



## Surface modification of nanocellulose: A brief overview

<sup>1</sup>Nurul Ain Nadirah Jamaluddin, <sup>2</sup>Latifah Jasmani, <sup>2</sup>Rafaedah Rusli and <sup>1</sup>Sarani Zakaria

<sup>1</sup>Bioresources and Biorefinery Laboratory, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia, Department of Chemistry, <sup>2</sup>Forest Product Division, Forest Research Institute (FRIM), 52109, Kepong, Selangor, Malaysia

### Abstract

The increased popularity in sustainable technology recently has resulted in the rapid use of renewable material in many application fields. Nanocellulose is considered as one of the alternative materials to minimize our dependency on fossil resources and has the highest potential to be green nanomaterial across various research disciplines. The tremendous level of attention from scientist to focus on nanocellulose is due to its amazing physicochemical properties such as high mechanical strength, high surface area and ease of modification. Nanocellulose is hydrophilic in nature thus can only be used in related water-based application field. Surface modification is necessary to confer functionality such as hydrophobicity on nanocellulose in order to provide extra feature as well as to broaden its use in various application industries. The ease of functionalization on nanocellulose is due to the presence of abundant hydroxyl group on its surface. This review summarizes the surface modification process that has been conducted to date which focusing on the physical and chemical modification.

**Keywords:** Nanocellulose, surface, modification, functionality

**Full length article** \*Corresponding Author, e-mail: [ainnadh@gmail.com](mailto:ainnadh@gmail.com)

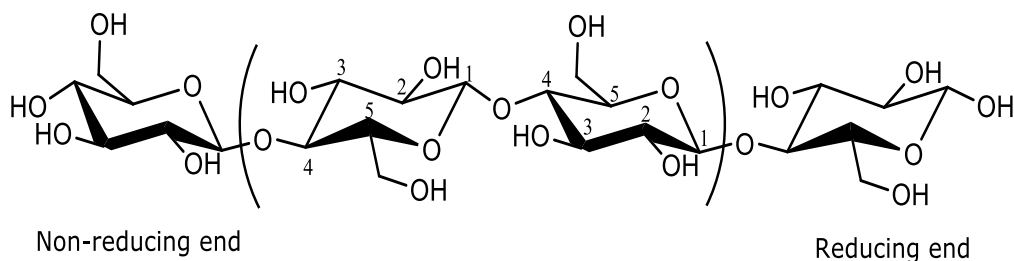
### 1. Introduction

Cellulose, the most abundant, renewable and sustainable organic material has become one of the promising materials to develop innovative products for both academic and industrial sectors as an alternative solution for environmental pollution, energy crisis and global warming. Cellulose has been utilized in various applications such as paper and packaging, food additives, personal care products, biomedical, lightweight composite for aerospace and automotive, building and construction, energy and water purification in the last 150 years [1]. It has been known for its availability, low cost, non-toxicity as well as its remarkable mechanical and physical properties such as high strength, high flexibility and stiffness, and lightweight. Due to its amazing capabilities, there are more than 700 patents on nanocellulose that have been filed in previous years by researchers and engineers [2] as well as rapid increased of scientific publication. Cellulose along with gelatin, chitin, chitosan, and starch have been revealed as the promising candidates due to its availability in nature [3]. However, among them, cellulose has long been regarded as the most abundant compound found on earth. In 2015, nanofibrillated cellulose (NFC) maintained as one of the largest segment

that accounted more than half share of the market, followed by nanocrystalline cellulose (NCC) that are widely used for packaging sector that exhibits its greatest demand, in which both nanocellulose was estimated to maintain USD 297 million for the global demand value and expected to reach USD 783 million by 2025 [4].

### 2. Cellulose

Cellulose can be extracted from various resources primarily wood, non-wood, flax, hemp cotton, algae, and marine animals. It has grown in popularity as a renewable resource to replace petroleum-based materials. Cellulose annual production is estimated to reach  $7.5 \times 10^{10}$  tons [5]. It is linear chain that is composed of  $\beta$ -D-glucopyranose units (anhydroglucose unit, AGU) that was covalently linked together. Cellobiose units are joined to form elementary fibrils, which are then bundled to produce micro-fibrils. These in turn form macro-fibrils. All chemical group (intra and intermolecular) impart cellulose its features i.e. hydrophilicity, chirality, infusibility and ease of chemical modification. The origin of cellulose and extraction process affects the degree of polymerization (DP) or number of glucose unit. Figure 1 shows the molecular formula for cellulose.

