Chapter 4
Biocomposite Reinforced with Nanocellulose for Packaging Applications

Anand Babu Perumal, Periyar Selvam Sellamuthu, Reshma B. Nambiar, Emmanuel Rotimi Sadiku and O. A. Adeyeye

1 Introduction

Food packaging is one of the most important areas in food technology dealing with the protection and preservation of all types of foods from microbial contamination and oxidative damage. In addition, packaging reduces food loss and increases the shelf life of food leading to a decreased economic loss for the distributor and consumer. Around 50% of agricultural produce are ruined due to the lack of packaging. Presently, the plastics that are commonly used in different packaging field are developed from petroleum-based products. However, these packaging materials are a threat to the environment as they are non-biodegradable, and they remain in the environment for 100–450 years [1]. At present, the technique used to manage the plastic wastes are burning and recycling; however, it is not enough for solving the environmental problems. An effort has been taken to decrease the waste disposal during the maintenance of food quality, as well as the production of eco-friendly packaging film using renewable sources. The increasing petroleum prices have also led to the search for an economical method for the development of packaging materials. Furthermore, there is a constant consumer demand to develop packaging materials that are biodegradable, as well as eco-friendly [2], thus encouraging researchers and industries to develop packaging materials derived from natural biopolymers. The natural polymers market value improved from 0.4 to 1.3 billion pounds in the year 2006–2013 [3]. To attain this growing trend, there is a need to venture resources that are sustainable and renewable. By the way, polysaccharides such as chitosan (CS)

A. B. Perumal (✉) · P. S. Sellamuthu · R. B. Nambiar
Department of Food Process Engineering, School of Bioengineering, SRM Institute of Science and Technology, Kattankulathur, Chennai 603203, Tamil Nadu, India
e-mail: anmicrobiology@gmail.com

E. R. Sadiku · O. A. Adeyeye
Department of Chemical, Metallurgical and Materials Engineering, Institute of Nano-Engineering, Tshwane University of Technology, Pretoria, South Africa

D. Gnanasekaran (ed.), *Green Biopolymers and their Nanocomposites*,
Materials Horizons: From Nature to Nanomaterials,
https://doi.org/10.1007/978-981-13-8063-1_4

and cellulose are the most important since these two are the most abundant natural polymer.

2 Chitosan

Chitosan is a natural polysaccharide derived from chitin that consists of *N*-acetyl glucosamine and D-glucosamine [4]. Chitosan is insoluble in water but only soluble in aqueous acidic solution which restricts its use. Chitosan has various exciting physicochemical and biological properties like biocompatibility, biodegradability, and non-toxicity, which makes CS more appropriate for use in many applications, like complementary foods, ingredients, drug delivery, wastewater treatment, cosmetics, and postharvest preservation of fresh produce [5, 6].

Generally, biopolymer-based packaging films are more sensitive to the environmental situation and usually have poor mechanical properties. To solve this problem, various researchers developed blend film based on the combination of biopolymers and synthetic polymers [7]. Poly(vinyl alcohol) [PVA] has been extensively used for the development of composites by blending with various natural polymers [8].

3 Polyvinyl Alcohol

The PVA is a water-soluble, semi-crystalline polymer widely used because of its excellent physical characteristics, which arise owing to the presence of hydroxyl groups and the formation of hydrogen bond [9]. It has good biodegradability, excellent resistance to chemicals, and better mechanical behavior [10]. Conversely, the usage of biopolymers for packaging of foods is still challenging due to its poor physical properties. The addition of nanocellulose (NC) as fillers to these composites might augment the physical properties. This paves a way for use of cellulose as a by-product of agricultural waste for the application in food industries.

4 Cellulose

Cellulose is one of the most plentiful natural biopolymers, which is actually prepared from plants sources and other novel resources of bacteria and tunicate [11–14], among which, the cotton fibers are most important fibers for the production of cellulose and nanocellulose. The fibers are primarily made up of three constituents like cellulose, hemicellulose, and lignin [15, 16]. Conversely, hemicellulose and lignin compounds are comparatively amorphous and cellulose material is more crystalline in nature [17]. The cellulose has both crystalline and amorphous section. Cellulose has a strong and long-chain polymer that are tightly arranged with inter- and intramolecular hydrogen bonding during the van der Waals forces [18, 19]. Cellulose microcrystals (CMCs) hold better mechanical behavior, as well as very cheap, low density, hydrophilicity, chirality, biodegradability, low thermal enlargement, and less toxicity [20–22].

