Basic Overview of Cellulose Nanocrystals

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ABSTRACT

This paper discusses the various aspects of cellulose nanocrystals, including its extraction, mechanical properties, surface modifications, and medical applications. Cellulose nanocrystals are extracted from cellulose, one of the most common polymers in nature. Cellulose nanocrystals are unique as they can be extracted from organic material making them widely abundant and renewable, but they also possess incredible mechanical properties. Cellulose nanocrystals' theoretical tensile strength could be around 10 GPa and its theoretical elastic modulus could be 120+ GPa. In addition to its already desirable mechanical properties the crystals can still be further modified to bestow them with specific characteristics such as oxidation to increase thermal stability. The crystals' combination of being organic, compatible with modifications, alongside its mechanical properties makes it a material of interest in a multitude of fields. One of the fields that cellulose nanocrystals can shine in is the biomedical field, where they can act as materials for biosensors, tissue reparation scaffolding, or drug delivery systems.

Introduction

Cellulose is the most common polymer in nature with possibly over a hundred billion tons produced each year from numerous organic sources. Its unique chemical structure endows it with properties that make it an integral component to most plant lives. Cellulose is formed by repeated glucopyranose units that are linked together by covalent bonds using β (1,4) links (George and Sabapathi, 2015). This particular way the glucopyranose units link together gives cellulose strength comparable to steel. In addition, every glucopyranose contains three hydroxyl groups. This combination gives cellulose a unique combination of extremely desirable mechanical properties such as high stiffness and strength whilst being completely renewable. However, there are methods to enhance the already impressive properties of cellulose which is by processing it into cellulose nanocrystals or CNC.

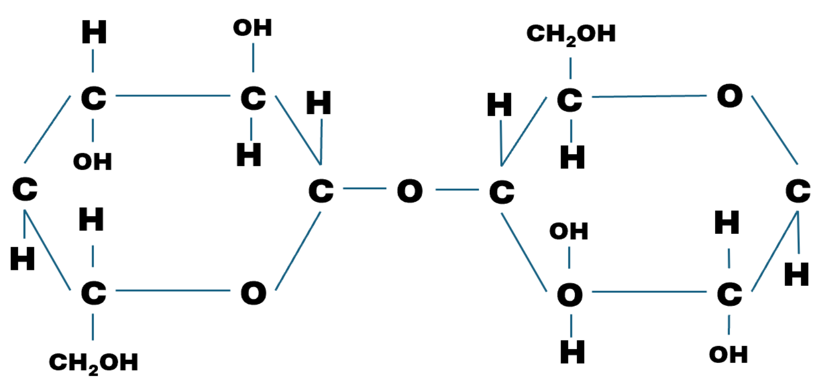

Figure 1. Structure of two bonded together glucopyranose units.

Natural cellulose is composed of microfibrils organised into amorphous and crystalline regions. The crystalline regions can be extracted to form nanocrystals through hydrolysis. Cellulose nanocrystals (CNC) are the crystalline regions of cellulose that are isolated through a combination of mechanical and chemical processes. The nanocrystals have a high aspect ratio, with lengths on the order of a few hundred nanometres, and widths on the order of a few nanometres. Their mechanical properties along with small size and biocompatibility make them sought-after materials for a wide range of applications. In this paper we review the extraction process, mechanical properties, modification and application of CNC.

Extraction

The use of cellulose as a widespread material is appealing as it can be extracted from a variety of natural sources such as tunicates, algae, cotton, bacteria, etc. Plants and organisms known for the production of cellulose often use it to form cellular walls, or protective layers around their body such is the case with tunicates and bacteria. While cellulose exists in a multitude of species the most common source for cellulose extraction are plants. Although bacteria have also been subjects of CNC extraction, plant-based cellulose extraction still remains to be the most common practice due to their low cost and availability (Norizan et al., 2022). Plants such as sisal, wood pulp, hemp, straw and certain fruits can all be subjects of cellulose extraction and experiments. Especially fruit husks or agricultural waste-based CNC extraction is a topic of interest for sustainability reasons as well as being able to acquire an abundant amount at a low cost.