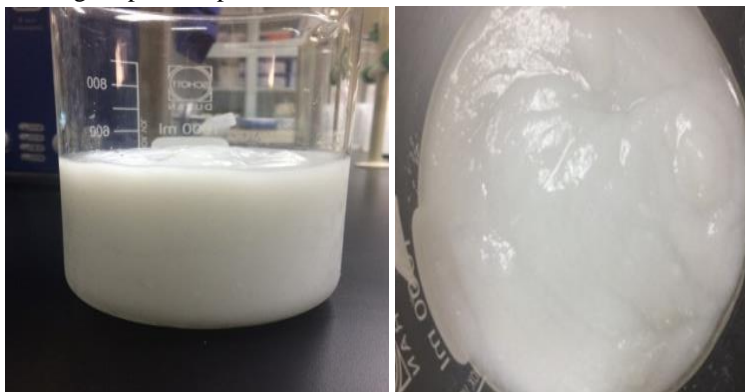


**Fig. 1:** Molecular structure of cellulose

### 3. Nanocellulose

Nanocellulose is cellulose-based material generally refers to particle having at least one of its dimension measuring from 1 to 100 nm. Earlier, the study of nanocellulose was first started in 1960s (Ranby 1951), where the nanocellulose was prepared via top-down approach from bulky cellulosic material. The study has regained more interest after 1999. Basically, there are three types of nanocellulose: nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC) and bacterial cellulose (BC). NCC and NFC are synthesized through top-down process, in

which the cellulose fibres are broken down to nanosize level while BC is produced via bottom-up approach. NCC is commonly prepared by bleached wood pulp via an acid hydrolysis using inorganic acids. As opposed to NCC, NFC is produced via mechanical methods using high pressure homogenizer, micro-fluidizer, cryocrushing and milling. The key difference of NCC and NFC is the method of extraction and their morphological structure [6][7]. BC on the other hand is synthesized extracellularly by microorganisms called *Gluconacetobacter xylinus*.



**Fig. 2:** Nanocellulose produced from *Macaranga gigantea* in suspension

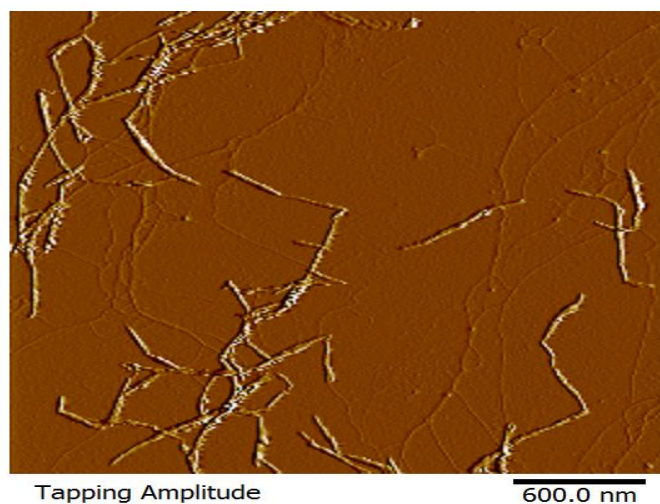
#### 3.1 Nanocrystalline cellulose (NCC)

Nanocrystalline cellulose (NCC) isolated via acid hydrolysis process also known as cellulose nanowhiskers has rod-like shape with a width of about 2-20 nm and 100-500 nm in length [8]. It consists of two regions namely amorphous and crystalline regions. The acid diffuses into the non-crystalline sections during the hydrolysis process and hydrolyzes the glycosidic link, leaving the crystals substantially intact due to their tight packing. The properties of resulting NCC strictly depend on acid concentration, acid type, reaction time and its temperature [9]. A few types of strong acid such as: hydrobromic [10], hydrochloric [11], phosphoric [12] and sulphuric acid have been used to prepare NCC. It is also best to note that mild conditions are important to avoid complete conversion of glucose.

#### 3.2 Nanofibrillated cellulose (NFC)

NFC was introduced by Turbak et al (1838) in which cellulose was produced with lateral dimensions in

nanometer through high-pressure homogenizer [13]. During the process, high shearing forces is produced, causing network of nano-fibrils to be entangled together having both crystalline and amorphous domains with 1-100 nm in diameter and 500-2000 nm in length [14]. In comparison to NCC, NFC preparation is relatively easy and straightforward, requiring just the use of mechanical disintegration techniques e.g. homogenization, micro-fluidization, and micro-grinding. Other techniques, such as high speed blending, cyro-crushing, high-intensity ultrasonication, and steam explosion. However, it was still under study and would be difficult to scale up [5]. The use of chemical via carboxy-methylation, TEMPO-mediated oxidation and enzyme as pre-treatment [15] prior to mechanical delamination is usually carried out to reduce energy consumption that limits the commercialization process [16][17]. Compared to NCC, the raw material has less influence on the properties of NFC however its effected the processing energy consumption [18].



