

# Promising Approaches from Cellulose to Nanocellulose in Reinforced Polymer Industry- A Comprehensive Study

## M. Surya<sup>1</sup>, A.J. Sunija<sup>2</sup> and S. Sivailango<sup>3</sup>

<sup>1</sup>Undergraduate Student, Department of Chemistry, Mannar Thirumalai Naicker College,

Madurai 625 004

<sup>2&3</sup>Assistant Professor, Department of Chemistry, Thiagarajar College of Engineering, Madurai 625 015

### Abstract

A move towards sustainability and greener approach and the widespread strengthening of SDG goals towards sustainability has urged researches to explore the potential of sustainable biomaterials for use as raw material in every industry. Fiber reinforced composites are one of the best frontrunners in the materials era from spacecrafts to electronics and medicine. Research shows that excellent properties of nanocellulose has proved it as frontrunner as reinforcement in composite industry. This paper is a review on the nanocellulose and its applications in polymer composites industry.

Keywords: Nanocellulose, fiber reinforced polymer

## Introduction

Nanocellulose is the herbal fiber in nano scale which may be extracted from cellulose, the primary structural factor of plant molecular walls. Nanocellulose shows promise as a new type of reinforcing agent in the field of composite industry. Nanocellulose have a characteristic shape and are  $\sim$ 3 nm in width and several micrometers in length. They have been demonstrated to have excellent mechanical and thermomechanical properties, with high strength (2–6 GPa), high elastic moduli (130–150 GPa) and low thermal expansion coefficients (4–6) ppm K<sup>-1</sup> making them a suitable material in polymer industry as reinforcement (1). Cellulose, one of the most abundant raw materials has excellent properties. The potential of cellulose is exploited in various industries and is found to be one of the most sustainable biomaterial of the future. Cellulose is present mainly from micro to macrolevel bioforms especially from bacterial, algae to higher



order woody plants. The plant fibre is composed of three secondary walls, a lumen in the centre, and a main cell wall on the exterior. Whereas the cellulose fibres in the secondary cell wall are oriented helically, the cellulose fibres in the primary cell wall are arranged randomly. In the secondary cell wall the fibers are oriented helically, the cellulose fibres in the primary cell wall are ordered haphazardly. Chemically, cellulose is a linear polysaccharide produced from ringed glucose monomers linked together through  $\beta$ -(1,4) glycosidic bonding. Morphology studies shows the presence of alternating regions of crystalline and amorphous zones, which, together, form the characteristic macroscopic fibrous structure of cellulose. The strength of cellulose is contributed by the highly ordered crystalline region which makes them more chemical resistance and decrease solubility in water (2, 3). Nanocellulose is synthesized from different sources under different reaction conditions. Categorically nanocellulose are classified into three types: cellulose nanocrystals (CNCs), nano-fibrillated cellulose (CNF), and bacterial nanocellulose (BNC) based on the function of their sources, the degree of crystallinity, and The extraction and manufacturing method, if a bottom-up or top-down method is used. CNCs are made up of cylindrical, elongated, inflexible, rod-like nanoparticles that are typically produced by hydrolysis. They have dimensions of 4-70 nm in width and 100-6000 nm in length, with a crystallinity index of about 54-68%. In order to extract cellulose nanocrystals, cellulose sources are often pre-treated to partially remove hemicellulose and lignin content (4). This is followed by acid hydrolysis or enzymatic treatment of the cellulose fibres. The crystalline content of the cellulose fibres is increased and the amorphous sections are removed with the aid of the acid treatment. Compared to enzymatic hydrolysis, it often requires harsher reaction conditions and less time. The surface functions of the nanocellulose are determined by the mineral acids utilised in acid hydrolysis. Because the cellulose chains are surrounded by negatively charged sulphate groups, the nanocellulose made from sulphuric acid has a high colloidal stability. These surface groups' repellent properties stop the cellulose chains from further aggregating. With a braided network structure and dimensions of 20–100 nm in width and >10,000 nm in length, nano-fibrillated cellulose (CNF), which is typically generated mechanically, is made up of longer, more flexible fibres with a low crystallinity index ( 88%, bacterial nanocellulose (BNC), microbial nanocellulose, is the most promising and economical biomaterial, particularly for the biomedical industry [5]. The BNC is made up of recognizing 3D networks made up of ultrafine nanofibers



