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Chapter

Production, Processes and Modification of Nanocrystalline Cellulose from Agro-Waste: A Review

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Abstract

Nanocrystalline cellulose is a renewable nanomaterial that has gained huge attention for its use in various applications from advanced biomedical material to food packaging material due to its exceptional physical and biological properties, such as high crystallinity degree, large specific surface area, high aspect ratio, high thermal resistance, good mechanical properties, abundance of surface hydroxyl groups, low toxicity, biodegradability, and biocompatibility. However, they still have drawbacks: (1) sources of raw materials and its utilization in the production of nanocomposites and (2) high chemical and energy consumption regarding the isolation of macro-sized fibers to nano-sized fibers. The incorporation of hydrophilic nanocrystalline cellulose within hydrophobic polymer limits the dispersion of nano-sized fibers, thus resulting in low mechanical properties of nanocomposites. Hence, surface modification on nano-sized fiber could be a solution to this problem. This review focuses on the advanced developments in pretreatment, nanocrystalline production and modifications, and its application in food packaging, biomedical materials, pharmaceutical, substitution biomaterials, drug excipient, drug delivery automotive, and nanopaper applications.

Keywords: nanocrystalline cellulose, nanocomposites, surface modification, hydrolysis, agro-waste

1. Introduction

During the past decades, huge efforts have been made to improve new chemicals and/or materials and replace broadly used petroleum-based products by utilizing biomass renewable feedstock [1–3]. Biocompatible composites and biodegradable plastics produced from biorenewable resources are regarded as promising biomaterials that could replace petrochemical-based polymers and hence reduce global dependence on nonrenewable sources (i.e., fossil fuels: coal, petroleum, and natural gas) and provide simplified recycling or end-of-life disposal [4–10].

Agro-based industry's function is to increase the value of raw agricultural products through downstream processing so that products are marketable, consumable, and

used to generate income and provide profit to the producer [11]. However, there is waste generated through the process of downstream and upstream of agro-industry. The composition of industrial wastes varies depending on the types of industry as different countries apply various categories for industrial waste which contribute adversely to air, soil, and water quality. This is due to some of the industrial wastes which are neither toxic nor hazardous. For example, organic wastes, such as corncob, sugarcane bagasse, sugar palm (fiber, frond, bunch, trunk), areca nut husk fiber, wheat straw fiber, soy hull fiber, pineapple leaf fiber, oil palm (mesocarp fiber, empty fruit bunch, frond), rubber wood thinning, curaua fiber, banana fiber, water hyacinth fiber, wheat straw, sugar beet fiber, etc. that are produced by agro-based industries are not hazardous in nature and thus have potential for other uses [12–14]. **Figure 1** shows the by-products of agro-industry that are used for sources of lignocellulose biomass.

Biomass renewable feedstocks are of great interest due to the possibility of nontoxicity, renewability, and biodegradability as well as sustainability [12–17]. Lignocellulosic can be classified as lower-value biomass (LVB). Lower-value biomass (LVB) in forest or agriculture industry constitutes noncommercial material traditionally left on site following harvesting of crops. However, emerging markets for energy, chemicals, and bioproducts have increased incentives to harvest and utilize this material in some cases [20–25]. Lignocellulosic biomass suppliers do not use any kind of wood indiscriminately due to economic and environmental reasons; they usually used mobilized woody biomass sourced from by-products of forest operations, agriculture, and crops' waste as well as the wood industry waste such as sawmills. Lignocellulosic biomass sector has been developed to work in synergy with other agro-based industry and wood-based industries to give value to non-mobilized and/or low-value biomass such as trunk, fiber, sugar cane bagasse, manure bedding, plant stalks, vines, hulls, leaves, vegetable matter, sawdust, mill

Figure 1.
By-products of agro-industry that are used for sources of lignocellulose biomass.

Figure 2.
By-products of forest operation that are used for sources of lignocellulose biomass. Adapted from Ref. [23]. http://www.europeanbioenergyday.eu/solid-bioenergy-in-questions-an-asset-to-eu-forests/.