**Fig. 3:** Atomic force microscopy (AFM) from a suspension of NFC obtained from *Macaranga gigantea* sample

### 3.3. Properties of nanocellulose

Nanocellulose has been greatly known for its unique properties; high surface area (more than  $30 \text{ m}^2\text{g}^{-1}$ ), high stiffness (220 GPa), low toxicity and lightweight. Theoretically, nanocellulose has higher tensile strength compared to cast iron which is 10 GPa and high ratio of strength to weight that is 8 times stronger than stainless steel [8]. Nanocellulose shows liquid crystalline property as it possesses birefringent behavior that gives rise to incandescent optical applications as well as possesses low coefficient thermal expansion ( $10^{-7} \text{ K}^{-1}$ ). Due to its excellent mechanical property and high optical transparency, nanocellulose has been applied in coatings and packaging field as well as substrates for optoelectronics [19]. Exceptional mechanical qualities, a high aspect ratio, and nanoscale dimension are some of the other advantages of nanocellulose [20][21].

### 4. Surface modification

Recently, there has been growing interest on nanocellulose due to its incomparable properties whenever material strength, high aspect ratio or flexibility is required. However, the hydrophilic nature of nanocellulose hinders its application in any process or product that could not use water and cannot be readily incorporated in most non-polar matrices [22]. In some cases, chemical functionalization was also carried out to target certain application [23] such as coating agent for textiles, paints and biomedical devices. Other drawbacks and challenges reported for nanocellulose include its difficulty to be characterized routinely, the gel-like structure with low solid content, high cost of production for bulk quantities, lack of standardization, agglomeration due to the strong hydrogen and moisture sensitivity [21], [24]. Modification needs to be performed under strict condition so that its crystallinity will not be affected while taking advantage of their intrinsic properties. Several modifications have been studied and tested on nanocellulose

to extend their compatibility in a diverse of matrices through physical adsorption or by chemical approach such as silylation, esterification acetylation, polymer grafting, adsorption of molecules and etc.

#### 4.1. Physical adsorption

Based on this method, the surface of cellulose nanoparticles is modified using surfactants or electrostatic interaction between an anionic substrate and cationic polyelectrolyte. These interactions with the nanocellulose are performed through electrostatic attractions, hydrophilic affinity, hydrogen bonds or van der Waals forces. The simplest technique to obtain a non-flocculated cellulose dispersion in non-polar matrices is to coat the surface of nanocellulose with surfactants. Surfactants are usually amphiphilic organic compound in which the compound contains both hydrophilic and hydrophobic group. In a study carried out by Syverud et al. the use of N-hexadecyltrimethylammonium bromide (also called cetyltrimethylammonium bromide CTAB) as a surfactant has been reported. The CTAB was later dissolved in water and deposited on a film [25][26]. As a result, it was discovered that the adsorbed layer of CTAB increased its hydrophobicity without degrading its mechanical properties. In another study, NCC was surface modified with four different types of quarternary ammonium cation surfactants with extended alkyl, glycidyl, phenyl and diallyl group. According to the findings, quarternary ammonium salts with  $\text{C}_{18}$  alkyl chains result in a significant increase in contact angle, as well as the ability to produce well-dispersed nanocomposites with non-polar polymers [27]. A number of studies have been conducted by several authors in employing quaternary ammonium salt for surface modification [26][28]. Recently, natural surfactant, rarasponins (RS) was attached on NCC from bamboo shoots to increase its hydrophobicity. The ability RS-modified NCC to disperse in THF confirmed the successful conversion of hydrophilic NCC to hydrophobic nanocrystals [29]. Beside

using surfactants, research has been carried out focusing on electrostatic interactions in which tailor-made block copolymer has been achieved, containing quarternized poly (dimethylaminomethylmethacrylate) (PDMAEMA) block [30], PDMAEMAb-polycaprolactone (PCL), poly(1,2-butadiene) (PB)-b-Qpdmaema, poly(di-ethylene glycol) methyl ether methacrylate) (PDEGMA) [30] or a poly((acrylamidopropyl)trimethylammonium chloride) (PAPTAC) block [31]. Cationic latexes have also been explored for their ability to modify nanocellulose. Past research has been conducted on core-shell latex particles with varying compositions of styrene, n-butyl acrylate, methyl methacrylate and etc. proved its efficiency in increasing the hydrophobicity as well as adsorption of cellulose fibers and incorporation into a polypropylene based-biocomposites [32].

#### 4.2. Chemical modification

Polymer grafting is another method that gain the interest of most researchers since it improves hydrophobicity while also forming enormous physical entanglements on the polymer-NCC phase interphase as well as providing better compatibility in the target polymer and improving target polymer compatibility [33]. For instance, the synthesis of NCC and poly-L-lactic acid (PLLA) via in-situ ring open polymerization (ROP), lead to hydrophobic PLLA-grafted-NCC and free PLLA homopolymer. The resulting hydrophobic NCC makes the process of incorporation of other polymer much easier which lead enhancement of nanocellulose-polymer property. In particular, properties such as interfacial and oxygen barrier were also improved [34].