with diameters ranging from 20 to 100 nm and lengths measured in micrometres Flexible fibres with alternating crystalline and amorphous domains with a high aspect ratio, diameter ranging from 5 to 30 nm, and length of several micrometres are known as nanofibrillated cellulose [NFC] or cellulose nanofibrils [6, 7]. Numerous sources, including microbes, plants, and animals, can provide NFC. The resulting fibrillated cellulose's size, crystallinity, and shape are primarily determined by the mechanical treatments and unprocessed natural sources [8]. Nanocellulose is a promising material that is essential to a variety of industries, including electronics and medical. Mali and Sherje reported that the biodegradability and biocompatibility of nanocellulose makes it non-toxic for humans and useful for the reconstruction of body tissues or for drug delivery and medicine. Industries typically employ nanocellulose as a strengthening agent. Omran et al. showed that these nanomaterials can modify the surfaces with various functional groups that enhance their compatibility with polymers to obtain various multifunctional composite materials. Nanocellulose has the potential to enhance the properties of poly(lactic acid) and poly-3hydroxybutyrate/poly-3-hydroxyvalerate. They have a high Young's modulus, and can be related to the Kevlar material, and used for the production of highly robust materials [8]. In order to enhance the qualities of natural or synthetic textile fibres, nanocellulose can also be applied as a surface treatment or incorporated as an addition into a polymer matrix [9]. In both environmental remediation and water treatment, nanocellulose is essential serving as a The nanocellulose surface has a large number of hydroxyl groups, which enable it to interact with organic molecules and heavy metals found in waste fluids and function as a filtering membrane. Nanocellulose can be utilised as a UV shield and possesses fire retardant qualities [9]. Moreover, they have good antimicrobial property and it can be used as in hospitals wallpapers and as food packaging materials and water filters [9]. In the field of cultural heritage, nanocellulose can be used in combination with some additives , such as silver nanoparticles ZnO and (AgNPs), thus providing an antibacterial and antifungal eect against commonly available fungi in archives or museums. Nanocellulose has use in the electrical industry since it can increase the conductivity and suppleness of composite materials [10]. For instance, polyaniline nanocellulose composite material finds extensive application in the production of electrical devices, paper-based sensors, flexible electrodes, and conductive adhesives [10].



#### **Characterization of Cellulose Nanomaterials**

Properties evaluation of cellulose nanomaterials are investigated and characterized using a variety of techniques. These most common properties investigated include surface morphology, size, dimensions (length, diameter, and aspect ratio), shape, thermal stability, surface charge, crystallinity, mechanical and optical qualities. For the morphological and topographic analyses of nanocellulose, Kumar et al. [11] demonstrate the use of field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), and transmission electron microscopy (TEM) techniques; Fourier transform infrared spectroscopy (FTIR) was used for the chemical and physical analyses. Elemental analysis was completed using energy dispersive X-ray diffraction (EDX) and X-ray diffraction (XRD). Thermogravimetric analysis (TGA), derivative thermogravimetry (DTG), and differential thermal analysis (DTA) are used to assess the thermal stability and thermal response to a change in temperature. These techniques allow us to assess the thermal stability of the consolidants. Specifically, XRD was used to determine the crystallographic structure of CNC and, consequently, the degree of crystallinity of nanocellulose [12, 14]. Singh et al. suggest using the DLS technique, also known as photon correlation spectroscopy, to analyse the particle size of isolated microcrystalline cellulose. Actually, the issue with the DLS technique is that, although this light scattering-based model performs well in characterising spherical particles with a single, constant rate of diffusion, it is not always able to accurately measure the size of particles in terms of their length or cross-section for nanocellulose structures, which have high aspect ratios and varying translational diffusion constants that are parallel to and perpendicular to one another. As a result, this method offers a hydrodynamic "apparent particle size" that is utilised to assess the aggregation and dispersion of NC suspensions. However, in order to obtain a more precise analysis, it is required to integrate the DLS results with those from other methods, like microscopy analyses . Huang et al. were able to differentiate between the morphological variations of the four polymorphic nanocelluloses produced with the four distinct treatments, in particular, because of the SEM and TEM investigations. Mishra et al. demonstrate the application of additional methods for the analysis of the particle dimension distribution in the study of the nanocellulose morphology, including dynamic light scattering (DLS), small-angle neutron scattering (SANS), small-angle X-ray scattering (SAXS), and wide-angle X-ray scattering (WAXS) [13]. Additionally, they talked