Cellulose is one of the most commonly available biopolymer globally, which is renewable and biodegradable. Cellulose is a natural polymer consisting of D-glucose in chain form (Fig. 1). Mostly, it is existing in the form of pure cellulose in cotton, whereas, in wood and plant materials, it is available in a combined form with lignin and hemicelluloses. Mechanical and chemical treatments of cellulose result in more valuable materials like CNC and CNF. The CNC has good mechanical properties, thermal behavior, aspect ratio, eco-friendly, and low cost [23]. CNC comprises of the highly crystalline rod-like structure with a large specific area and length in the range of tens to hundreds of nanometers and 1–100 nm in diameter [24]. Moreover, CNC holds ample of OH groups on its surfaces, creating a hydrophilic nanomaterial that may enable their diffusions in the water-soluble polymer matrices [25]. Earlier, some researchers have stated the use of nanofibers from agricultural residue as reinforcement in polymer matrices such as CS [26] and PVA [27].

5 Nanocellulose

With the progress of nanotechnology, cellulose is the most important natural biopolymer on earth, which gains more attention in the form of nanocellulose (Fig. 2). Based on the size and shape, NC is grouped as CNC, cellulose nanofibers (CNF), and bacterial cellulose [BC] [28, 29]. The lignocellulosic fibers acquired from agricultural residues have a great importance due to its abundance, low cost, renewability, and biodegradability [30]. The plant fibers containing relatively high cellulose content make it an attractive material for the use in the development of biocomposites that may efficiently reduce the environmental pollution, saving the limited forest and petroleum resources, and thus encourage the added value of agricultural waste fibers.

CNC and CNF can be obtained from the same cellulose source by two different methods (Fig. 3). CNC can be prepared by acid hydrolysis of wood fiber or any other

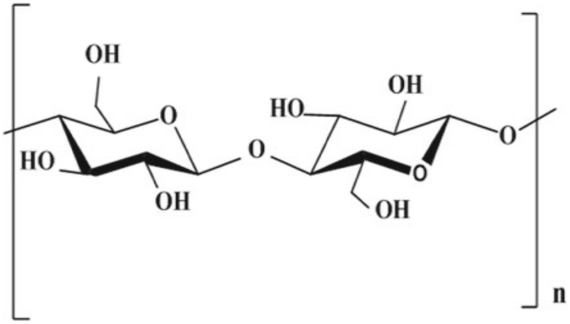

Fig. 1 Cellulose structure

cellulosic materials, resulting in a rod-like nanoscale structure with 3–20 nm width and 50–500 nm in length [31]. CNF can be produced using mechanical processes, with or without chemical and biological treatments, yielding 4–50 nm width and greater than 500 nm in length of linear or branched chains [31]. In addition to CNC and CNF, there are two more types of cellulose nanomaterials: microcrystalline cellulose (MCC) consisting of purified and partially depolymerized cellulose particles with an average degree of polymerization between 200 and 450 and microfibrillated cellulose (CMF), obtained from cellulose fibers which are submitted to high mechanical shearing forces.

5.1 Cellulose Nanocrystals

The CNC is a natural biological polysaccharide, having great potential in many applications due to its various key properties, e.g., better tensile and modulus value, high surface area, good optical properties, eco-friendly, and good biodegradable properties [33]. Usually, CNC has been described as reinforcing filler for the production of polymer composites [34, 35]. Nanocellulose is commonly used as a reinforcing agent; however, they might also be used as matrixes for several types of composites including films for the applications of food packaging.

Generally, CNCs can be synthesized from many sources, like plants [36, 37], animals [38], and bacteria [38–41]. Recently, numerous agricultural and industrial residues have gathered much interest in the production and utilization of CNC; these residues include sugarcane bagasse [42], rice husk [43], rice straw [44] and wastepaper [45, 46].