This type of modification consists of two types of route: 'grafting from' and 'grafting to'. 'Grafting from' indicate that the monomers are being polymerized directly from the surface of nanocellulose. According to Lönnberget al. (2008), the polymer chains are formed by in situ surface initiated polymerization from immobilized initiators on the substrate [35]. Here, cellulosic nanoparticles are combined with monomer and initiator agent to induce polymerization of the monomer from the nanoparticle surface. Based on this route, high grafting density is obtained as the viscosity of the medium is low resulting to less steric hindrance effect. The only problem that need to be encountered is its difficulty to control (in terms of the length of the polymer chains and polydispersity) and to determine the molecular weight of the grafted polymer due to low degree of polymerization and quantity of homo-polymer (non-grafted) [23]. Past attempts on this type of route have been conducted by Peltzer et al. (2013) [36], in which they used L-lactide by ring-opening polymerization (ROP) method. However, at high concentrations, their optical changes change from an isotropic to anisotropic chiral nematic liquid crystalline phase leading to birefringent phenomenon. Other examples include the research on grafting microfibrillated *Jamaluddin et al., 2021*

cellulose (MFC) with poly( $\epsilon$ -caprolactone) (PCL) [37] and grafting of PCL polymer onto the surface of NCC by Sn(Oct)<sub>2</sub>-catalyzed-ROP [38]. Apart from ROP, another approach involving radical polymerization are atom transfer radical polymerization (ATRP) [39][40] and single-electron transfer living radical polymerization (SET-LP) [41].

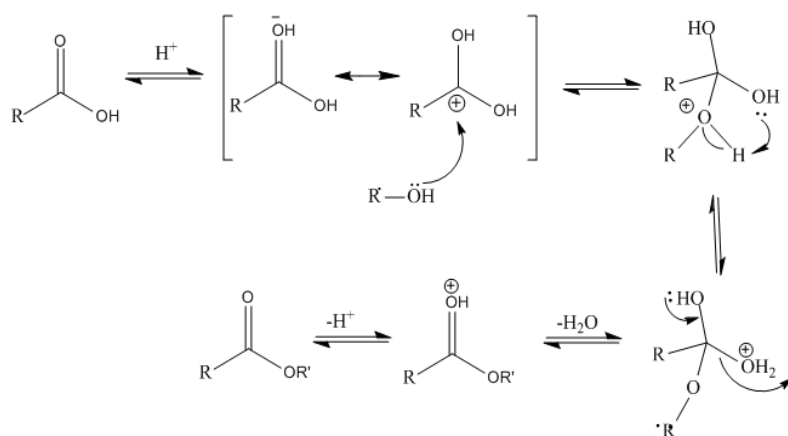
Grafting onto' means that the polymers are covalently attached on the surface of the nanocellulose instead of the monomer with the presence of coupling agent. In this process, the chance to get high grafting density is quite low due to the steric hindrance induced by the polymeric chains in which it has to diffuse through the layer of already attached brushes to reach the available reactive sites at the surface as well as the high viscosity of the reaction medium in the presence of macromolecular chains [23]. The nature of the produced material is fully controlled since the molecular weight of the polymer is determined before the grafting process, and the reaction and product purification procedures are both economical and efficient.

Covalent modification generally involves esterification (acetylation, butyration and palmitoylation), carbonylation, amidation and silylation. Owing to its simple and straightforward reaction, esterification has been widely studied. Among all esterification process, acetylation has been considered as one of the best methods to modify the hydrophilicity of cellulose fibers as it helps in reducing the absorption of moisture in fibers [35]. Originally, acetylation process is applied to wood cellulose [35], later, it was observed that pre-treating nanocellulose with acetic anhydride modified the surfaces by replacing the polymer hydroxyl group with an acetyl group.

Bulota et al. (2012) for instance, conducted an acetylation process employing acetic anhydride against isolated NFC, claiming that nanofibers with a higher degree of substitution influenced the poly-lactic acid-acetylated NFC properties such as mechanical and tensile strength [42]. Other than acetic anhydride, succinic anhydride, vinyl stearate, vinyl acetate and vinyl acrylate also have been used through transesterification in N,N-dimethylacetamide (DMAc) using lipase from *Pseudomonas cepacia* [43]. Esterification was prepared in another work using an iodine-catalyzed, single-step, solvent-free esterification process [44]. The acetylated crystalline nanocellulose (Ac-NCC) was reinforced in epoxy (EPON 828) resin with Epikure 3140 as a hardener to create the epoxy nanocomposite. To confirm Ac-NCC hydrophobicity, the dispersibility and contact angle measurements of NCC were performed. According to the findings, the Ac-NCC was well disseminated in most of the organic solvents, with no evidence of sedimentation over time. It forms transparent solution in ethanol, ethyl acetate, toluene, DMSO and acetone and formed white flocculent which settles as precipitate when DMF is added. Apart from dispersion in solvent, contact angle result showed an exceptional

hydrophobicity of 76.54 to 88.78°. The morphological and integrity of the cellulose during the high degree of

esterification was maintained and confirmed via TEM and XRD observation.



