Materialising Nanocellulose - A Potential Sustainable Material of the Future- A Review

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Abstract

The rising environmental concerns due to the excessive usage of petroleum-based materials have driven research for sustainable, renewable, and biodegradable products. Cellulose is one of the most abundant natural polymers, extracted mainly from plants, tunicates, bacteria, and algae. Nanocellulose has the remarkable properties such as low density, biodegradability, and non-toxicity; along with great mechanical and thermal stability, self-assembly in aqueous dispersion media, reinforcing capabilities and long-lasting nature. This paper gives a review on nanocellulose and materising them for different application.

Key words: Cellulose, Nanocellulose, Sustainability

Introduction

Cellulose is one of the most abundant natural polymers. It is abundantly available in woody and non-woody residues. Large amount cellulose is present in the residues of both woody and non-woody plants [1]. Bio-nanostructure of cellulose can be obtained from cellulose extracted from various natural sources, such as plants, algae, small marine animals (tunicate), straw (rice), seeds (cotton), cane (bamboo, bagasse), and some bacteria.

It has been discovered that the cell walls of some algal species, including Rhodophyta, Phaeophyceae, Dinophyta, and Charophyceae, contain cellulose, which is primarily present in Iα

form [2]. Similar to plant cellulose, tunicates' cellulose is predominantly found in the Iβ form of cellulose [3].Bacteria are the source of bacterial cellulose, with Acetobacter xylinum being the most productive. High crystallinity, elastic modulus, and degree of polymerization are characteristics of bacterial cellulose. Compared to amorphous cellulose, it has ordered crystalline domains that are more resistant to mechanical, chemical, and enzymatic treatments; these crystalline regions are stabilised by hydrogen bonds, which also reduce cellulose's solubility in water and other solvents.

Different factors including effective surface area, crystallinity, and mechanical strength alter when the size decreases from micrometres, as in cellulose polymer chains, to nanometers, as in nanocellulose. As a result, cellulose synthesised at the nanoscale has superior qualities to cellulose [4].

The cellulose supply, the concentration of mineral acid, the length of treatment, and the temperature of hydrolysis are all significant factors that affect the size and structure of the nanocellulose. The presence of hydroxyl groups on the surface, surface area, aspect ratio, crystallinity, and mechanical properties of cellulose nanocrystals are the primary determinants of their attributes [5]. The cellulose nanocrystals' strength, stiffness, and crystallinity are provided by the robust inter- and intra-chain hydrogen bonds. The market for nanocellulose was valued at $291.53 million in 2019 and is expected to grow at a thrilling rate of 19.9% to reach $1,053.09 million by 2027[6].

Pre-Treatments of Cellulose Sources

The main technique used to break down the lignocellulosic biomass's interior tissues and cell walls through biochemical conversion processes is pre-treatment [7]. Internal structures are upset by this treatment, which also creates an opening for additional therapies. Therefore, during the pre-treatments, the cellulose sources are amenable to size reduction, structural modification, increased crystallinity, and improved swelling capacity in water [8].

Pre-treatments fall into three categories: chemical, biological, and physical. Mechanical, pyrolysis, sonication, microwave radiation, and spray drying are examples of physical pre-treatments [9]. As mechanical pre-treatments, three distinct techniques are typically used: grinding, chipping, and milling. To bring the particle size down to a few millimetres, chipping is done. While the particle size is reduced to 0.2 mm by the high shearing forces generated by milling and grinding techniques, a consistent size distribution is provided. The type and duration of milling processes used determine the specific surface area, degree of polymerization, and crystallinity of the nanocellulose [10]. Plant fibres can be made smaller by using a variety of milling techniques, including dry, wet disc, and vibratory milling. Because mechanical treatment is both economically feasible and produces no harmful by-products, it is a reasonable choice for a pre-treatment. The biological method consists of picking, enzymatic therapy, fungal action, and bacterial treatment. Hemicellulose and lignin are the results of the biological treatments. Alkali pre-treatment and bleaching are the two primary chemical pre-treatments used for cellulose extraction. Among the chemical pre-treatments employed are carboxymethylation, carbonylation, alkali treatment, acid hydrolysis, sulfonation, and quaternization. Defibrillation is aided by the large shearing pressures that the mechanical treatment imparts to the cellulose bundles [11]. High-pressure homogenization, microfluidization, micro grinding, steam explosion, cryo-crushing, and high-intensity ultrasound are among the mechanical treatments employed for nanofibrillation. Nanocellulose is highly hydrophilic and amenable to modification through a variety of chemical and physical techniques due to its abundance of hydroxyl groups (-OH) that can form hydrogen bonds either intramolecularly or between different chains . Its hydrophilicity may occasionally be a disadvantage, particularly in situations where humidity may be an issue. Chemical changes to hydroxyl groups are frequently made to reduce nanocellulose's hygroscopicity [12]. Because of their high reactivity, the hydroxyl groups can be altered through surface chemical functionalization, which enhances the compatibility of the nanocellulose with the non-polar polymer matrix.