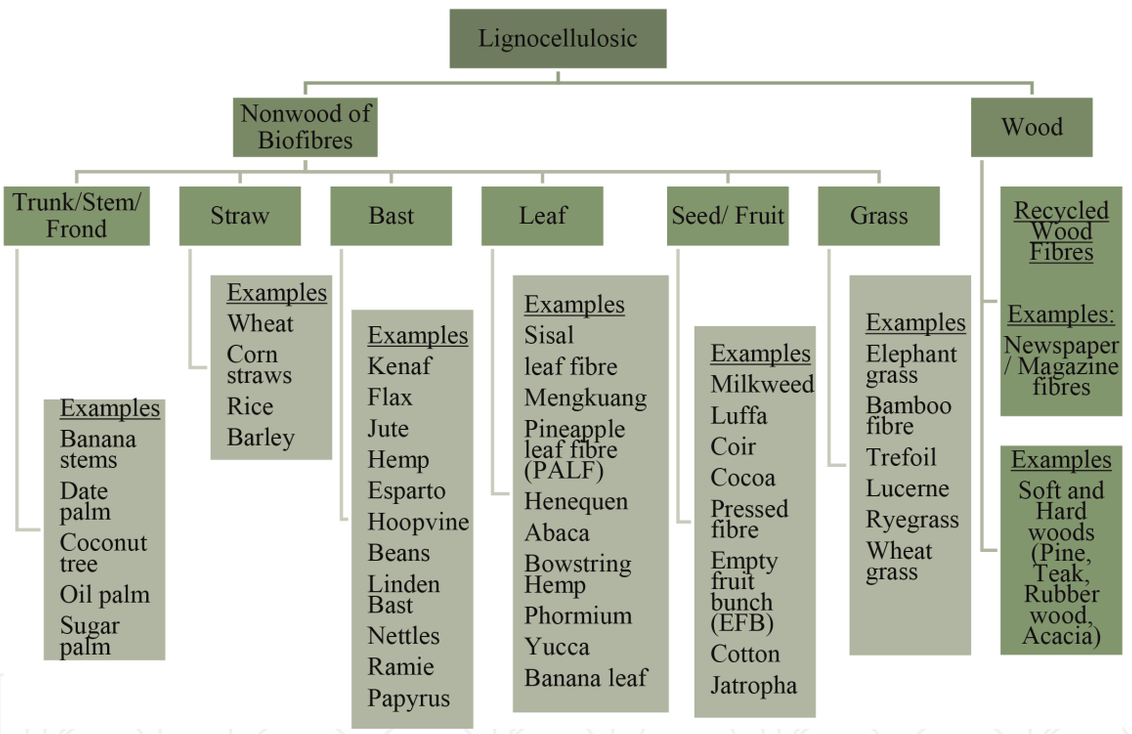

Figure 3.
Schematic representation of lignocellulosic agro-waste and by-product of forest classification. Adapted from Ref. [7].

residues, thinnings, low-quality wood, tops, and limbs. Biomass generators do not use high-quality timber or main agricultural products, as using lumber or major crops would make the price of biomass wholly uncompetitive for end consumers. **Figure 2** shows the by-products of forest operation that are used for sources of lignocellulose biomass. Natural fibers or lignocellulosic fibers can be classified into two main groups that are wood and non-wood bio-fibers (**Figure 3**). This review will be focusing on production, processes, modification, and application of nanocrystalline cellulose from agro-waste.

2. Lignocellulosic biomass from agro-waste fiber and forest by-products

Lignocellulosic biomass comprises of three major chemical components that are cellulose, lignin, and hemicellulose [18–21]. The chemical compositions of

Fibers	Holocellulose (wt%)		Lignin (wt%)	Ash (wt%)	Extractives (wt%)	Crystallinity (%)	Ref.
	Cellulose (wt%)	Hemicellulose (wt%)					
Sugar palm fiber	43.88	7.24	33.24	1.01	2.73	55.8	[6]
Sugar palm frond	66.49	14.73	18.89	3.05	2.46	—	[28]
Sugar palm bunch	61.76	10.02	23.48	3.38	2.24	—	[28]
Sugar palm trunk	40.56	21.46	46.44	2.38	6.30	—	[28]
Wheat straw fiber	43.2 ± 0.15	34.1 ± 1.2	22.0 ± 3.1	—	—	57.5	[29]
Soy hull fiber	56.4 ± 0.92	12.5 ± 0.72	18.0 ± 2.5	—	—	59.8	[29]
Areca nut husk fiber	34.18	20.83	31.60	2.34	—	37	[14]
Helicteres isora plant	71 ± 2.6	3.1 ± 0.5	21 ± 0.9	—	—	38	[30]
Pineapple leaf fiber	81.27 ± 2.45	12.31 ± 1.35	3.46 ± 0.58	—	—	35.97	[31]
Ramie fiber	69.83	9.63	3.98	—	—	55.48	[32]
Oil palm mesocarp fiber (OPMF)	28.2 ± 0.8	32.7 ± 4.8	32.4 ± 4.0	—	6.5 ± 0.1	34.3	[33]
Oil palm empty fruit bunch (OPEFB)	37.1 ± 4.4	39.9 ± 0.75	18.6 ± 1.3	—	3.1 ± 3.4	45.0	[33]
Oil palm frond (OPF)	45.0 ± 0.6	32.0 ± 1.4	16.9 ± 0.4	—	2.3 ± 1.0	54.5	[33]
Oil palm empty fruit bunch (OPEFB) fiber	40 ± 2	23 ± 2	21 ± 1	—	2.0 ± 0.2	40	[34]
Rubber wood	45 ± 3	20 ± 2	29 ± 2	—	2.5 ± 0.5	46	[34]
Curaua fiber	70.2 ± 0.7	18.3 ± 0.8	9.3 ± 0.9	—	—	64	[35]
Banana fiber	7.5	74.9	7.9	0.01	9.6	15.0	[36]
Sugarcane bagasse	43.6	27.7	27.7	—	—	76	[37]
Kenaf bast	63.5 ± 0.5	17.6 ± 1.4	12.7 ± 1.5	2.2 ± 0.8	4.0 ± 1.0	48.2	[38]
Phoenix dactylifera palm leaflet	33.5	26.0	27.0	6.5	—	50	[39]

Fibers	Holocellulose (wt%)		Lignin (wt%)	Ash (wt%)	Extractives (wt%)	Crystallinity (%)	Ref.
	Cellulose (wt%)	Hemicellulose (wt%)					
Phoenix dactylifera palm rachis	44.0	28.0	14.0	2.5	—	55	[39]
Kenaf core powder	80.26	23.58	—	—	—	48.1	[40]
Water hyacinth fiber	42.8	20.6	4.1	—	—	59.56	[41]
Wheat straw	43.2 ± 0.15	34.1 ± 1.2	22.0 ± 3.1	—	—	57.5	[42]
Sugar beet fiber	44.95 ± 0.09	25.40 ± 2.06	11.23 ± 1.66	17.67 ± 1.54	—	35.67	[43]
Mengkuang leaves	37.3 ± 0.6	34.4 ± 0.2	24 ± 0.8		2.5 ± 0.02	55.1	[44]

Table 1.
Chemical composition of agro-waste fibers and forest by-products from different plants and different parts.