**Fig. 4:** Esterification method of nanocellulose

Silylation is another method performed for hydrophobic surface modification [45]. In these study, silylation was conducted using various quantities of methyltrimethoxysilane-sols and as a result, the silylated sponges exhibit hydrophobic (contact angle reading increased by 20°) and oleophilic properties. The hydrophobic sponge was then used to remove dodecane spills from water surface.

Covalent grafting is another known method that has been conducted by researcher to modify the surface of nanocellulose through chemical. The term 'Sol-React' was first named by Domenek et al. (2014) [46]. In this study, solvent-free esterification of cellulose is investigated with carboxylic acid act as grafting agent and solvent media. Phenylacetic acid and hydrocinnamic acid was tested and subjected to a closed distillation system and heated above its melting point for 20 hours. Results from the XRD showed that only a slight decrease of crystallinity (less than 10%) was observed which could be attributed due to the acid environment and high temperature used throughout the esterification process [47]. Apart from that, XPS results evidently proved the presence of ester group formed during esterification process between carboxylic acid and the hydroxyls on the NCC surface. The contact angle was reported in the range of 75-80°. Berlioz et al. (2009) have previously investigated the solvent-free gas-phase esterification of palmitoyl chloride [48]. However, this strategies lead to drying process which favor agglomeration thus limits their application in which redispersion is required. Covalent grafting using rosin was also reported for surface modification of cellulose [49]. Based on this method, it is fascinating to highlight, the in situ solvent exchange by evaporation process of water in the esterification method does not lead to drying of NCC which could cause aggregation as moderate reaction temperature is

proposed, 130°. TGA result showed, the surface modification of nanocellulose affected the thermal stability, as proven by [28] due to presence of corrosive species upon heating most likely due to the presence of thiol and bromine moieties and consequently accelerated the process of degradation of cellulose. Niu et al. (2018) adopted the same approach using rosin as a grafting agent and solvent media but in nitrogen ambient and longer stirring time [50]. Based on the research, the modified NFC increased its hydrophobicity, improved its dispersion in PLA matrix and also increased in mechanical properties.

Shang et al. (2012) has conducted a novel approach in which it uses castor oil (CO), a natural vegetable oil to modify the surface of nanocellulose [51]. This study was carried out to functionalize the surface of nanocellulose with hydrophobic group from easily available vegetable oil. The success of grafting was confirmed by the increased change of contact angle which increased from 44.60° to 96.85°. The modified nanocellulose was analysed with FTIR, <sup>13</sup>C-NMR and XPS to further prove the surface modification by castor oil. Based on TEM result, morphology of the cellulose was essentially preserved. However, this particular method involved many steps and required a lot of solvent. Another study concerned on urethanization that involves the reaction between isocyanate and the hydroxyl group on the surface of the nanocellulose that lead to the formation of covalent bonds (urethanization linkage). In this study, the modification was performed using n-octadecyl isocyanate (C<sub>18</sub>H<sub>37</sub>NCO) using two different methods in which one of its consists of an in-situ solvent exchange [52]. It was found that the hydrophobicity of nanocellulose was enhanced and dispersibility in organic solvent improved.

A simple method for hydrophobic surface modification of NCC was conducted in which dodecyl-trimethylsilane (DTMOS) act as a silanation modifier was

grafted on the NCC through two step using KH560 (7-(2,3-epoxypropyl) propyltrimethoxysilane as a linker. It is reported that its water contact angle increase from 0° to 140° as well as enhanced its thermal stability compared to the unmodified NCC [53].

### 5. Application of surface modified nanocellulose

For the past few years, nanocellulose has been widely studied in many fields such as coatings, optical films, pulp and paper, electronic devices, pharmaceuticals, food and cosmetics additives etc. However, due to its hydrophilicity attribute, certain application might be limited. Thus, surface modification is necessary to broaden its applicability in different fields.

Modified nanocellulose has been contributing in nanocomposites area in which it helps in preventing separation problem between reinforcement and matrix and avoids the usage of a large amount of additives [34]. The high surface area to volume ratio of nanocellulose as well as its non-toxic behavior, has been useful in medical applications such as tissue engineering, bone implant and as drug delivery carrier [54].

Recently, hydrophobic nanocellulose also has been studied as water repellent paper for printable paper and packaging [55], water purification, oil absorbents, biotechnological and also electrical and electronic devices such as dielectric material [56]. Due to its hydrophobic behavior, nanocellulose are best suit in coating activity for marine equipment such as offshore rig, jetties and watercraft which can help in reducing wetting behavior that may minimize the attack from marine organism and corrosion [57].