In its natural state, cellulose exists in the form of fibrils. Within the cellulose fibrils there exists microfibrils organised in both amorphous regions and ordered regions, and the proportions vary depending on the source of cellulose. Ridding the cellulose of amorphous regions to form CNC which achieves more desirable mechanical properties (George and Sabapathi, 2015). As cellulose is composed of hydrogen bonds, disrupting the bond is a pivotal step in creating CNC. The ordered regions consist of tightly packed chains in the form of crystallites which are held together by intra- and intermolecular hydrogen bonds.

Generally, two forms of hydrolysis, H2So4 and HCl are used to perform acid hydrolysis to extract CNC from their natural sources (Ribeiro et al., 2019). The cellulose would have to first undergo delignification, bleaching, and hemi-cellulose removal before undergoing acid hydrolysis. Hydrolysis is a reaction where a water molecule is used to break one or more chemical bonds. When cellulose is hydrolysed by an acid, the amorphous regions, which lack order, and the para-crystalline regions, which contain short range order, are hydrolysed (Xing et al., 2018). The crystalline regions, on the other hand, are left intact. Once the hydrolysis process is completed the tightly packed, highly-ordered crystalline region is left, this post-hydrolysis crystalline region is known as cellulose nanocrystals. After hydrolysis putting the crystals through dialysis ensures the resulting CNCs are pure.

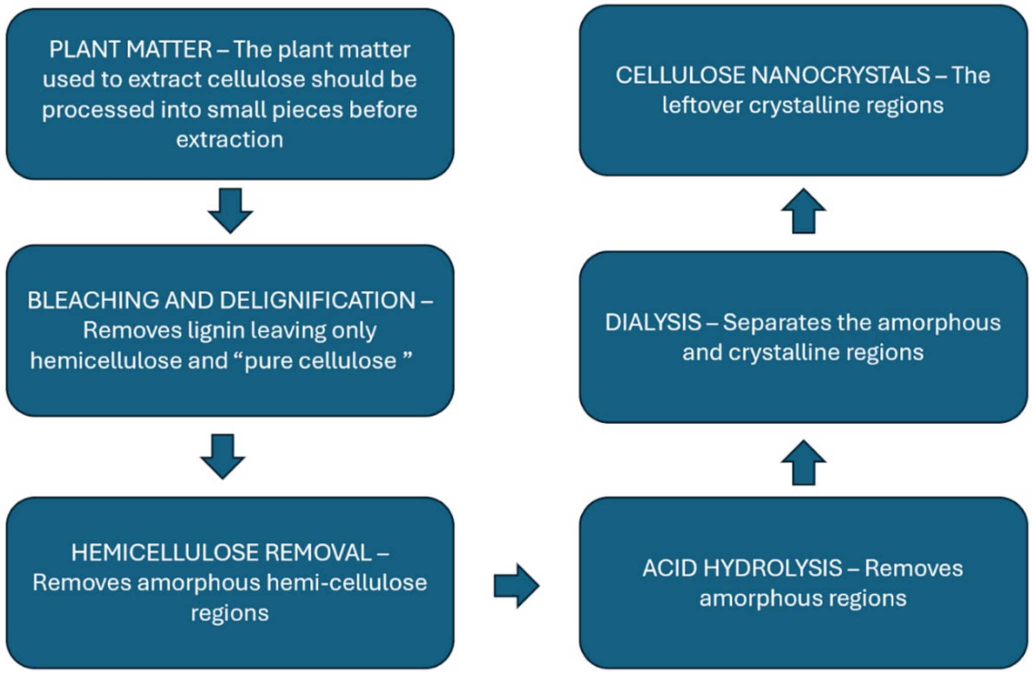

Figure 2. Flow chart of CNC extraction

4 types of cellulose structures exist (I - IV), cellulose I and cellulose II are the most relevant polymorphs. Cellulose I, or native cellulose, is the original form of cellulose found in nature or the common product after acid hydrolysis. Cellulose II contains an antiparallel chain arrangement that contains more hydrogen bonds relative to cellulose I but can only be obtained through processing cellulose I (Gautam et al., 2010). The synthesis of cellulose II involves acid hydrolysis that is performed under specific conditions and consumes much more energy. While cellulose I is more widely abundant and easier to synthesise, cellulose II has great thermal stability due to its additional inter-chain hydrogen bonds. However, cellulose I contains a larger elastic modulus, i.e. a resistance to stretching, due to the larger number of hydrogen bonds running parallel to a cellulose chain. With the two types of cellulose each having distinct characteristics, the two polymorphs are used for different applications. For example, since cellulose I is more susceptible to surface modification and can be used to reinforce other polymers while cellulose II having greater heat and structural resistance could be used as bioethanol fuel or feedstock.