Materilising Nanocelluose

Ming et al. synthesised nanocellulose that was separated from cotton stalks using acid hydrolysis. The findings using FTIR, AFM, XRD, and TA, demonstrated the smooth surface and rod-like forms of nanocellulose. The interior chemical linkages of cellulose macromolecules were impacted by the acid hydrolysis, particularly the (3)-OH and (5)-OH bonds. Decrease in particle size caused hydrogen bonds to break and reunite. Thermal characteristics were influenced by nanocellulose size. When the size of the nanocellulose particles was reduced, the overall thermal property dropped [13].

Al-Hagar and Abol-Fotouh [14] used an economical technique to synthesise bacterial cellulose from Komagataei bacterhansenii KO28. Using this technique, the scientists exposed the bacterial strain to varying levels of gamma radiation. After 10 days of incubation, the bacteria strain subjected to 0.5 kGy of gamma radiation twice (low dosage) yields the maximum, or 475% more than the control culture. The properties of the synthesised nanocellulose were also examined, and they matched those of the control nanocellulose.

Using nanocellulose and extract from mango leaves, Bastante et al. [15] created bioactive films by using Super-critical impregnation technology or solvent casting were used to create the bioactive films from extract of mango leaf. Since the extracted mango leaf has antibacterial and antioxidant qualities, the nanocellulose films that were made have antimicrobial characteristics against both Gram-positive and Gram-negative bacteria, including Staphylococcus aureus. In addition to their antioxidant and antibacterial qualities, the films made using super-critical impregnation technique have strong UV light barrier qualities, which helps to preserve food better for longer periods of time. In an effort to substitute hazardous dyes, scientists have recently started experimenting with biomaterials like cellulose or modified forms of cellulose [16].

Acid-hydrolysis was used to recover nanocellulose from water hyacinth. Hydrogels were recovered from nanocellulose when treated with urea and NaOH. Afterwards, borax was applied to the hydrogels to create crosslinked hydrogels. The crosslinked nanocellulose's SEM morphology revealed a more porous structure. The uncross-linked hydrogels displayed a swelling ratio of 325.2%, but the cellulose hydrogel crosslinked with borax exhibited a swelling

ratio of around 900% because of the borax's increased generation of OH groups on the crosslinked nanocellulose. Because there were more OH groups and a higher degree of polymerization in the crosslinked nanocellulose, there was also an increase in the water content and gel fraction. When it comes to antibacterial efficacy against Gram-positive bacteria (S. aureus), the crosslinked hydrogels also demonstrated a respectable degree of thermal stability (the majority of thermal breakdown happens between 250 and 400 °C) and transmittance [17]. Consequently, a highly adsorbent hydrogel derived from nanocellulose was created, which may find use in flame-retardant coating, agricultural applications, and wound dressing.

Using acid hydrolysis, Abdelaziz et al. [18] wastepaper was converted into nanocrystals, which were then utilised to make hydrogels by adding epichlorohydrin as a crosslinker. The nanocrystal hydrogels are positively charged at lower pH and are negatively charged at higher pH. The electrostatic interaction provides the basis for the dye's specific adsorption onto cellulose. Because sulfonic groups are present, the acid red anionic dye exhibits great adsorption at lower pH values, according to the researchers. However, at higher pH values (alkali washing), the dye will desorb. The hydrogels' reusability was examined as well, and after four cycles, the dye removal percentage was cut in half as a result of the films' deterioration from alkali washing. Additionally, the kinetic characteristics of the dyes' adsorption were examined; pseudo-second-order and Langmuir isotherm models demonstrated good fit to the experimental data using azide dyes and a triazine-alkyne linker.

3D printed self-healing hydrogels were synthesised using oxidised cellulose nanofibers, chitin nanofibers, and carboxyl methyl chitosan by Heidarian et al. [19]. The formation of nanohybrid hydrogels was brought about by the imine crosslinks that were formed between the nanomaterials. Tannic acid (TA) and Fe III solution were added to the nanohybrid hydrogels to increase their impart conductivity. The gel demonstrated strong strain-sensing capabilities, good self-thinning qualities, up to 89% self-healing, and 100% self-recovery (in the absence of outside stimuli).

The impact of fibre length, orientation, fiber-fiber interaction, and loading direction on the mechanical characteristics of cellulose nanocrystals (CNC) films was investigated by

Shishehbor. The researchers found that the primary factor governing the mechanical properties is the interfacial strength (fiber–fiber contact) between the cellulose nanocrystals. Babi et al. successfully labelled the nanocellulose fluorescently without changing the cellulose's structure.