about assessing NC's structure and crystallinity using Raman analysis. In order to examine the impact of chemical alterations on the surface polarity resulting from the nanocellulose, Moran et al. present the contact angle measurement of starch films functionalized with nanocellulose. Gond et al. measured the optical characteristics of nanocellulose using UV/visible spectroscopy. The antimicrobial hobby of nanoparticles or different nanomaterials, including nanocellulose, is commonly completed via way of means of optical and electronical microscopy [13]. Nanocellulose in Reinforced Polymer

Literature shows that nanocellulose is a promising reinforcement with polymers for manufacturing composites. The distribution and dimension of nanoparticles entails critical factors during reinforcement. If the scale is simply too large, the nanometer impact is weakened, which incorporates a lower withinside the quantity of segment interfaces, a weakening of the bond energy among The reinforcing section and the matrix and a deterioration of the strain conduction effect [15]. Because of the high surface activity and hydrophilicity of nanocellulose, self-aggregation is inevitable without a certain amount of processing, it easily self-aggregates, which makes dispersion more difficult to disperse. If the particle length distribution is simply too wide, the fast plate impact may be prominent, and the enhancement impact may be reduced. In addition to the distribution mode, the association mode of nanocellulose additionally has a widespread have an effect on the composites. Nanocellulose is a kind of nanomaterial with a excessive element ratio in maximum cases, composed of linear molecules, and its axial and radial mechanical residences are extensively distinct. Literature shows that many work has been done by using nanocellulose as reinforcement. Boufi etal. insulated nanofibrillated cellulose( NFC) and cellulose nanocrystals( CNCs) from both the alfa factory and rachis of the date win tree. For the medication of CNC, the pre-treated filaments were acid hydrolyzed with H<sub>2</sub>SO<sub>4</sub> and for the medication of NFC, the pre-treated filaments were TEMPO- oxidized and latterly homogenized at high pressure (16). The morphologyof CNC and NFC turned into depending on the form of the source. The CNC and NFC of the date palm tree reported the loftiest aspect rate compared to the alfa factory. The poly( styrene-co- butylacrylate) mixes were fabricated using the casting system. The DMA studies reported asignificant buttressing effect of the nanofiller on the storehouse modulus of the mixes. Zielińska etal. enzymatically hydrolyzed micrometric



cellulose (Cel\_A) with 20  $\mu$ m particle size and micrometric cellulose (Cel\_B) with 18  $\pm$  3  $\mu$ m flyspeck size usingcellulases. Cellulases from the bitsy fungus trichoderma reesei ATCC 26,921 and Aspergillussp. were used for the hydrolysis. The attained cellulose become in addition used to reinforce the PP matrix. Rao etal. fabricated polymer mixes with a high quantum of( 60 to 90) CNC in epox ide oligomer. The mixer become ultrasonicated and bureaucracy a gel. It was also 3D published or cast andlater thermally cured( performing in crosslinking between the OH groups of cellulose and epoxide groups of epoxy resin monomers). Complex structures with cellulose nanocrystals with high strength, stiffness, durability, and hardness can be developed by this approach. Somseemee and co-workers studied the impact of UV radiation at the cellulose nanocrystal's reinforcement on epoxidized herbal rubber (ENR). The cellulose nanocrystals were extracted from Napier lawn stems. The insulated cellulose nanocrystals and maleic anhydridemodified cellulose nanocrystals were used as the underpinning for epoxidized natural rubber. The ENR and ENR mixes were cured using ultraviolet irradiation. The maleic anhydride- grafted cellulose nanocrystals( 5 wt) modified epoxidized natural rubber showed the stylish tensile strength, modules, and hardness due to better underpinning caused by the better interaction among changed cellulose nanocrystals and epoxidized herbal rubber advised by UV irradiation (17).