Mechanical Property

In addition to being biodegradable, easily modified, and renewable, CNCs possess impressive mechanical properties. In particular, they have high tensile strength, hardness, and surface area to volume ratio and are nearly elastic. What gives rise to the high tensile strength and hardness of CNCs are the layers of intramolecular hydrogen bonds on each cellulose chain (figure 1). The hydrogen bonding gives CNCs a tensile strength on the order 10 GPa and a Young's modulus on the order 150 GPa (Shojaeiarani et al., 2021). The mechanical properties of CNCs are also heavily influenced by the size of the crystals.

Though many of the measurements of CNC are available, many of them are theoretical since it is extremely difficult to measure the specific properties of a material at a nanoscale. For example, X-ray diffraction has been used to calculate the elastic modulus of the crystals and while the resulting 120+ GPa elastic modulus is extremely high the experiment assumes perfect orientation and stress transfer onto the crystals (Moon et al., 2011). Other methods of measurements such as the AFM and Raman Spectroscopy resulted in lower values. AFM measures the force required to deform a material and Raman spectroscopy reveals the crystallinity of the cellulose nanocrystals as many mechanical properties such as hardness, stiffness, or strength are related to how crystalline a solid is.

Larger crystals experience more optimized mechanical properties. The size of cellulose nanocrystals could vary based on the sources they are extracted from and the process they are extracted by acid or enzymatic hydrolysis (Listyanda et al., 2020). Despite all its mechanical upsides CNC has slightly lower thermal stability compared to materials with similar strengths such as steel at around 300 degrees Celsius and Kevlar at around 560 degrees Celsius; structural degradation of CNC begins to occur at around 150 and reaches its peak at around 320 degrees Celsius (Nagy et al., 2020). Certain surface modifications of CNC could lower its thermal resistance bringing the temperature for degradation down to around 260 degrees Celsius (Moon et al., 2011). Extraction process can also vary the thermal stability, for example CNC extracted with hydrochloric acid hydrolysis has higher thermal stability than CNC extracted with sulfuric acid hydrolysis.

Surface Modification

One of the most desirable features of CNCs is its ability to be modified for use in a variety of applications. Recall that a CNC is a hydrophilic material by nature. This restricts it from being compatible with hydrophobic materials. However, because of its high surface area to volume ratio, the surface of a CNS tends to be highly reactive and easy to functionalize. Functionalizing the surface of a CNC can allow it to be used in applications involving hydrophobic matrices. In addition, surface modifications of CNCs can improve their thermomechanical properties. Methods to modify CNCs include but are not limited to esterification, etherification, amination, oxidation, silylation, carbamation, polymer grafting, phosphorylation, sulfonation, cross-linking, fluorescent labelling, and surfactant modification (Mujtaba et al., 2023).

An example of how surface modification can improve the properties of CNCs is oxidation. Oxidation at the surface of a CNC has been shown to increase the zeta potential and thermal stability of the crystals (Marwanto et al., 2021). The two most common types of oxidations are nitroxyl and periodate based. (Eyley and Thielemans, 2014). Oxidation occurs on the surface of the crystals when oxidising agents are introduced and form functional groups. In the case of nitroxyl and periodate-based oxidation, aldehyde or dehydrated alcohol functional groups are formed.