CNF was extracted from Eucalyptus globulus kraft pulp by Alves et al. [20] using three distinct techniques: (i) mechanical treatment by high-pressure homogenization; (ii) enzymatic treatment followed by mechanical treatment; and (iii) TEMPO oxidation followed by mechanical treatment. The researchers created films using either the solvent casting approach or vacuum filtering followed by hot pressing by combining separated nanocellulose with clay (sepiolite). When compared to solvent casting, the films made via filtering and hot pressing have higher Young's modulus and tensile strength. The researcher suggests using artificial films in place of plastics.

Nanocellulose films could be employed as the foundation material for flexible electronic devices.According to Uetani et al. [21], tunicate nanocellulose sheets have a thermal conductivity of 2.5 W/m K, which is higher than that of other polymeric films used in electronic devices. Flexible electronics based on cellulose were created by Fu et al. [22] using balsa wood (Ochroma pyramidale). After the hemicellulose and lignin were chemically removed from the balsa wood, it was compressed under high pressure to create a flexible, translucent wood film with an excellent modulus and strength. Before being turned into an amyloid/lignin-based carbon ink, the electron-spun lignin was carbonised into a conductive carbon fibre. The flexible, translucent wood film was then printed with the ink to create an electronic circuit. According to the researchers, the flexible electronics they developed are sustainable and favourable to the environment, making them suitable for use in applications like flexible circuits and sensors.

Yuen et al. [23] used bacterial nanocellulose to create ultra-thin biosensors. The circuit boards were effectively mounted on the nanocellulose using electroless plating and inkjet printing. The new circuit boards based on nanocellulose are recommended by the researchers for use in temperature sensor, electronics, and healthcare applications.

Carter etal. [24] created a CNF manufacturing facility that uses mechanical defibrillation technology to generate consistent CNF slurry. Subsequent CNF sheets were made using calendar or non-calendar procedures from CNF slurry. Because the calendared sheets have a minimal thickness, they are more transparent. Researchers that changed the slurry's solids concentration or adjusted the knife applicator's height saw differences in the films' transparency. Ethylene oxide was used to further sterilise the nanosheets so they could be used as animal implants in mice and non-human primates.It was noted that the animals treated with the nanosheet implants showed no signs of irritation or inflammation and were completely biocompatible.

Hence literature shows that nanocellulose prepared from various sources finds various applications in different such as food packaging, chemical industry as viscosity modifier, biomedicine and drug delivery, electrochemical devices, as mechanical reinforcement of matrices, and membrane filtration and environmental remediation [25, 26].

Conclusion

Nanocellulose is an attractive and high-value-added product. Nanocellulose is an excellent material with good biodegradability, antibacterial, antifungal, has good fire retardant, high tensile strength, mechanical robustness, low weight, high surface area, biodegradability, hydrophilicity, and tunable optical properties that has a broad range of applications from an industrial, technological, and academic perspective. It has unique characteristics makes it a promising sustainable material for commercial markets.

Reference

1. Aiswarya Poulose et al., Nanocellulose: A Fundamental Material for Science and Technology Applications *Molecules* **2022**, *27*(22), 8032; https://doi.org/10.3390/molecules27228032,
2. Zanchetta, E.; Damergi, E.; Patel, B.; Borgmeyer, T.; Pick, H.; Pulgarin, A.; Ludwig, C. Algal cellulose, production and potential use in plastics: Challenges and opportunities. Algal Res. **2021**, 56
3. Trache, D.; Hussin, M.H.; Haafiz, M.M.; Thakur, V.K. Recent progress in cellulose nanocrystals: Sources and production. Nanoscale **2017**, 9, 1763–1786.