	Cellulose	Hemicellulose	Lignin
Structure	• Cellulose is assembled together with pectin fibers, which function to bind the cellulose together to produce tighter cell walls in natural fibers, accounting for their strength providing resistance to lysing in the presence of water • Hemicelluloses consist of long chain—7000–15,000 glucose molecules per polymer	• Hemicellulose is a cell wall polysaccharide that has the capacity to bind strongly to cellulose microfibrils by hydrogen bonds • Hemicelluloses consist of short chains—500–3000 glucose molecules per polymer	• Lignin is a cross-linked polymer with molecular masses in excess of 10,000 u
Function	• Connecting cells to form tissue • Provide structural support • Provides a strong resistance to stress • Prevents the cell from bursting in hypotonic solution	• Responsible for the moisture absorption, biodegradation • Microfibrils are cross-linked together by hemicellulose homopolymers	• Responsible for UV degradation • Lignin assists and strengthens the attachment of hemicelluloses to microfibrils • Lignin plays a crucial part in conducting water in plant stems
Properties	• Thermal stability (occurred from 315 to ~400°C)	• Thermal stability occurred from 220 to ~315°C	• Thermal stability occurred from 165 to ~900°C

Table 2.
Functions and properties of cellulose, hemicellulose, and lignin. Adapted from Refs. [6, 7, 27].

agro-waste fibers are different depending on the type of fiber as summarized in **Table 1**. Besides that, it can be concluded in **Table 1** that the highest cellulose contents are pineapple leaf fibers (81.27%), followed by kenaf core powder (80.26%). Besides that, from **Table 1** also we can summarize that the chemical composition of natural fibers is 30–80% cellulose, 7–40% hemicellulose, and 3–33% lignin. Cellulose, hemicellulose, and lignin have their own properties and functionality. **Table 2** shows the functional properties of the cellulose, hemicellulose, and lignin. The physical, thermal, and mechanical properties of the natural fibers are diverse between each other as they are mostly depending on cellulose crystallinity. Intra- and intermolecular hydrogen bonding among the cellulose chains affects the packing compactness of cellulose crystallinity. **Table 1** shows the chemical composition of natural fibers and their crystallinity. From the abovementioned lignocellulosic, particularly, the hemicellulose and cellulose have promising features such as existing refining agro-forest or agro-waste factories. For centuries, cellulose has been utilized in the form of non-wood plant fibers and wood as building materials, clothing, textile, and paper.

3. Nanocrystalline cellulose

Nanocrystalline cellulose (NCC) has several notable optical, chemical, and electrical properties due to their needlelike shape, high surface area, high aspect ratio

(length/diameter), high crystallinity, nanoscale size, high strength and stiffness, low density, and highly negative charge which lead to unique behavior in solutions. The high chemical reactivity of the surface makes NCC customizable for various applications, besides their heat stability which allows high-temperature applications. Moreover, they also have huge surface OH groups which provide active sites for hydrogen bonding through the interlocking with nonpolar matrix [4, 7, 10, 45, 46]. Nanocrystalline cellulose can be isolated from cellulose as shown in **Figure 4**. The nanocellulose can be obtained through two approaches: top-down by the disintegration of plant fiber or bottom-up by biosynthesis [46]. For bottom-up biosynthesis approach, fermentation of low-molecular-weight sugars occurred by using bacteria from *Acetobacter* species. Meanwhile, for the top-down approach, the production of nanocrystalline cellulose is chemically induced via removing amorphous region. The chemical or mechanical treatments or a combination of both treatments involves enzymatic treatment, grinding, high-pressurized homogenization, acid hydrolysis, TEMPO-mediated oxidation, microfluidization, cryocrushing, and high-intensity ultrasonification. **Table 3** shows the hydrolysis approaches from various sources of agro-waste and forest by-product for NCC isolation.

Figure 4.
Schematic representation of lignocellulosic agro-waste and by-product of forest classification. Adapted from Ref. [47].

Source	Process	References
Acacia mangium	H_2SO_4 hydrolysis	[56]
Algae	H_2SO_4 hydrolysis	[57]
Areca nut husk fiber	HCl hydrolysis	[14]
Bacterial cellulose	H_2SO_4 hydrolysis	[58]
Bamboo	H_2SO_4 hydrolysis	[59]
Bamboo (*Pseudosasa amabilis*)	H_2SO_4 hydrolysis	[60]
Banana fiber	$H_2C_2O_4$ hydrolysis	[31]
Banana pseudo-stem	TEMPO-mediated oxidation, formic acid hydrolysis	[61]
Cassava bagasse	H_2SO_4 hydrolysis	[62]

Source	Process	References
Coconut husk	H_2SO_4 hydrolysis	[63]
Colored cotton	H_2SO_4 hydrolysis	[64]
Corncob	H_2SO_4 hydrolysis	[13]
Cotton (cotton wool)	H_2SO_4 hydrolysis	[65]
Cotton linters	HCl hydrolysis	[66]
Cotton Whatman filter paper	H_2SO_4 hydrolysis	[67]
Cotton (*Gossypium hirsutum*) linters	H_2SO_4 hydrolysis	[68]
Cotton stalk	TEMPO-mediated oxidation and H_2SO_4 hydrolysis	[69]
Cotton fiber	H_2SO_4 hydrolysis	[70]
Curaua fiber	H_2SO_4, H_2SO_4/HCl, HCl hydrolysis	[35]
Eucalyptus kraft pulp	H_2SO_4 hydrolysis	[71]
Grass fibers	H_2SO_4 hydrolysis	[72]
Grass fibers (*Imperata brasiliensis*)	H_2SO_4 hydrolysis	[73]
Groundnut shells	H_2SO_4 hydrolysis	[74]
Hibiscus sabdariffa fibers	Steam explosion H_2SO_4 hydrolysis	[75]
Humulus japonicus stem	H_2SO_4 hydrolysis with high-temperature pretreatment	[76]
Industrial bioresidue	H_2SO_4 hydrolysis	[77]
Industrial bioresidue (sludge)	H_2SO_4 hydrolysis	[78]
Kraft pulp	H_2SO_4 hydrolysis	[79]
Kenaf core wood	H_2SO_4 hydrolysis	[40]
MCC	H_2SO_4 hydrolysis	[55]
Mengkuang leaves	H_2SO_4 hydrolysis	[44]
Mulberry	H_2SO_4 hydrolysis	[80]
Oil palm trunk	H_2SO_4 hydrolysis	[81]
Oil palm empty fruit bunch (OPEFB)	H_2SO_4 hydrolysis	[82]
Phormium tenax (harakeke) fiber	H_2SO_4 hydrolysis	[83]
Potato peel waste	H_2SO_4 hydrolysis	[84]
Flax fiber	H_2SO_4 hydrolysis	[83]
Ramie	KOH hydrolysis	[85]
Ramie	H_2SO_4 hydrolysis	[86]
Ramie	H_2SO_4 hydrolysis	[87]
Rice husk	H_2SO_4 hydrolysis	[63]
Rice straw	H_2SO_4 hydrolysis	[88]
Sesame husk	H_2SO_4 hydrolysis	[89]
Sisal fiber	H_2SO_4 hydrolysis	[90]
Soy hulls	H_2SO_4 hydrolysis	[91]
Sugar palm fiber	H_2SO_4 hydrolysis	[6]
Sugar palm frond	H_2SO_4 hydrolysis	[92]