Cellulose can also be easily bonded with other molecules to improve its properties. One such molecule is polyethylene glycol or PEG (Figure 2). PEG is a widely used synthetic compound that can be found in cosmetic or pharmaceutical products. Combining CNC with PEG tackles the issue of re-dispersing dried cellulose in water (Cheng et al., 2015). Through grafting PEG onto CNC with a polydopamine (PDA), the mechanical properties of the crystals can be altered. The shorter grafts increased the stiffness, and the longer grafts increased the toughness of the crystal and also provided an external rubber coating (Zheng et al. 2021).

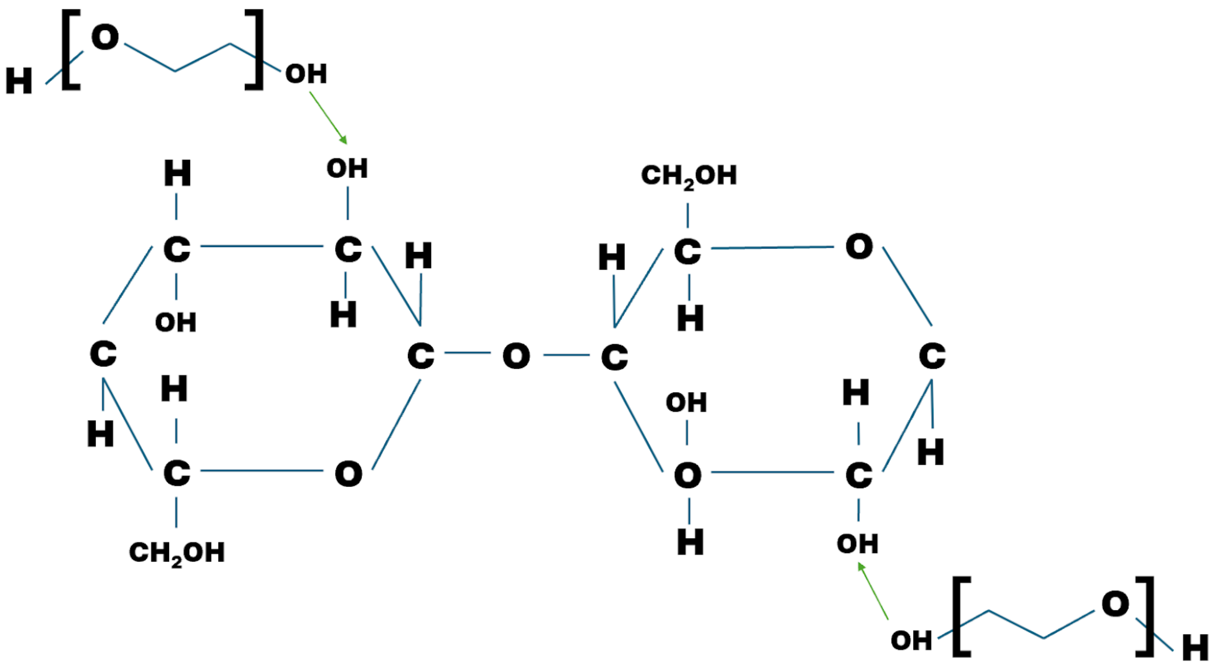

Figure 3. Structure of two glucopyranose units bonded with two PEG molecules

Medical Applications

Since cellulose is composed of hydroxyl groups, which can be readily modified, CNCs find use in many medical applications. The ease of surface modification in addition to other qualities such as high tensile strength, high surface area to volume ratio, etc. makes cellulose nanocrystals a prime candidate for drug deliveries, biosensors, tissue repairs or other forms of medical application. For example, using CNCs as films or membranes provides a slow-releasing binding site for drugs to deliver into the body (Munawaroh et al., 2023). A drug called Phycocyanin was developed as an anti-inflammatory/ anti-cancer agent however its effects are reduced due to the low PH environment in the human gastrointestinal system. By using CNC extracted from bacteria the drug is able to be administered while being shielded from the acid gastro environment.

Tissue reparations is another biomedical use where the biocompatibility and strength of CNC is once again highlighted. When paired with aerogel, the [aerogel and CNC] composite could act as a scaffolding for bone tissue reparation (Sunasee et al., 2016). In the same way that the films or membrane of cellulose can be engineered to be carriers of drugs, the material could also act like a carrier of living cells. This usage of cellulose is still in its infancy but shows promise in fixing bone or muscle tissue. CNC's mechanical properties are also desirable for this task as the high strength of CNC improves the structural integrity of the scaffolding (Murizan et al., 2020). With addition of CNC scaffold in tissue reparations, the regeneration process can be sped up immensely.