4. Icot-Allain, M.C.N.; Emmambux, M.N. Isolation, characterization, and application of nanocellulose from agro-industrial by-products: A review. Food Rev. Int. **2021**, 1–29.
5. Brinchi, L.; Cotana, F.; Fortunati, E.; Kenny, J.M. Production of nanocrystalline cellulose from lignocellulosic biomass: Technology and applications. Carbohydr. Polym. **2013**, 94, 154–169.
6. https://www.fortunebusinessinsights.com/nanocellulose-market-104565 downloaded on 7/02/2024
7. Agu, O.S.; Tabil, L.G.; Meda, V.; Dumonceaux, T.; Mupondwav, E. Pretreatment of crop residues by application of microwave heating and alkaline solution for biofuel processing: A review. In Renewable Resources and Biorefineries; Jacob-Lopes, E., Zepka, L.Q., Eds.; IntechOpen: Rijeka, Croatia, 2018; pp. 47–67.
8. Zimmermann, T.; Bordeanu, N.; Strub, E. Properties of nanofibrillated cellulose from different raw materials and its reinforcement potential. Carbohydr. Polym. **2010**, 79, 1086–1093.
9. Kucharska, K.; Rybarczyk, P.; Hołowacz, I.; Łukajtis, R.; Glinka, M.; Kamiński, M. Pretreatment of lignocellulosic materials as substrates for fermentation processes. Molecules **2018**, 23, 2937.
10. Kumar, A.K.; Sharma, S. Recent updates on different methods of pretreatment of lignocellulosic feedstocks: A review. Bioresour. Bioprocess. **2017**, 4, 7.
11. Nechyporchuk, O.; Belgacem, M.N.; Bras, J. Production of cellulose nanofibrils: A review of recent advances. Ind. Crops Prod. **2016**, 93, 2–25.
12. Ferreira, D.; Cruz, J.; Fangueiro, R. Surface modification of natural fibers in polymer composites. In Green Composites for Automotive Applications; Woodhead Publishing: Sawston, UK, 2019; pp. 3–41
13. Ming Li*, Physicochemical Properties of Nanocellulose Isolated from Cotton Stalk Waste, ACS Omega 2021, 6, 39, 25162–25169, 2021, https://doi.org/10.1021/acsomega.1c02568
14. Al-Hagar, O.E.; Abol-Fotouh, D. A turning point in the bacterial nanocellulose production employing low doses of gamma radiation. Sci. Rep. **2022**, 12, 7012.
15. Bastante, C.C.; Silva, N.H.; Cardoso, L.C.; Serrano, C.M.; de la Ossa, E.J.M.; Freire, C.S.; Vilela, C. Biobased films of nanocellulose and mango leaf extract for active food packaging: Supercritical impregnation versus solvent casting. Food Hydrocoll. **2021**, 117, 106709.
16. Tavakolian, M.; Wiebe, H.; Sadeghi, M.A.; van de Ven, T.G. Dye removal using hairy nanocellulose: Experimental and theoretical investigations. ACS Appl. Mater. Interfaces **2019**, 12, 5040–5049.
17. Tanpichai, S.; Phoothong, F.; Boonmahitthisud, A. Superabsorbent cellulose-based hydrogels cross-liked with borax. Sci. Rep. **2022**, 12, 8920.

18. Abdelaziz, R.M.; El-Maghraby, A.; Sadik, W.A.A.; El-Demerdash, A.G.M.; Fadl, E.A. Biodegradable cellulose nanocrystals hydrogels for removal of acid red 8 dye from aqueous solutions. Sci. Rep. **2022**, 12, 6424.
19. Heidarian, P.; Gharaie, S.; Yousefi, H.; Paulino, M.; Kaynak, A.; Varley, R.; Kouzani, A.Z. A 3D printable dynamic nanocellulose/nanochitin self-healing hydrogel and soft strain sensor. Carbohydr. Polym. **2022**, 291, 119545
20. Alves, L.; Ramos, A.; Rasteiro, M.G.; Vitorino, C.; Ferraz, E.; Ferreira, J.; Puertas, M.L.; Gamelas, J.A. Composite Films of Nanofibrillated Cellulose with Sepiolite: Effect of Preparation Strategy. Coatings **2022**, 12, 303
21. Uetani, K.; Okada, T.; Oyama, H.T. Crystallite size effect on thermal conductive properties of nonwoven nanocellulose sheets. Biomacromolecules **2015**, 16, 2220–2227.
22. Fu, Q.; Chen, Y.; Sorieul, M. Wood-based flexible electronics. ACS Nano **2020**, 14, 3528–3538
23. Yuen, J.D.; Shriver-Lake, L.C.; Walper, S.A.; Zabetakis, D.; Breger, J.C.; Stenger, D.A. Microbial nanocellulose printed circuit boards for medical sensing. Sensors **2020**, 20, 2047.
24. Carter, N.; Grant, I.; Dewey, M.; Bourque, M.; Neivandt, D.J. Production and Characterization of Cellulose Nanofiber Slurries and Sheets for Biomedical Applications. Front. Nanotechnol. **2022**, 3, 729743
25. Liu, K.; Takagi, H.; Osugi, R.; Yang, Z. Effect of physicochemical structure of natural fiber on transverse thermal conductivity of unidirectional abaca/bamboo fiber composites. Compos. Part A Appl. Sci. Manuf. **2012**, 43, 1234–1241.
26. Rojas, J.; Bedoya, M.; Ciro, Y. Current trends in the production of cellulose nanoparticles and nanocomposites for biomedical applications. Cellul. Fundam. Asp. Curr. Trends **2015**, 193–228.