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NANOCELLULOSE: VERSATILE AND AGELESS BIOPOLYMER FOR THE FUTURE

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INTRODUCTION

Cellulose is the world's most abundant and sustainable organic compound (ACS 2009). Cellulose can be extracted primarily from wood (hardwood and softwood) and non-wood (flax, kenaf, bamboo, cotton etc.) and also to some extent algae and marine animals (tunicate). Cellulose is a linear, semicrystalline polysaccharide and macromolecule that consists of 1000-30000 chains of glucose monomers. It has been one of the most studied biopolymers to tackle issues and challenges related to material biodegradability, renewability, energy and cost. Cellulose availability is estimated to reach one trillion tonnes (Klemm et al. 2005) and this numbers keep on increasing as it is renewable in nature as a result of biosynthesis. Cellulose has been recognised for years as a source of energy, building and clothing material possessing properties such as low price, low density and high strength. Derivatives of cellulose have also been used for coatings, films, membranes, new building materials, pharmaceuticals and food products. It has been used for a long time to strengthen polymer mainly due to economic and environmental issues. It is polysaccharide with molecular formula of $C_6H_{10}O_5$ and molecular weight of 162.1406 g/mol per glucose unit. Figure 1 shows the molecular structure of cellulose.

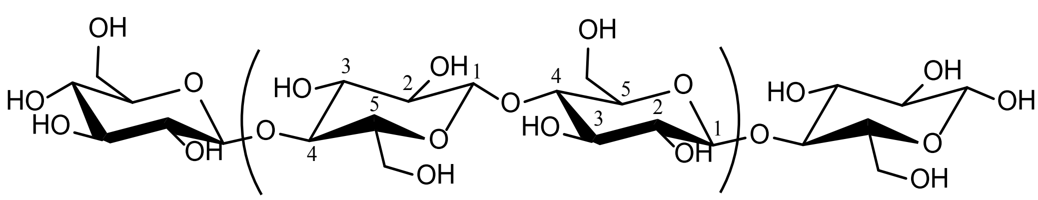

Figure 1 Molecular structure of cellulose. (Source: Borjesson & Westman 2015)

Nanocellulose on the other hand is cellulose at nanosized level. The difference between cellulose and nanocellulose is regarding the dimension in which nanocellulose has at least one of its dimensions measuring from 1 to 100 nm (1 nanometer is equivalent to $1x10^{-9}$ meter). It has received tremendous level of attention nowadays due to the increased demands for high value added and high performance materials. Nanocellulose possesses remarkable mechanical and physical properties due to its unique structure. Nanocellulose consists of two parts: highly crystalline structure (ordered part) and amorphous regions (disordered part). Crystalline part contributes to high stiffness and strength while amorphous region bring flexibility to the bulk material. Nanocellulose consists of three types namely nanocrystalline cellulose (NCC), nanofibrillated cellulose (NFC), and bacterial nanocellulose (BNC).

Nanocellulose is commonly prepared from bleached wood pulp. The properties of nanocellulose (NCC and NFC) such as morphology and crystallinity depend on the method of extraction and their source (Abitbol et al. 2016). NCC is extracted mainly by acid hydrolysis using sulphuric acid (H_2SO_4) under strictly controlled hydrolysis condition. Sulphuric acid has been the most utilized acid for preparation of NCC, but the use of other acids such as hydrochloric acid and bromic acid has also been reported.

During hydrolysis, acid hydrolyses the amorphous part of the cellulose chain leaving the crystalline region intact. NCC has been reported to have crystallinity between 54 to 88 %. It has a short rod-like shape with 2-20 nm diameter and 100-500 nm in length. Schematic diagram of NCC which was extracted from cellulose fibrils by acid hydrolysis is shown in Figure 2.

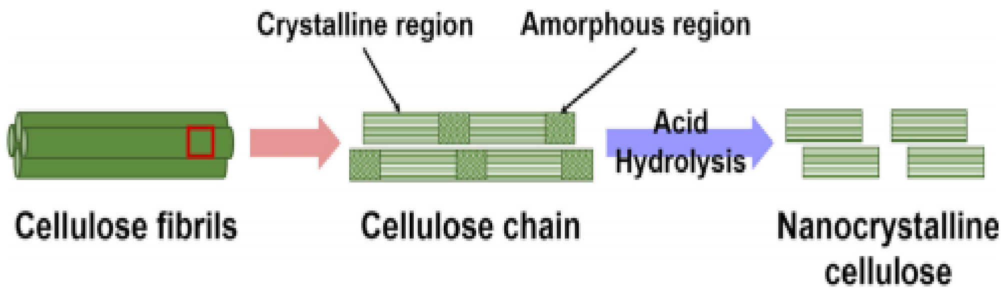

Figure 2 Schematic diagram of nanocrystalline cellulose (NCC). Source: (Phanthong et al. 2018)

The morphology of NCC is commonly determined using transmission electron micrographs (Figure 3).