Source	Process	References
Sugarcane bagasse	H_2SO_4 hydrolysis	[37]
Sago seed shells	H_2SO_4 hydrolysis	[93]
Tunicate	H_2SO_4 hydrolysis	[94]
Water hyacinth fiber	HCl hydrolysis	[48]
Wood pulp	TEMPO oxidation followed by HCl hydrolysis	[95]
Wheat straw	H_2SO_4 hydrolysis	[96]
Valonia ventricosa	HCl hydrolysis	[97]

Table 3.
Available process of extraction approaches from different sources for NCC isolation.

4. Processes of nanocrystalline cellulose

Recently, researchers are exploring the potential utilization of agriculture or forest wastes as NCCs' sources. As a consequence, the various local sources are used to investigate the potential of NCC in certain technologies. The isolation of NCC needs intensive hydrolysis chemical treatment. However, according to the degree of processing and raw material, physical, chemical, enzymatic, and ionic pretreatments are performed before nanocrystalline cellulose synthesis. **Figure 5** shows the sources, pretreatments, synthesis, and application of nanocrystalline cellulose. It is good to know that appropriate pretreatments of cellulosic fibers promote the accessibility of hydroxyl group, alter crystallinity, increase the inner surface, and break cellulose hydrogen bonds and hence improved the reactivity of the fibers [6, 7, 10]. Several approaches to diminish cellulosic fibers into nanofibers can be divided into several techniques such as acid hydrolysis, alkali treatment, mechanical treatments, and combination of mechanical and chemical treatments. Common methods for isolate NCC are hydrolysis methods which are a chemical method. **Figure 6** shows

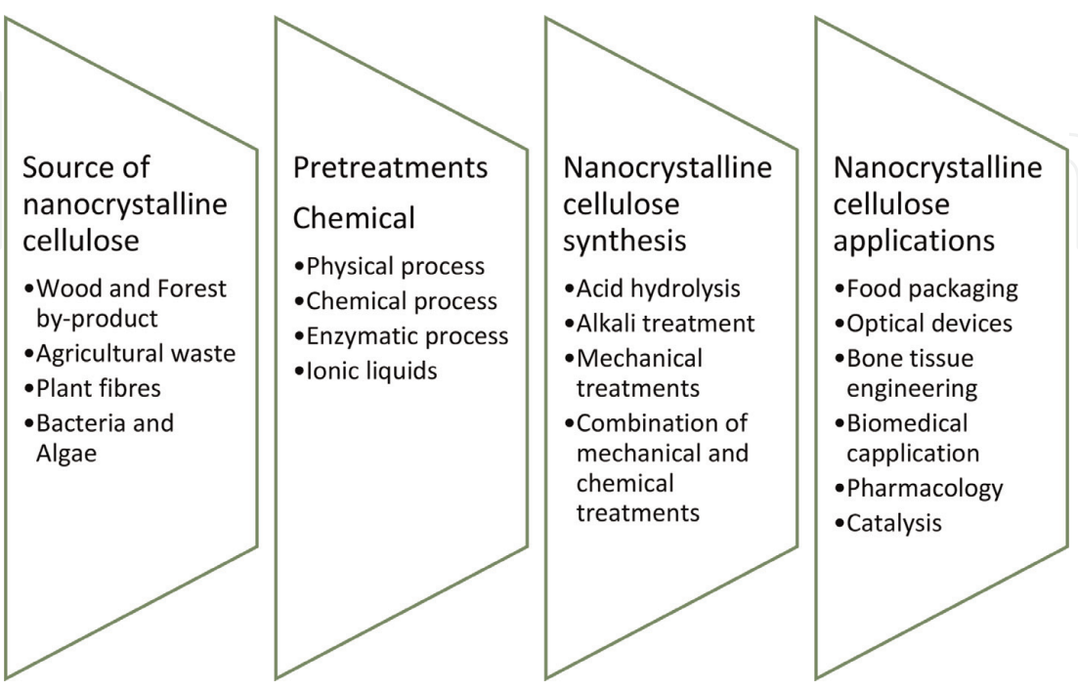

Figure 5.
Sources, pretreatments, synthesis, and application of nanocrystalline cellulose. Adapted from Refs. [6, 7, 10].