### Conclusions

Nanocellulose is perceived as one of the most fascinating, biodegradable, renewable and sustainable polymer due to its inherent properties. A lot of studies have been conducted by researchers and engineers to address its capabilities in diverse field and area to be utilized as a precursor to minimize global warming as well as for the conservation of environment. This reviews, provided an overview to alter the surface of nanocellulose using two types of pathway, physical and chemical modification in which both focused to modify its hydrophilicity properties. Surface modification i.e. Hydrophobization is able to widen the application of nanocellulose not only in polar solvents but also in non-polar matrices.

### Acknowledgements

The authors would like to acknowledge the funding from Ministry of Higher Education (MOHE) through Fundamental Research Grant Scheme (FRGS) (FRGS/1/2019/WAB07/NRE/02/1) and technical assistance from Pulp and Paper Branch staff, FRIM.

### References

- [1] S. Afrin, Z. Karim (2017). Isolation and surface modification of nanocellulose: Necessity of enzymes over chemicals. *Chem Bio Eng Reviews*. 4(5): 289-303.
- [2] A.W. Carpenter, C.F. de Lannoy, M.R. Wiesner, (2015). Cellulose nanomaterials in water treatment technologies. *Environmental Science and Technology*. 49(9): 5277-5287.
- [3] D. Trache, M.H. Hussin, M.M. Haafiz, V.K. Thakur (2017). Recent progress in cellulose nanocrystals: sources and production. *Nanoscale*. 9(5): 1763-1786.
- [4] R.S. Baghel, C.R.K. Reddy, R.P. Singh (2021). Seaweed-based cellulose: Applications and future perspectives. *Carbohydrate Polymers*. 267: 118241.
- [5] Habibi, Y (2014). Key advances in the chemical modification of nanocelluloses. *Chemical Society Reviews*. 43(5): 1519-1542.
- [6] M. Jonoobi, R. Oladi, Y. Davoudpour, K. Oksman, A. Dufresne, Y. Hamzeh, R. Davoodi (2015). Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: a review. *Cellulose*. 22(2): 935-969.
- [7] Xu, X., Liu, F., Jiang, L., Zhu, J.Y., D. Haagenson, D.P. Wiesenborn (2013). Cellulose nanocrystals vs. cellulose nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents. *ACS Applied Materials and Interfaces*. 5(8): 2999-3009.
- [8] P. Phanthong, P. Reubroycharoen, X. Hao, G. Xu, A. Abudula, G. Guan (2018). Nanocellulose: Extraction and application. *Carbon Resources Conversion*. 1(1): 32-43.
- [9] N. Lavoine, L. Desloges, A. Dufresne, J. Bras (2012). Microfibrillated cellulose—Its barrier properties and applications in cellulosic materials: A review. *Carbohydrate polymers*. 90(2): 735-764.
- [10] B.L. Carpenter, E. Feese, H. Sadeghifar, D.S. Argyropoulos, R.A. Ghiladi (2012). Porphyrin-cellulose nanocrystals: a photo-bactericidal material that exhibits broad spectrum antimicrobial activity. *Photochemistry and Photobiology*. 88(3): 527-536.
- [11] J. Araki, M. Wada, S. Kuga, T. Okano (1999). Influence of surface charge on viscosity behavior of cellulose microcrystal suspension. *Journal of Wood Science*. 45(3): 258-261.
- [12] S. Camarero Espinosa, T. Kuhnt, E.J. Foster, C. Weder (2013). Isolation of thermally stable cellulose nanocrystals by phosphoric acid hydrolysis. *Bio-macromolecules*. 14(4): 1223-1230.