CNC is a derivative of cellulose which comprises of nanofiber, which determines the product characteristics and its functionality. The nanofibers are very useful material for the development of low cost, lightweight, and strong nanocomposite materials [47]. Usually, CNC is prepared by the bioformation of cellulose via bacteria as well as by the breakdown of plant celluloses using shear forces in refiner techniques.

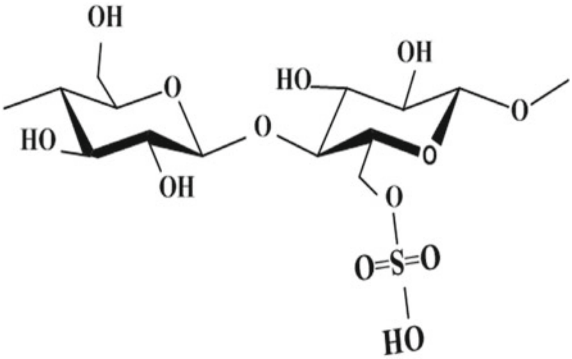

Fig. 2 Chemical structure of nanocellulose

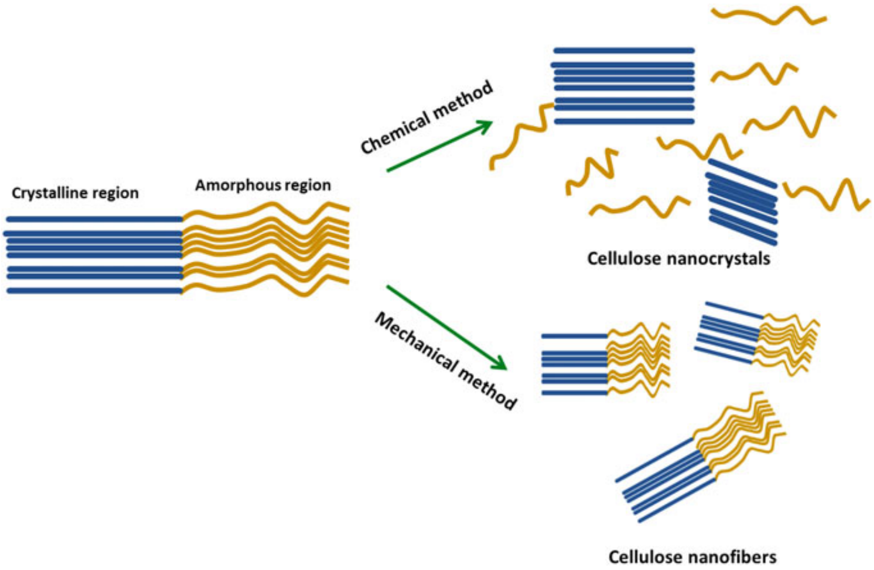

Fig. 3 Mechanism of chemical and mechanical methods for producing the CNC and CNF [32]

CNC derived from wood pulp can also be produced by electrospinning [48] or by controlled acid hydrolysis of bleached fibers [49].

5.2 Cellulose Nanofibers

CNF is documented as more efficient materials than microfibers to strengthen the composite because of their interactions between the nanomaterials which may form a percolated network formed by hydrogen bonds, only if there is a good dispersal of nanofibers in the composites and their large specific area in the arrangement of various 100 m^2/g. It is expected that NC as reinforcing filler in the composites could offer value-added particles with greater characteristics and wide applications for the next generation of biodegradable materials. CNC is likely to exhibit better stiffness since the tensile modulus of the CNC is as high as 134 GPa. The tensile strength of the CNC was evaluated to be nearly 0.8 up to 10 GPa [50–52]. Polymer matrices are the combinations of polymers with inorganic or organic materials holding particular geometries like fibers, flakes, spheres, and particulates. The usage of nanofillers is leading to the production of polymer composites and denotes a radical substitute to the conventional polymer nanocomposites [53].