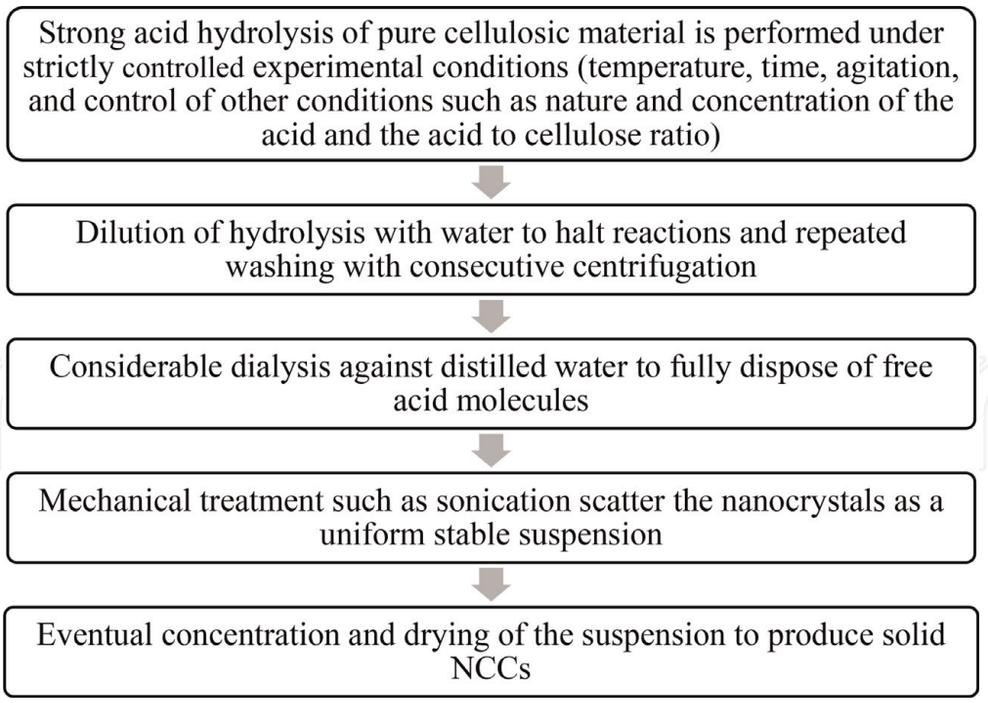

Figure 6.
Typical process for the production of nanocrystalline cellulose. Adapted from Refs. [4, 5, 8].

the typical process for the production of nanocrystalline cellulose. Hydrolysis process includes inserting raw plant fibers into a strong acidic environment with the help of mechanical agitation. Concentrated acid and shear forces on solution generate shear rates in the stream and decrease the size of fibers to the nanoscale. Sulfuric acid (H_2SO_4) is commonly used in the isolation process of NCC besides other chemicals such as HCL [48], HBr [49], and H_3PO_4 [50]. Hydrolysis process using sulfuric acid solution resulted in a high number of negatively charged sulfate groups on the surface of NCC. This process limits the agglomeration and flocculation of NCC in an aqueous medium [51]. The drawback from this process is that the NCC displays moderate thermostability. Hence to overcome this drawback, the NCC will either undergo dialysis process using distilled water to fully dispose free acid molecules or use sodium hydroxide (NaOH), which functions to neutralize nanoparticles [52]. **Figure 7** displays three steps in the mechanism of acid hydrolysis [53]:

1. Development of conjugated acid by reactions between oxygen protons and glycoside acid

2. Breaking down of C-O bonds and segregation of conjugated acid into cyclic carbonium ions

3. Release of the proton and free sugar after the addition of water

There are numerous studies that have been conducted on the effects of concentration of acid, acid-to-fiber ratio, and temperature and time of the hydrolysis process on the dimensions and morphological properties of yielded nanocrystalline cellulose. According to Azizi et al. [29], there is a strong relationship between the hydrolysis time and acid-to-fiber ratio to the length and dimensions of nanocrystalline cellulose, which by increasing the hydrolysis time and acid-to-fiber ratio would reduce the dimension and length of nanocrystalline cellulose.

Besides that, there are large numbers of published studies [51, 54] that describe the dimension, size, and shape of NCC that were affected by the conditions of hydrolysis process (purity of the material, temperature, time, and ultrasound

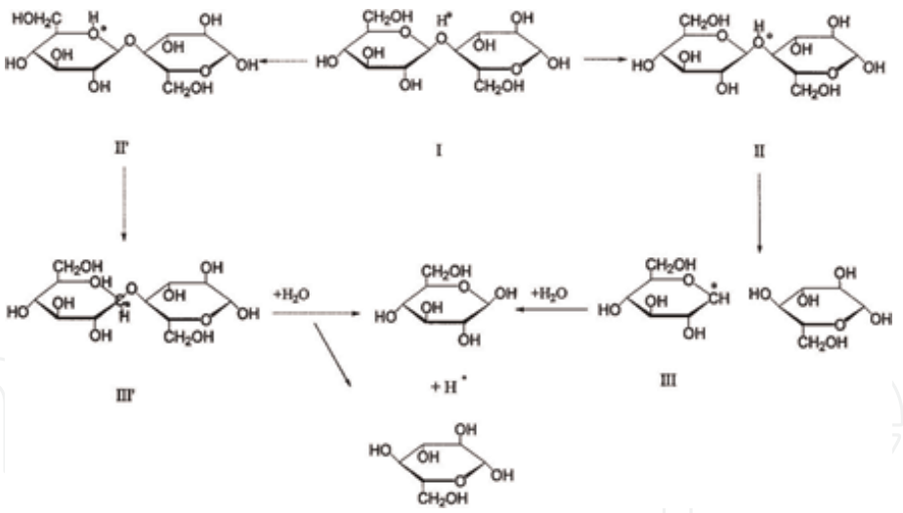

Figure 7.
Mechanism of hydrolysis of acid [53].

treatment) and a variety of cellulosic fiber sources. Bondeson et al. [55] conducted an experiment on the isolation of NCC and found that the optimized condition is at a concentration of 63.5% H_2SO_4, which yielded 38 wt.% of NCCs with a width of 10 nm. Another experiment that is conducted by Ilyas et al. [6] found that the optimum yield for isolating sugar palm nanocrystalline cellulose is at a concentration of 60 wt% H_2SO_4 and duration hydrolysis of 45 min, with length and diameters of 130 ± 30 and 9 ± 1.96 nm, respectively. **Table 3** shows the preparation of NCC using various acid hydrolysis processes from different cellulosic sources. Typical procedures for NCC extraction are composed of several steps: strong acid hydrolysis, dilution, dialysis, sonification, and drying of NCC.