- [13] A.F. Turbak, F.W. Snyder, K.R. Sandberg (1983). Microfibrillated cellulose, a new cellulose product: properties, uses, and commercial potential. *J. Appl. Polym. Sci.: Appl. Polym. Symp.* 37, 815
- [14] O. Nechyporchuk, M.N. Belgacema, Bras, J. (2016). Production of cellulose nanofibrils: A review of recent advances. *Industrial Crops and Products.* 93: 2-25.
- [15] M.N. Angles, A. Dufresne (2000). Plasticized starch/tunicin whiskers nanocomposites. 1. Structural analysis. *Macromolecules.* 33(22): 8344-8353.
- [16] M. Ioelovich (2017). Characterization of various kinds of nanocellulose. *Handbook of nanocellulose and cellulose nanocomposites.* 1: 51-100.
- [17] L. Siró, D. Plackett (2010). Microfibrillated cellulose and new nanocomposite materials: a review. *Cellulose.* 17(3): 459-494.
- [18] K. Missoum, M.N. Belgacem, J. Bras (2013). Nanofibrillated cellulose surface modification: a review. *Materials.* 6(5): 1745-1766.
- [19] T. Abitbol, A. Rivkin, Y. Cao, Y. Nevo, E. Abraham, T. Ben-Shalom, O. Shoseyov (2016). Nanocellulose, a tiny fiber with huge applications. *Current opinion in biotechnology.* 39: 76-88.
- [20] S.J. Eichhorn (2011). Cellulose nano-whiskers: promising materials for advanced applications. *Soft Matter.* 7(2): 303-315.
- [21] R.J. Moon, A. Martini, J. Nairn, J. Simonsen, J. Youngblood (2011). Cellulose nanomaterials review: structure, properties and nanocomposites. *Chemical Society Reviews.* 40(7): 3941-3994.
- [22] M. Mariano, C. Chirat, N. El Kissi, A. Dufresne (2016). Impact of cellulose nano-crystal aspect ratio on crystallization and reinforcement of poly (butylene adipate-co-terephthalate). *Journal of Polymer Science Part B: Polymer Physics.* 54(22): 2284-2297.
- [23] G. Morandi, W. Thielemans (2012). Synthesis of cellulose nanocrystals bearing photo-cleavable grafts by ATRP. *Polymer Chemistry.* 3(6): 1402-1407.
- [24] L. Siró, D. Plackett (2010). Micro-fibrillated cellulose and new nanocomposite materials: A review. *Cellulose.* 17(3): 459-494.
- [25] J. Chuan, Y. Li, L. Yang, X. Sun, Q. Zhang, T. Gong, Z. Zhang (2013). Enhanced rifampicin delivery to alveolar macrophages by solid lipid nanoparticles. *Journal of Nanoparticle Research.* 15(5): 1-9.
- [26] K. Xhanari, K. Syverud, G. Chinga-Carrasco, K. Paso, P. Stenius (2011). Reduction of water wettability of nano-fibrillated cellulose by adsorption of cationic surfactants. *Cellulose.* 18(2): 257-270.
- [27] M. Salajková, L.A. Berglund, Q. Zhou (2012). Hydrophobic cellulose nano-crystals modified with quaternary ammonium salts. *Journal of Materials Chemistry.* 22(37): 19798-19805.
- [28] A. Boujemaoui, S. Mongkhontreerat, E. Malmström, A. Carlmark (2015). Preparation and characterization of functionalized cellulose nanocrystals. *Carbohydrate Polymers.* 115: 457-464.
- [29] C.J. Wijaya, S. Ismadji, H.W. Aparamarta, S. Gunawan (2020). Hydrophobic modification of cellulose nanocrystals from bamboo shoots using rarasaponins. *ACS omega.* 5(33): 20967-20975.
- [30] E. Larsson, C.C. Sanchez, C. Porsch, E. Karabulut, L. Wågberg, A. Carlmark (2013). Thermo-responsive nano-fibrillated cellulose by polyelectrolyte adsorption. *European Polymer Journal.* 49(9): 2689-2696.
- [31] J. Engström, F.L. Hatton, L. Wågberg, F. d'Agosto, M. Lansalot, E. Malmström, A. Carlmark (2017). Soft and rigid core latex nanoparticles prepared by RAFT-mediated surfactant-free emulsion polymerization for cellulose modification—a comparative study. *Polymer Chemistry.* 8(6): 1061-1073.
- [32] Y. Pan, H. Xiao, Y. Zhao, Z. Wang (2013). CTMP-based cellulose fibers modified with core-shell latex for reinforcing biocomposites. *Carbohydrate Polymers.* 95(1): 428-433.
- [33] L. Zhou, H. He, M.C. Li, S. Huang, C. Mei, Q. Wu (2018). Grafting poly-caprolactone diol onto cellulose nanocrystals via click chemistry: enhancing thermal stability and hydrophobic property. *Carbohydrate Polymers.* 189: 331-341.
- [34] .C. Miao, W.Y. Hamad (2016). In-situ polymerized cellulose nanocrystals (CNC)—poly (l-lactide)(PLLA) nanomaterials and applications in nanocomposite processing. *Carbohydrate Polymers.* 153: 549-558.
- [35] M.T. Islam, M.M. Alam, M. Zoccola (2013). Review on modification of nanocellulose for application in composites. *International Journal of Innovative Research in Science, Engineering and Technology.* 2(10): 5444-5451.
- [36] M. Peltzer, A. Pei, Q. Zhou, L. Berglund, A. Jiménez (2014). Surface modification of cellulose nanocrystals by grafting with poly (lactic acid). *Polymer International.* 63(6): 1056-1062.
- [37] H. Lönnberg, L. Fogelström, M.A.S.A Samir, L. Berglund, Malmström, E. and Hult, A. (2008). Surface grafting of microfibrillated cellulose with poly ( $\epsilon$ -caprolactone)—Synthesis and characterization. *European Polymer Journal.* 44(9): 2991-2997.