Ghasemi andco-workers reused PLA with nanocellulose along with the compatibilizer maleated PLA( PLA- g- Mama) through melt mixing and extrusion and the test specimens were prepared by injection molding. The composition of maleated PLA was 5 wt, while that of the cellulose nanofibers was 3 and 5 wt. Among the mixes, PLA/ CNF5/ PLA- g- MA5exhibited maximum HDT, maximum enhancement in impact strength, maximum tensile strength (138 enhancement), and a 40 enhancement in Young's modulus when compared to neat PLA.

de Souza, etal. in their study, punctuate the insulation of nanocellulose from both cotton waste and artificial paper wastes using acid hydrolysis. The cotton waste(10 wt), artificial paper wastes(3 wt), and isolated nanocellulose from cotton waste(10 wt) and insulated nanocellulose from industrialpaper wastes(3 wt) were incorporated in the PLA matrix as underpinning. The study revealed an enhancement in tensile strength and extension at break with the objectification of nanocellulose. The increase in the parcels was due to the better distribution of the filler and due to the chemical cling of the OH group of nanocellulose and the CO group of the PLA matrix.



Lammetal. explored the operation of chitin as a binary- cling padding in PLA/ nanocellulose mixes. The study reported that on one hand, chitosan formed hydro word bonds with cellulose, and on the other hand, it formed amide bonds with poly( lactic acid) therefore perfecting the interfacial commerce between the PLA and nanocellulose, and improving significantly the mechanical parcels with a small quantum of chitin(2.5 wt).

Further, nanocellulose modified polyvinylalcohol(PVA) mixes were fabricated using the solvent casting system. Water is used as the detergent for making mixes. The thermal stability of PVA/nanocellulose mixes reported bettered declination temperature. The increased thermal stability was due to the hydrogen cling between the cellulose and PVA. The tensile strength and extension at break of the mixes were also reported. It was observed that the mixes with 2 wt percentage nanocellulose showed bettered tensile strength followed by a drop at a advanced percent age of the nanocellulose. This was due to the aggregation of nanocellulose at higher concentrations. On the other hand, the extension at break of PVA gradationally reduced with the incorporation of nanocellulose. The gradational reduction in extension at break was due to the restricted movement of polymer chains in the presence of the nanofillers.

In another study, Gong etal. reported enhancement in tensile strength, tensile modulus, storage modulus, and bettered creep resistance of polyvinyl acetate with the objectification of 10 wt percentage nanocellulose. Ethylene vinyl alcohol is known for its gas hedge parcels, but it has poor humidity resistance that limits its operation in food packaging.

Tang and Liu prepared PVA mixes with a non-transparent electron- spun cellulose nanofibrous mat. The mechanical parcels and translucency were estimated. The PVA com posites with 40 wt percentage cellulose nanofibrous mat showed the stylish tensile strength and modulus, and improved translucency. The high number of OH groups in nanocellulose mats and PVA was responsible for the bettered mechanical parcels and translucency.

Nuruddin etal. developed ethylenevinyl alcohol/ cellulose nanocrystal mixes modified with food- grade compatibilizer( monolaurin) by melt compounding process for implicit food packaging operations. It is observed that the mixes modified with monolaurin showed excellent comity with improved thermo- mechanical and humidity hedge parcels (18).

All these studies proved that nanocellulose reinforced polymer composites have improved properties.



### Conclusion

Nanocellulose makes an ideal nanofiller due to its extremely low particle size, high specific surface area, high modulus, high strength and ease of modification. Nanocellulose reinforced polymers have the ability of improving the strength of the material while not significantly reducing or even enhancing the toughness of the material, which provides more possibilities for the application of the material and being a best competitor to its couterpart. If the existing preparation processes with high energy consumption can be further improved, nanocellulose can also be a widely available cheap natural biomass, biodegradable, nontoxic, biocompatible and environmentally friendly raw material. Hence nanocellulose these factors make nanocellulose an important choice in the fields of biodegradable plastics, bioscaffolds, catalysts and drug carriers. There is an inherent compatibility problem between hydrophilic nanocellulose and most hydrophobic polymer matrices, which greatly affects the dispersion of nanocellulose with the polymer matrix. If these properties are compromised with better modilication, nanocellulose can lead to a more diverse composite design and improve performance. This is both an opportunity and a challenge that researchers also face as challenge in developing modified materials with higher value-added materials. Thus, with further research, nanocellulose reinforced polymer composites are expected to become the most valuable composite material in the coming era in industries.

