckar, S., Gindl, W., Veigel, S., Keckes, J., Yano, H., Abe, K., Nogi, M., Nakagaito, A.N., Mangalam, A., Simonsen, J., Benight, A. S., Bismarck, A., Berglund, L.A., and Peijs, T., "Review: Current international research into cellulose nanofibres and nanocomposites", *J. Mater. Sci., 2010, 45, 1-33,.*

[5] Habibi Y, Lucia LA, Rojas OJ Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev,* 2010, *110:3479–3500.*

[6] Siro´ I, Plackett D. Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose,* 2010, *17:459–494.*

[7] S. P. Dong and M. Roman, *J. Am. Chem. Soc., 2007, 129, 13810*.

[8] Siqueira G, Bras J, Dufresne A, Cellulosic bionanocomposites: a review of preparation, properties and applications. *Polymers,* 2010a, *2:728–765.*

[9] H. Fukuzumi, T. Saito, T. Wata, Y. Kumamoto and A. Isogai, *Biomacromolecules, 2009, 10, 162–165.*

[10] M. Nogi, S. Iwamoto, A. N. Nakagaito and H. Yano, *Adv. Mater., 2009, 21, 1595–1598.*

[11] H. Yano, J. Sugiyama, A. N. Nakagaito, M. Nogi, T. Matsuura, M. Hikita and K. Handa, *Adv. Mater., 2005, 17, 153–155*.

[12] Fortunati, E., Puglia, D., Monti, M., Peponi, L., Santulli, C., Kenny, J.M., and Torre, L., "Extraction of Cellulose Nanocrystals from Phormium tenax Fibres", *J. Polym. Environ, 2013,21, 319-328.*

[13] Dong, H., Snyder, J. F., Tran, D.T., and Leadore, J. L., "Hydrogel, aerogel and film of cellulose nanofibrils functionalized with silver nanoparticles", *Carbohydr. Polym, 95, 760-767, 2013.*

[14] Bledzki AK, Gassan J (1999) Composites reinforced with cellulose based fibres. *ProgPolym Sci (Oxford)24:221–274.*

[15] Mohanty AK, Misra M, Hinrichsen G (2000) Biofibres, biodegradable polymers and biocomposites: an overview.*Macromol Mater Eng 276–277:1–24.*

[16] S. J. Eichhorn, J. Sirichaisit and R. J. Young, *J. Mater. Sci., 2001,36, 3129–3135.*

[17] Panshin AJ, de Zeeuw C *Textbook of wood technology:structure, identification, properties, and uses of the commercial woods of the United States and Canada*. (Mcgraw- Hill College, New York, 1970).

[18] Akil HM, Omar MF, Mazuki AAM, Safiee S, Ishak ZAM, Abu Bakar A, Kenaf fiber reinforced composites: a review. *Mater Des, 2011, 32:4107–4121.*

[19] Kumar, A., Negi, Y. S., Bhardwaj, N. K., and Choudhary, V., "Synthesis and characterization of cellulose nanocrystals/PVA based bionanocomposite", *Adv. Mater. Lett, 2013, 4, 626-631.*

[20] Faruk, O., Bledzki, A. K., Fink, H. P., & Sain, M. (2012). Biocomposites reinforced withnatural fibers: *2000–2010. Progress in Polymer Science, 37, 1552–1596.*

[21] Jawaid, M., & Abdul Khalil, H. P. S. Cellulosic/synthetic fibre reinforced poly-mer hybrid composites: A review. *Carbohydrate Polymers,2011, 86, 1–18.*

[22] John, M. J., & Thomas, S. Biofibres and biocomposites. *Carbohydrate Polymers, 2008, 71, 343–364.*

[23] Khan, A., Huq, T., Khan, R. A., Riedl, B., & Lacroix, M. Nanocellulose-basedcomposites and bioactive agents for food packaging. *Critical Reviews in FoodScience and Nutrition, 2014, 54, 163–174.*

[24] Siqueira, G., Bras, J., &Dufresene, A. Cellulosic bionanocomposites: A reviewof preparation properties and applications. *Polymers, 2010, 2, 728–765.*

[25] Festucci-Buselli, R.A., Otoni, W.C., Joshi, C.P., Structure, Organization, and Functions of Cellulose Synthase Complexes in HigherPlants.*Brazillian Journal of Plant Physiology, 2007, 19(1).*