5. Limitation and modification of nanocrystalline cellulose

There are several limitations when using natural fibers as reinforcement filler in the polymer matrix such as single-particle dispersion, barrier properties,

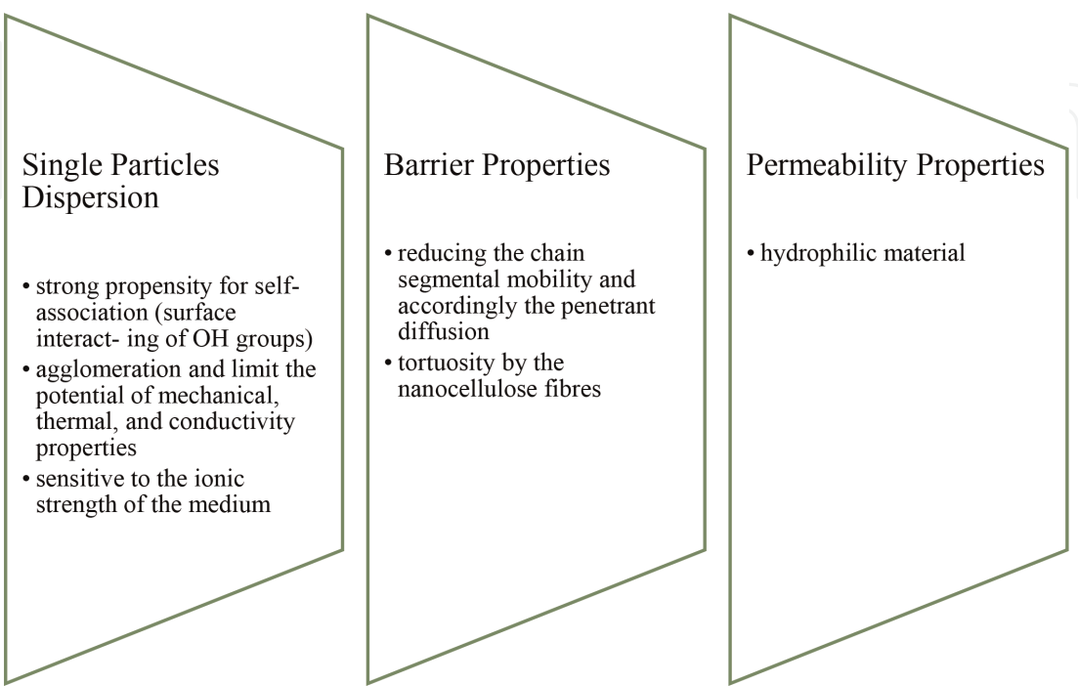

Figure 8.
Limitation of nanocellulose. Adapted from Refs. [6, 7, 10].

permeability properties, and poor interfacial adhesion (**Figure 8**). Nanocrystalline cellulose has a strong propensity of self-association due to the interaction of abundance OH groups within its surface, which causes agglomeration and limits its potential applications. Besides, hydrophilic properties of nanocrystalline cellulose make it difficult to disperse homogenously within any medium and matrix. Therefore, in order to overcome the incompatible nature, poor interfacial adhesion, and difficult dispersion of nanocrystalline cellulose in a polymer matrix, surface modification of fibers or modification of matrix is introduced. Nanocellulose displays a high surface area valued more than 100 m^2/g. This gives advantages to nanocellulose for surface modification in order to introduce any desired surface functionality. However, according to Postek et al. [98], the surface chemistry of nanocellulose is primarily controlled by the process of isolation that used to prepare these nanocelluloses from raw cellulose substrate. **Figure 9** shows the most common surface chemical modifications of nanocrystalline cellulose. Surface modification of NCC can be categorized into three typical groups, namely, (1) polymer grafting based on "grafting onto" strategy with different coupling agents (as indicated with blue arrows in **Figure 9**), (2) substitution of hydroxyl group with small molecules (as indicated with red arrows in **Figure 9**), and (3) polymer grafting