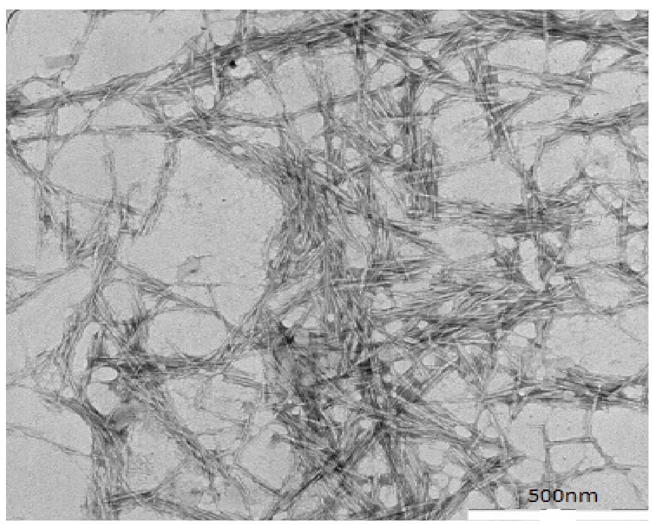

Figure 3 Transmission electron micrographs of NCC obtained from *Acacia mangium*. Source: (Latifah & Sharmiza 2017)

NFC has a long fibril shape with 1-100 nm in diameter and 500-2000 nm in length which can be extracted via mechanical disintegration techniques such as homogenization, grinding, milling, cryocrushing and microfluidization. The use of chemical and enzyme as a pre-treatment process prior to mechanical delamination is usually carried out to reduce energy consumption. As oppose to nanocrystalline cellulose, nanofibrillated cellulose maintains both crystalline and amorphous regions. Figure 4 shows schematic diagram of cellulose nanofibrils synthesized by mechanical methods.

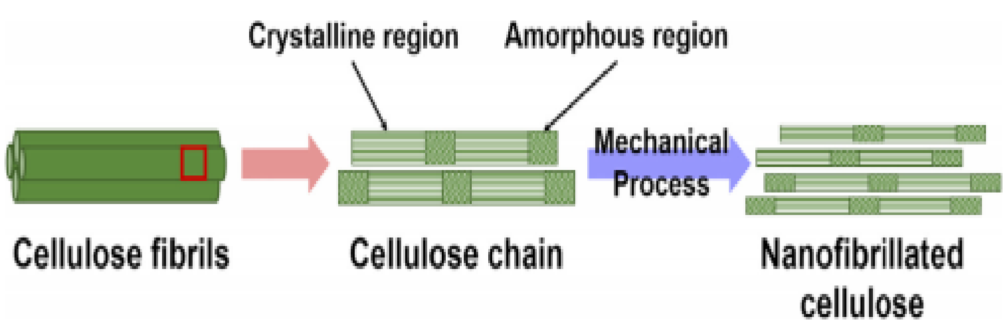

Figure 4 Schematic diagram of cellulose nanofibrils (NFC). Source: (Phanthong et al. 2018)

Figure 5 shows the morphology of NFC of *Opuntia Ficus-indica* that has been studied by past researchers.

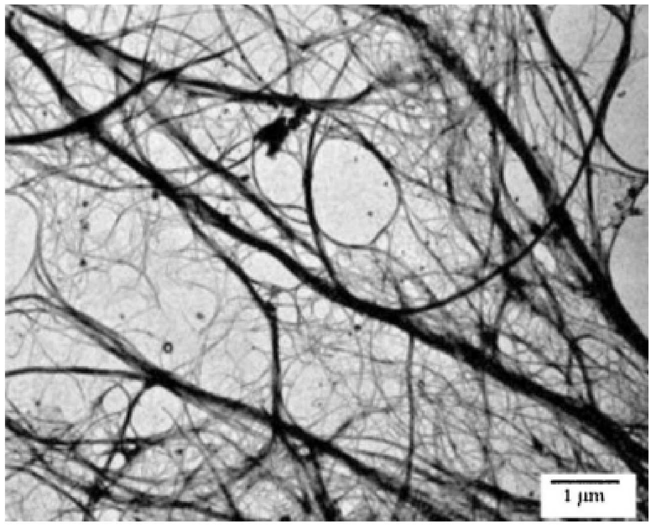

Figure 5 Transmission electron micrograph of NFC after high mechanical treatment of *Opuntia Ficus-indica*. Source: (Krishnamachari et al. 2011)

Bacterial nanocellulose (BNC) is another type of cellulose produced by bacteria that belongs to the genus *Acetobacter, Agrobacterium, Alcaligenes, Pseudomonas, Rhizobium* or *Sarcina*. The most efficient bacterial cellulose called *Gluconacetobacter xylinus*, is synthesized during a time period of days (few days or up to two weeks) in aqueous culture medium. BNC is in the form of randomly assembled (twisting) ribbon with diameter of 20-100 nm. BNC is applicable in cosmetic field as moistening mask, in medicine and veterinary areas as biocompatible implants (Ioelovich, 2017). The morphology of bacterial cellulose by scanning electron microscope is shown in Figure 6.