- [38] Y. Habibi, A.L. Goffin, N. Schiltz, E. Duquesne, P. Dubois, A. Dufresne (2008). Bio-nano-composites based on poly ( $\epsilon$ -caprolactone)-grafted cellulose nanocrystals by ring-opening polymerization. *Journal of Materials Chemistry*. 18(41): 5002-5010.
- [39] A. Carlmark, E. Malmström (2002). Atom transfer radical polymerization from cellulose fibers at ambient temperature. *Journal of the American Chemical Society*. 124(6): 900-901.
- [40] D. Nyström, J. Lindqvist, E. Östmark, A. Hult, E. Malmström (2006). Superhydrophobic bio-fibre surfaces via tailored grafting architecture. *Chemical Communications*. (34): 3594-3596.
- [41] A. Dufresne (2013). Nanocellulose: a new ageless bionanomaterial. *Materials Today*. 16(6): 220-227.
- [42] K.H. Hong, K.W. Oh, T.J. Kang (2005). Preparation of conducting nylon-6 electrospun fiber webs by the in situ polymerization of polyaniline. *Journal of Applied Polymer Science*. 96(4): 983-991.
- [43] B. Thomas, M.C. Raj (2018). Nanocellulose, a versatile green platform: From biosources to materials and their applications. *Chemical Reviews*. 118: 11575-11625.
- [44] E. Abraham, Y. Nevo, R. Slattegard, N. Attias, S. Sharon, S. Lapidot, O. Shoseyov (2016). Highly hydrophobic thermally stable liquid crystalline cellulosic nanomaterials. *ACS Sustainable Chemistry and Engineering*. 4(3): 1338-1346.
- [45] Z. Zhang, G. Sèbe, D. Rentsch, T. Zimmermann, P. Tingaut, (2014). Ultralightweight and flexible silylated nanocellulose sponges for the selective removal of oil from water. *Chemistry of Materials*. 26(8): 2659-2668.
- [46] E. Espino-Pérez, S. Domenek, N. Belgacem, C. Sillard, J. Bras (2014). Green process for chemical functionalization of nanocellulose with carboxylic acids. *Biomacromolecules*. 15(12): 4551-4560.
- [47] M.F. Rosa, E.S. Medeiros, J.A. Malmonge, K.S. Gregorski, D.F. Wood, L.H.C. Mattoso, S.H. Imam (2010). Cellulose nano-whiskers from coconut husk fibers: Effect of preparation conditions on their thermal and morphological behavior. *Carbohydrate Polymers*. 81(1): 83-92.
- [48] S. Berlioz, S. Molina-Boisseau, Y. Nishiyama, L. Heux (2009). Gas-phase surface esterification of cellulose micro-fibrils and whiskers. *Biomacromolecules*. 10(8): 2144-2151.
- [49] D.O. de Castro, J. Bras, A. Gandini, N. Belgacem (2016). Surface grafting of cellulose nanocrystals with natural antimicrobial rosin mixture using a green process. *Carbohydrate Polymers*. 137: 1-8.
- [50] X. Niu, Y. Liu, Y. Song, J. Han, H. Pan (2018). Rosin modified cellulose nanofiber as a reinforcing and co-antimicrobial agents in polylactic acid/chitosan composite film for food packaging. *Carbohydrate Polymers*. 183, 102-109.
- [51] W. Shang, J. Huang, H. Luo, P.R. Chang, J. Feng, G. Xie (2013). Hydrophobic modification of cellulose nano-crystal via covalently grafting of castor oil. *Cellulose*. 20(1): 179-190.
- [52] G. Siqueira, J. Bras, A. Dufresne (2010). New process of chemical grafting of cellulose nanoparticles with a long chain isocyanate. *Langmuir*. 26(1): 402-411.
- [53] W. Lin, X. Hu, X. You, Y. Sun, Y. Wen, W. Yang, H. Chen (2018). Hydrophobic modification of nano-cellulose via a two-step silanation method. *Polymers*. 10(9): 1035.
- [54] S. Tortorella, V.V. Buratti, M. Maturi, L. Sambri, M.C. Franchini, E. Locatelli (2020). Surface-modified nanocellulose for application in biomedical engineering and nanomedicine: A review. *International Journal of Nanomedicine*. 15: 9909.
- [55] H. Ogihara, J. Xie, J. Okagaki, T. Saji (2012). Simple method for preparing super-hydrophobic paper: spray-deposited hydrophobic silica nanoparticle coatings exhibit high water-repellency and transparency. *Langmuir*. 28(10): 4605-4608.
- [56] M. Kaushik, A. Moores (2016). Nano-celluloses as versatile supports for metal nano-particles and their applications in catalysis. *Green Chemistry*. 18(3): 622-637.
- [57] P. Panchal, E. Ogunsona, T. Mekonnen (2019). Trends in advanced functional material applications of nanocellulose. *Processes*. 7(1): 10.