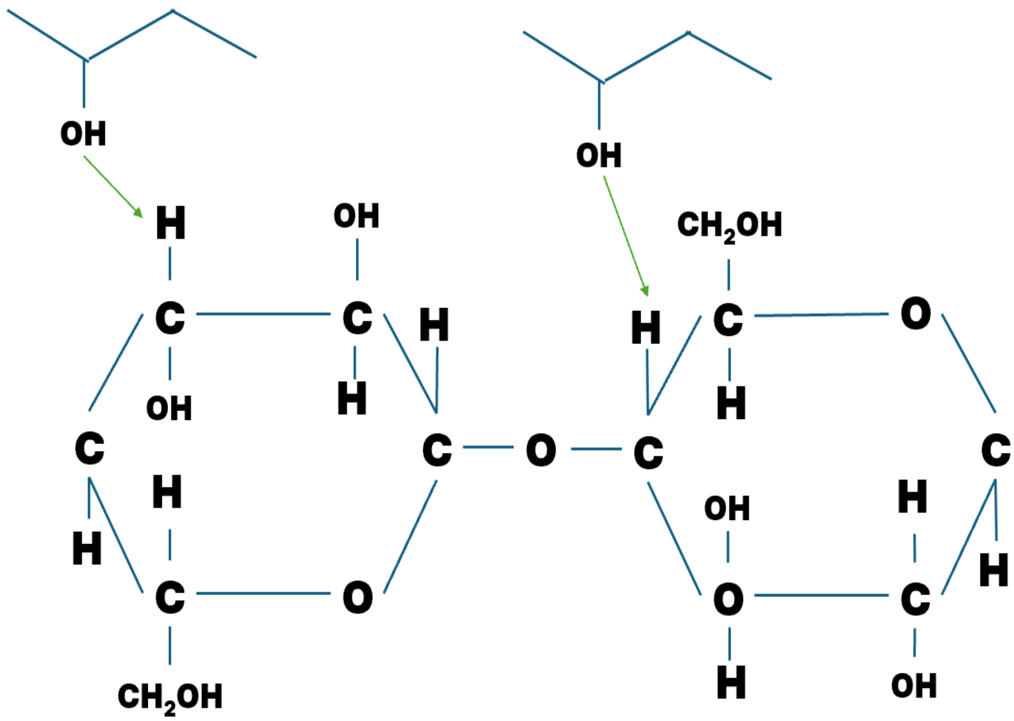

Figure 4. Structure of two glucopyranose units bonded with two aerogel molecules.

Biosensors are devices made out of organic material that output a response when coming into contact with a specific chemical. The sensors are important as they can help detect early stages of certain diseases or viruses in the human body. CNC due to its ease of modification could be used as a platform to host chemicals for biosensors. In the modern age where a plethora of people have issues with high levels of blood sugar, a cheap method of measuring blood sugar level is in high demand. There have been developments of CNC films binded with magnetite as a way to orally or dermally detect high blood sugar levels (Tracey et al., 2020). When exposed to a high level of glucose level the Magnetite would oxidise resulting in a green colour change. In addition to sensing the development of diseases and viruses, CNC has the possibility to be developed into sensors that detect hazardous gases, metals, or solvents.

Conclusion

With its unique and desirable properties CNC could be applied in a multitude of fields, currently the material has great unexplored and undeveloped potential. Cellulose inherently has a multitude of desirable traits and can be extracted from a myriad of organisms. Upon processing into nanocrystals, the traits of the material can be further enhanced. Not only is CNC already an improved version of cellulose, but even further modification can also be implemented to specialise the material for purposes that range from biomedical to energy. Though there are many areas for improvement and further research such as the technology to extract cellulose in abundance or further testing on how it could be broken down in the human body when applied in the medical field. CNC is a material with largely untapped potential and presents opportunities for research and innovation.

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