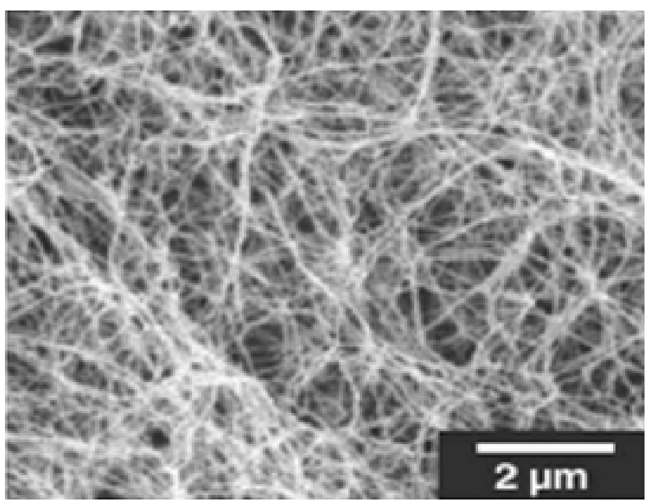

Figure 6 Scanning electron microscope (micro scale order) of a bacteria cellulose pellicles. Source: (Habibi, 2014)

In general, both NCC and NFC are produced by breaking down the cellulose fibres into nanosize (top down process) while BNC is synthesised using bottom-up approach through enzymatic polymerisation of organic substrates such as sugar and glycerol. BNC is synthesised as pure cellulose as it does not require pre-treatment to remove lignin and hemicellulose.

Each type of nanocellulose exhibits distinct properties that are useful for specific applications and functions. It is interesting to note that certain nanocellulose is better suited for particular functions than the others. This is due to their unique properties and potential compatibility with materials such as polymer, protein and living cells. The advancement of nanocellulose has opened up new field and directions in research area which has not been fully utilized yet.

PROPERTIES OF NANOCELLULOSE

Nanocellulose has been known for its high surface area and high tensile strength up to 10 GPa (greater than cast iron). Its ratio of strength is 8 times higher than stainless steel, and it has high stiffness (220 GPa). Its other beneficial attributes are high flexibility, high thermal and electrical strength (Deepa et al. 2011). It is of low toxicity, renewable, good biocompatibility, and it has been commercially used in medical field (Lavoine et al. 2012).

Furthermore, one of the special properties of nanocellulose is that it is a lightweight biodegradable nanofiber and of low density with value of around 1.6 g/cm^3. Nanocrystalline cellulose is also of interest in photonic technology due to the liquid crystalline property which gives rise to incandescent optical applications.

APPLICATION AREAS FOR NANOCELLULOSE

Due to the excellent properties of nanocellulose, it has attracted various applications in field such as nanocomposite, automotive, construction, cosmetic, food, pharmaceutical, packaging, biomedical and electronic devices. Apart from that, nanocellulose can be widely used as reinforcement material for plastic, papermaking and textile industries and also as adsorbent in environment field (waste water treatment) (Pui et al. 2018).

Nanocellulose can be used as reinforcing filler in composites since synthetic filler has issues related to disposal and recycling. Cellulose is considered as one of the alternatives as it is biodegradable, low cost and of low density. In a recent study, nanocomposite material that used nanocellulose was found to have high mechanical strength and high thermal properties, and it was also lightweight and transparent (Phanthong et al. 2018). Due to its high surface area and nanoscale dimension, nanomaterial can improve stiffness, strength, toughness, barrier properties and flame retardancy compared to pure polymer material with addition of only a few percent (1–5 % weight) (Alexandre & Dubois, 2000). In another study, nanocellulose used in the matrix of polylactic acid (PLA) and nanocellulose has enhanced the interaction among matrix fillers and improved the thermal properties as well as the crystallization.

LIMITATIONS OF NANOCELLULOSE

Hydrophilic property of nanocellulose limits its applications for any process or product that could not use water. Hence, modification on nanocellulose could solve this issue to broaden its application. Several chemical modifications have been studied such as silylation, carbamylation, etherification and amidation. The abundance of hydroxyl group on the surface of nanocellulose helps to introduce new functionalities.

With regards to bacterial cellulose, although it possesses many excellent properties, it might have obstacles to scale up due to the inefficiency to synthesize bacteria at large scale. New process development needs to be studied to produce a large scale of bacterial nanocellulose as the traditional method cannot produce required quantities that are needed for commercialisation.

SUMMARY

Nanocellulose is perceived as a milestone in the field of material science and engineering due to its unique characteristic and high availability in nature. Nanocellulose has great potential across many applications. The new trend and search for biodegradable, sustainable and recyclable material has made nanocellulose as one of the promising alternative materials to minimize environmental impact issue and potential to be truly green nanomaterials with many functional properties. Evidently, more observation and attention should be focused on the development of nanocellulose to enhance their usage in a diverse range of fields due to their inherently attractive properties.

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Nanocellulose is cellulose at nanosized level that can be prepared from lignocellulosic materials, marine animals, algae and bacteria. It has become an interesting nanomaterial because of its remarkable mechanical, physical and chemical properties. Nanocrystalline cellulose (NCC), Nanofibrillated cellulose (NFC) and Bacterial cellulose (BNC) are the three types of nanocellulose that produced by different methods, and each type of nanocellulose exhibits distinct properties that are useful for specific applications and functions.

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