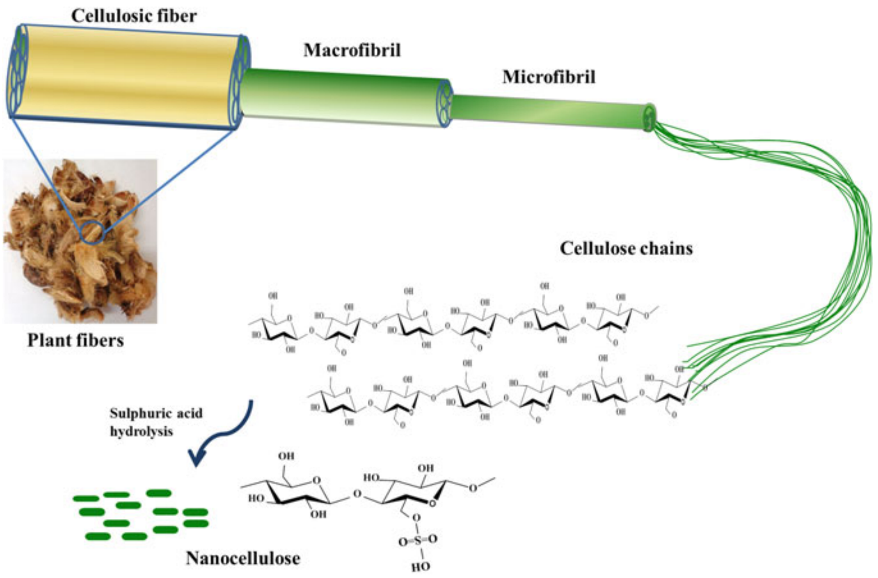

Fig. 4 Synthesis of nanocellulose from cellulosic fibers [103]

5.3 Bacterial Cellulose

Previously, bacterial cellulose (BC) is produced in the form of nanomaterial by *Gluconacetobacter* species which is grown in a medium containing carbon and nitrogen sources. Though it is chemically similar to plant cellulose, BC is formed as a bottom-up process, in that the bacteria produce cellulose and form a bunch of nanofibrils and gathering of a nano-sized ribbon-shaped fibrils in the range of 70–80 nm width [54] preparing a pellicle membrane which has a water-holding capacity of 60–700 times its dry weight [55]. The BC is also synthesized in pure form which is not combined with hemicellulose and lignin components, decreasing the purifying costs and environmental pollutions resulting from the usage of harsh chemicals reagents [56]. It might also be used to prepare composites in various methods.

5.4 Preparation of Nanocellulose

Various techniques have been stated for the isolation of NC fibers from agricultural residues (Table 1). Alemdar and Sain [57] synthesized CNF from agricultural wastes like wheat straw and soy hulls to utilize as reinforcing filler in biocomposites by the chemo-mechanical method. Fahma et al. [58] prepared CNF by hydrolyzing oil palm empty fruit bunch (OPEFB) with H_2SO_4 hydrolysis (Fig. 4). They noted a decline in crystallinity and degree of polymerization during the acid hydrolysis.