#### References

- 1. Shuji Fujisawa, Material design of nanocellulose/polymer composites via Pickering emulsion templating, *Polymer Journal* volume 53, pages103–109 (2021)
- Eichhorn SJ, Dufresne A, Aranguren M, Marcovich NE, Capadona JR, Rowan SJ, et al. Review: Current international research into cellulose nanofibres and nanocomposites. J Mater Sci. 2010;45:1–33
- Siró I, Plackett D. Microfibrillated cellulose and new nanocomposite materials: a review. Cellulose. 2010;17:459–94



- Arindam Chakrabarty, Recent Advances in Nanocellulose Composites with Polymers: A Guide for Choosing Partners and How to Incorporate Them, *Polymers* 2018, *10*(5), 517; https://doi.org/10.3390/polym10050517
- Jonoobi, M.; Oladi, R.; Davoudpour, Y.; Oksman, K.; Dufresne, A.; Hamzeh, Y.; Davoodi, R. Different preparation methods and properties of nanostructured cellulose from various natural resources and residues: A review. *Cellulose* 2015, 22, 935–969.
- Grishkewich, N.; Mohammed, N.; Tang, J.; Tam, K.C. Recent advances in the application of cellulose nanocrystals. *Curr. Opin. Colloid Interface Sci.* 2017, 29, 32–45.
- Herrick, F.W.; Casebier, R.L.; Hamilton, J.K.; Sandberg, K.R. Microfibrillated cellulose: Morphology and accessibility. In Proceedings of the Ninth Cellulose Conference, Syracuse, NY, USA, 24–27 May 1982; Volume 37, pp. 797–813.
- Turbak, A.F.; Snyder, F.W.; Sandberg, K.R. Microfibrillated cellulose, a new cellulose product: Properties uses, and commercial potential. In Proceedings of the Ninth Cellulose Conference, Syracuse, NY, USA, 24–27 May 1982; Volume 37, pp. 815–827.
- 9. Miao, C.; Hamad, W.Y. Cellulose reinforced polymer composites and nanocomposites: A critical review. *Cellulose* **2013**, *20*, 2221–2262.
- 10. Manjunathan Alagarsamy, Reinforcement of Nanocellulose as Green Agent in the Electronic Applications Associated with the Composites of Polymer Matrix, Volume 2023 | Article ID 9645190 | <u>https://doi.org/10.1155/2023/9645190</u>
- Kumar, V.; Pathak, P.; Bhardwaj, N. K. Waste paper: An Underutilized but Promising Source for Nanocellulose Mining. *Waste Manage*. 2020, *102*, 281–303, DOI: 10.1016/j.wasman.2019.10.041
- Mao, Y.; Liu, K.; Zhan, C.; Geng, L.; Chu, B.; Hsiao, B. S. Characterization of Nanocellulose Using Small-Angle Neutron, X-ray, and Dynamic Light Scattering Techniques. J. Phys. Chem. B 2017, 121, 1340–1351, DOI: 10.1021/acs.jpcb.6b11425
- Zhao, C.; Zhang, Y.; Wang, C.-C.; Hou, M.; Li, A. Recent Progress in Instrumental Techniques for Architectural Heritage Materials. *Herit. Sci.* 2019, 7, 36



- Oh, S. Y.; Yoo, D. I.; Shin, Y.; Seo, G. FTIR Analysis of Cellulose Treated with Sodium Hydroxide and Carbon Dioxide. *Carbohydr. Res.* 2005, 340, 417–428, DOI: 10.1016/j.carres.2004.11.027
- Lu, P.; Hsieh, Y.-L. Preparation and characterization of cellulose nanocrystals from rice straw. Carbohydr. Polym. 2012, 87, 564–573
- Saito T, Nishiyama Y, Putaux JL, Vignon M, Isogai A. Homogeneous suspensions of individualized microfibrils from TEMPO catalyzed oxidation of native cellulose. Biomacromolecules. 2006;7:1687–91.
- 17. Renjie Shen, Research Progress and Development Demand of Nanocellulose Reinforced Polymer Composites, *Polymers* 2020, *12*(9), 2113; https://doi.org/10.3390/polym12092113
- Karmaker N., Islam F., Islam M.N., Razzak M., Koly F.A., Chowdhury A.M.S., Khan R.A. Fabrication and Characterization of PVA-Gelatin-Nano Crystalline Cellulose based Biodegradable Film: Effect of Gamma Radiation. J. Res. Updates Polym. Sci. 2019;8:7–14. doi: 10.6000/1929-5995.2019.08.02