[26] Azizi Samir MAS, Alloin F, Dufresne A. Review of recent research into cellulosic whiskers, their properties and their application in nanocomposite field. *Biomacromolecules, 2005, 6:612–626.*

[27] Mehdi Jonoobi ,Reza Oladi , YaldaDavoudpour ,Kristiina Oksman , Alain Dufresne ,YahyaHamzeh , Reza Davoodi. Cellulose, *Springer, DOI 10.1007/s10570-015-0551-0.*

[28] Nishino, T., Takano, K., and Nakamae,K. *J. Polym. Sci., Part B: Polym.Phys., 1995, 33, 1647–1651.*

[29] Herrick FW, Casebier RL, Hamilton JK, Sandberg KR (1983) Microfibrillated cellulose: morphology and accessibility.*J Appl Polym Sci Appl PolymSymp 37:797–813.*

[30] Turbak AF, Snyder FW, Sandberg KR. Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. *J Appl Polym Sci Appl PolymSymp, 1983, 37:815–827.*

[31] Dufresne A, Dupeyre D, Vignon MR. Cellulose microfibrils from potato tuber cells: processing and characterization of starch–cellulose microfibril composites. *J Appl Polym Sci, 2000, 76:2080–2092.*

[32] Ferrer A, Filpponen I, Rodrı´guez A, Laine J, Rojas OJ Valorization of residual Empty Palm Fruit Bunch Fibers (EPFBF) by microfluidization: production of nanofibrillated cellulose and EPFBF nanopaper. *Bioresour Technol. 2012a, 125:249–255.*

[33] Lee SY, Chun SJ, Kang IA, Park JY. Preparation of cellulose nanofibrils by high-pressure homogenizer and cellulose-based composite films. *J IndEng Chem 2009a, 15:50–55.*

[34] Leitner J, Hinterstoisser B, Wastyn M, Keckes J, Gindl W. Sugar beet cellulose nanofibril-reinforced composites *Cellulose, 2007, 14:419–425.*

[35] Habibi Y, Lucia LA, Rojas OJ Cellulose nanocrystals: chemistry, self-assembly, and applications. *Chem Rev, 2010, 110:3479–3500*.

[36] Moon, R.J., Martini, A., Nairn, J., Simonsen, J., and Youngblood, J., “Cellulose nanomaterials review: structure, properties and nanocomposites”, *Chem. Soc. Rev., 2011, 40, 3941-3994.*

[37] Peng, B. L., Dhar, N., Liu, H.L., and Tam, K. C., “Chemistry and applications of nanocrystalline cellulose and its derivatives: a nanotechnology perspective”, *Can. J. Chem. Eng., 2011,89, 1191-1206.*

[38] Bhatnagar A, Sain M. Processing of cellulose nanofiber reinforced composites. *J ReinfPlast Compos, 2005, 24:1259–1268.*

[39] Chakraborty A, Sain M, Kortschot M Cellulose microfibrils:a novel method of preparation using high shear refining and cryocrushing. *Holzforschung, 2005, 59:102–107.*

[40] Iwamoto, S., Kai, W., Isogai, A., & Iwata, T. Elastic modulus of single cellulose microfibrils from tunicate measured by atomic force microscopy. *Biomacromolecules, 2009,10(9), 2571–2576.*

[41] Jonoobi M, Harun J, Shakeri A, Misra M, Oksmand K.Chemical composition, crystallinity, and thermal degradation of bleached and unbleached kenaf bast (Hibiscus cannabinus) pulp and nanofibers. *BioResources, 2009, 4:626–639.*

[42] Dufresne A, Cavaille´ JY, Vignon MR (1997) Mechanical behavior of sheets prepared from sugar beet cellulose microfibrils. *J Appl Polym Sci. 1997, 64:1185–1194*.

[43] Iwamoto S, Nakagaito AN, Yano H, Nogi M, optically transparent composites reinforced with plant fiber-based nanofibers. *Appl Phys A Mater Sci Process, 2005, 81:1109–1112.*

[44] Nakagaito AN, Yano H,The effect of morphological changes from pulp fiber towards nano-scale fibrillated cellulose on the mechanical properties of high-strength plant fiber based composites. *Appl Phys A Mater Sci Process, 2004, 78:547–552.*

[45] Eldho Abraham, B. Deepa, L.A. Pothen, J. Cintil, S. Thomas, M.J. John, R. Anandjiwala, S.S. Narine. Environmental friendly method for the extraction of coir fiber and isolation of nanofiber. *Carbohydrate polymers 92(2013) 1477-1483.*