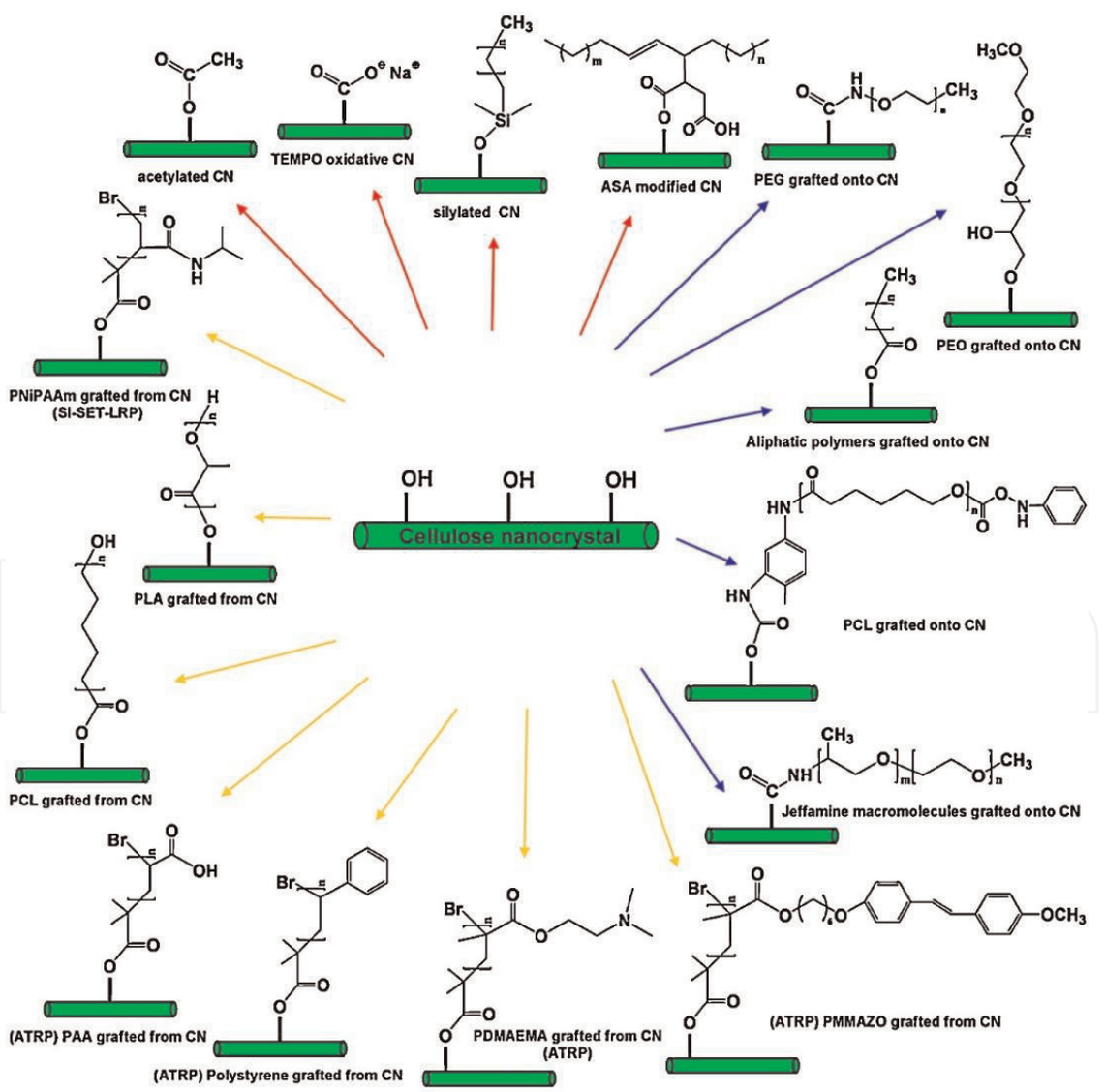

Figure 9.
Schematic diagram illustrating nanocellulose surface functionalization modification. PEG, poly(ethylene glycol); PEO, poly(ethylene oxide); PLA, poly(lactic acid); PAA, poly(acrylic acid); PNiPAAm, poly(N-isopropylacrylamide); PDMAEMA, poly(N,N-dimethylaminoethyl methacrylate). Adapted from Ref. [99].

based on the "grafting from" approach with a radical polymerization involving single-electron transfer-living radical polymerization (SET-LP), ring opening polymerization (ROP), and atom transfer radical polymerization (ATRP) (as indicated with yellow arrows in **Figure 9**). The enhancement of NCC-polymer matrix interaction is predicted to improve the stress transfer from the matrix to the dispersed phase and hence enhances the capability of load bearing material. Besides, the chemical modification of NCC can be dispersed in the low polarity of organic solvent and mixed with a polymer matrix solution or directly introduced into the polymer melt after drying. Nevertheless, two effects ascend from this process: (1) allow the improvement of dispersion of modified NCC in the polymer matrix and (2) limit the interaction between NNC and matrix through hydrogen bonding which is the basis of the outstanding mechanical properties of nanocellulose-based nanocomposites.

6. Applications of nanocrystalline cellulose from agro-waste fiber and forest by-products

The incorporation of nanocrystalline cellulose in biopolymers for the nanocomposite production provides huge advantages with superior performance which would extend their applications in various applications. This is due to their outstanding thermal and mechanical properties. NCC also can reduce the water vapor permeability of the composites due to its high gas permeability [26]. Besides that, NCC can be used to stabilize the encapsulated bioactive compounds in biopolymers for allowing better control in food applications which can improve the food quality, extend the shelf-life of food, and serve as active substance carriers such as antifungal, antioxidant compounds, antimicrobial, and insecticide.

The utilization of natural cellulose-based materials continues today as verified by the various industry players from forest product to make pulp and paper to the advanced technology used in biomedical applications. These uses have been reported extensively as summarized in **Table 4**. NCC can be used as a drug delivery

Polymer component	Manufacturing technique	Applications	References
Cellulose esterified with lauroyl chloride	Solution casting and thermopressing	Interface melting	[101]
Ethyl acrylate; methyl-methacrylate	Solution mixing	Drug carrier	[100]
Ethylene-co-vinyl acetate rubber	Solution mixing and vulcanization	Transparent, rubbery materials	[102]
Maleic-anhydride grafted PLA	Electrospinning	Bone tissue engineering	[103]
Methylcellulose	Hydrogel by aqueous dispersion	Thermoreversible and tunable nanocellulose-based hydrogels	[104]
PC	Masterbatch melt extrusion process	Optical devices	[105]
PC-based polyurethane blend	Solution casting	Smart actuators and sensors	[106]
Plasticized PLA	Twin-screw extruder	Film blowing, packaging	[107]
Plasticized starch	Solution casting	Transparent materials	[108]

Polymer component	Manufacturing technique	Applications	References
PU	Solution casting	High temperature biomedical devices	[109]
PVA	Solution casting	Stretchable photonic devices	[110]
PVA	Solution casting	Wound diagnosis/biosensor scaffolds	[111]
PVA	Solution casting	Conductive materials	[112]
Starch	Blending, solution casting	Air permeable, resistant, surface-sized paper, food packaging	[113, 114]
Starch	Solution casting	Food packaging	[60]
Cassava starch	Solution casting	Food packaging	[62]
Sugar palm starch	Solution casting	Food packaging	[115]
Wheat starch	Solution casting	Food packaging	[87]
Tuber native potato	Solution casting	Packaging	[116]
Cereal corn	Solution casting	Packaging	[116]
Legume pea	Solution casting	Packaging	[116]
Waterborne acrylate	Solution mixing	Corrosion protection	[79]
Wheat straw hemicelluloses	Solution casting	Packaging	[96]
PVA	Solution casting	Food packaging	[83]
Chitosan	Solution casting	Food coating/packaging	[70]

Table 4.
Polymer component reinforced NCCs and its manufacturing technique and applications.

excipient; Burt et al. [100] investigated the capability of pure NCC to bind water-soluble antibiotics (tetracycline and doxorubicin) and the potential of cationic NCC to bind non-ionized hydrophobic anticancer agents (docetaxel, paclitaxel, and etoposide). Moreover, besides direct use as drug delivery excipient, NCC can also be used as co-stabilizer to improve the physicochemical and flow properties of polymeric excipients. Acrylic beads prepared via emulsion polymerization using NCC as co-stabilizer were proven to be a suitable excipient.

Table 5 shows several nanocelluloses, NFCs, and NCCs that have been used as reinforcement fillers in polymer matrices. The polymer matrices used are from both synthetic and natural polymers. **Table 6** shows examples of NCCs used as fillers in polymeric matrices.

Source	Filler	Polymer matrix	Ref.
Sugar palm	NCC	Sugar palm starch	[117]
Sugar palm	NFC	Sugar palm starch	[115]
Acacia mangium	NCC	PVA	[56]
Bacteria	NCC	CAB (0–10 wt% filler)	[58]
Cotton	NCC	PVA (0–12 wt% filler)	[118]
Flax	NFC/NCC	PVA (10 wt% filler), waterborne polyurethanes (0–30 wt% filler)	[119, 120]
Hemp	NFC	PVA (10 wt% filler)	[120]
Kraft pulp	NCC	Waterborne acrylate	[79]

Source	Filler	Polymer matrix	Ref.
MCC	NCC	PLA (5 wt% filler)	[121]
Potato pulp	NFC	Starch/glycerol (0–40 wt% filler)	[122]
Ramie	NFC	Unsaturated polyester resin	[85]
Ramie	NCC	Starch/glycerol (0–40 wt% filler)	[87]
Rutabaga	NFC	PVA (10 wt% filler)	[120]
Soy hulls	NFC	No attempts were made with composites	[29]
Sugar beet	NFC/NCC	Styrene/butyl acrylate (6 wt% filler)	[123]
Tunicate	NCC	Styrene/butyl acrylate (6 wt% filler), starch/sorbitol (25 wt% filler), waterborne epoxy (0.5–5 wt% filler)	[94, 124–126]
Water hyacinth fiber	NCC	Yam bean starch	[48]
Water hyacinth fiber	NFC	Yam bean starch	[127]
Wheat straw	NFC	No attempts were made with composites	[29]
Wheat straw	NCC	Wheat straw hemicelluloses	[96]
Wood pulp	NFC/NCC	PVA (10 wt% filler), PLA (5 wt% filler)	[120, 128]
Cassava bagasse	NCC	Cassava starch	[62]
Ramie	NCC	Wheat starch	[87]
Phormium tenax (harakeke) fiber	NCC	PVA	[83]
Flax fiber	NCC	PVA	[83]
Potato peel fiber	NCC	Starch	[84]

Table 5.
Different nanocellulose sources of reinforcement fillers in polymer matrices.

Polymer	References
Cellulose acetate butyrate	[58, 129]
Cellulose	[130]
Chitosan	[131–133]
Poly(acrylic) acid, PAA	[134]
Poly-(allylmethylamine hydrochloride), PAH	[135]
Poly-(dimethyldiallylammonium chloride), PDDA	[136]
Poly(ethylene-co-vinyl acetate), EVA	[137]
Poly(hydroxyalkanoate), PHA	[133, 138]
Poly(hydroxyoctanoate), PHO	[139]
Poly(lactic acid), PLA	[118, 121, 140–144]
Poly(methyl-methacrylate), PMMA	[145, 146]
Poly(oxyethylene), PEO	[147, 148]

Polymer	References
Poly(styrene-co-butyl acrylate)	[94, 149, 150]
Poly(vinyl alcohol) (PVA)	[56, 83, 151]
Poly(vinyl alcohol), PVOH	[67, 152–154]
Polycaprolactone, PCL	[155–157]
Polypropylene, PP	[158, 159]
Polystyrene	[160]
Polysulfone	[161]
Polyurethane, PU	[162–164]
Polyvinyl chloride, PVC	[165–167]
Regenerated cellulose	[168, 169]
Soy protein	[170]
Starch-based polymers	[60, 62, 84, 152, 171–173]
Waterborne acrylate	[79]
Xylan	[174–176]
Hemicellulose	[96]

Table 6.
NCC used as filler in polymeric matrices.

7. Conclusion

Agro-waste is an unavoidable by-product that arises from various agricultural and agro-forest activities' operation. However, different kinds of agro-product industries, change of lifestyle, and population growth are assumed to be within the main factors that increase the rate of waste generation globally and locally. Therefore, proper waste management selections are very important based on the types of wastes and cost-effective factors in order to reduce the damage to the ecosystem. One of the alternatives to reduce agro-waste disposal is converting it to high-end value products such as nanocrystalline cellulose. In the present work, an overview of the production, processes, modification, and application of nanocrystalline cellulose from different agricultural wastes was proposed and leads to the following main concluding remarks: (1) it is important to select the proper raw material of agro-waste fiber, due to a broad variety of structure and chemical composition and its pretreatment process before the extraction process of nanocellulose begin; (2) the surface charge and morphology of nanocrystalline cellulose are affected by the production conditions such as hydrolysis time, temperature, and the acid-to-fiber ratio; and (3) nanocrystalline cellulose can be used in various applications including in hydrophobic polymer after some modification is made. The utilization of several lignocellulosic wastes from agricultural and forest by-product activities becomes the best proposal regarding cost/energy savings and economic development. The agricultural residue is available worldwide, abundant, cheap, and an unexploited source of cellulose that could be used as large-scale production of nanocellulose products.

Acknowledgements

The authors would like to thank Universiti Putra Malaysia for the financial support through the Graduate Research Fellowship (GRF) scholarship, Universiti

Putra Malaysia Grant scheme Hi-CoE (6369107), FRGS/1/2017/TK05/UPM/01/1 (5540048) and iRMC UNITEN (RJO10436494). The authors are grateful to Dr. Muhammed Lamin Sanyang for guidance throughout the experiment. The authors also thank Dr. Rushdan Ibrahim for his advice and fruitful discussion.

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