Table 1 Preparation of nanocellulose from different sources and various methods

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 acid hydrolysis	Sugarcane bagasse	CNC	5 ± 1.1, 275 ± 73	Achaby et al. [42]
Enzymatic hydrolysis	Sugarcane bagasse	CNC	14–18, 193–246	Camargo et al. [63]
Acid hydrolysis	Red algae	CNC	5.2–9.1, 285.4–315.7	Achaby et al. [27]
H_2SO4 hydrolysis	Rice straw	CNC	3–11, 39–117	Lu and Hsieh [12]
H_2SO4 hydrolysis	Rice husk	CNC	10–15	Johar et al. [43]
H_2SO4 hydrolysis	Cassava bagasse	CNF	2–11, 360–1700	Teixeira et al. [64]
H_2SO4 hydrolysis	Grain straws	CNC	10–25, 120–800	Oun and Rhim [65]
H_2SO4 hydrolysis	Kenaf bast fibers	CNC	12, 158	Kargarzadeh et al. [66]
H_2SO4 hydrolysis	Kenaf fibers	CNC	12 ± 3.4, 70–190	Zainuddin et al. [67]
Acid hydrolysis (H_2SO4 and HCl) and ultrasound assisted extraction	Waste cotton cloth	CNC	3–35, 28–470	Wang et al. [68]
H_2SO4 hydrolysis	Industrial waste cotton	CNC	10 ± 1, 180 ± 60	Thambiraj and Ravi Shankaran [69]
Chemo-mechanical fibrillation via griding and homogenization	Areca nut husk fibers	CNF	1–10	Chandra et al. [30]
H_2SO_4 hydrolysis and chemical, enzymatic pretreatment	Barley straw and husk	CNC	5–15, 40–270	Fortunati et al. [70]
H_2SO_4 hydrolysis, Microbial degradation	Okra fibers	CNC	–	Fortunati et al. [71]
H_2SO_4 hydrolysis	Kiwi pruning stalks	CNC	10–15, 100–150	Luzi et al. [72]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 hydrolysis	Cotton	NCC	25, 450,	Shamskar et al. [73]
Ethanol and peroxide + ultrasonication	Wood	CNC	1 ± 9, 500	Li et al. [74]
H_2SO_4 hydrolysis	Hemp	CNC	1–4.5, 20–120	Luzi et al. [75]
NaOH and H_2SO_4 hydrolysis	Miscanthus giganteus	CNC	8.5, 2.8	Cudjoe et al. [76]
NaOH and H_2SO_4 hydrolysis	Ramie fibers	CNC	3–15, 100–300	Habibi et al. [77]
H_2SO_4 hydrolysis	Sugarcane	CNC	20–60, 250–480	Kumar et al. [78]
H_2SO_4 hydrolysis mechanical treatment	Wheat straw	CNF	30–70, 90–110	Kaushik et al. [79]
H_2SO_4 hydrolysis	Tunicate	CNC	30–40, 500–3000	Roman and Gray [80]
Enzymatic hydrolysis	Tunicate	CNC	16.04	Zhao et al. [81]
NaOH and H_2SO_4 hydrolysis, steam extraction	Coconut coir fiber	CNF	5–50	Abraham et al. [15]
H_2SO_4 hydrolysis	Soy hulls	CNC	4.9, 503	Neto et al. [82]
H_2SO_4 hydrolysis	Mengkuang leaves	CNC	5–25, 5–80	Sheltami et al. [83]
H_2SO_4 hydrolysis	Corncob	CNC	4.15, 210.8	Silvério et al. [84]
H_2SO_4 hydrolysis	Bamboo fibers	CNC	5–8, 100–130	Brito et al. [85]
H_2SO_4 hydrolysis	Banana pseudostem	NCC	1.9–7.2, 12–135	Pereira et al. [86]
Acid and ball milling methods	Sugarcane bagasse	CNC and CNF	160–400, 20–30	Sofla et al. [32]
Chemo-mechanical method	Wheat straw and soy hull	CNF	10–120	Alemdar and Sain [57]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
H_2SO_4 hydrolysis	Oil palm empty fruit	CNF	10–80	Fahma et al. [58]
Chemo-mechanical method	Oil palm empty fruit	CNF	5–10	Fatah et al. [59]
Chemical ultrasonic method	Wood, bamboo, wheat straw and flax fibers	CNF	10–40	Chen et al. [60]
TEMPO oxidation mediated system	Hardwood celluloses	CNF	3–4	Saito et al. [61]
Chemical, grinder and homogenizer method	Coir	CNF	18–20	Kanoth et al. [87]
H_2SO_4 hydrolysis	Rice straw	CNC	15 ± 1.3	Anand babu et al. [88]
H_2SO_4 hydrolysis	Cotton wool	CNC	–	Popescu [89]
Chemo-mechanical process	Cotton fibers	NCF	70–300	Savadekar et al. [90]
Grinding and homogenization	Kenaf fibers	CNF	15–80	Jonoobi et al. [91, 92]
Disintegration in a Waring blender; homogenization, TEMPO	Sugar beet pulp	NC	–	Habibi and Vignon [93]
Enzymatic pretreatment, high shear refining, cryocrushing	Bleached kraft pulp	CMF	100	Janardhnan and Sain [94]
Mechanical pretreatments followed by homogenization	Rubber wood	CNF	10–90	Jonoobi et al. [92]
Mechanical pretreatments followed by homogenization	Empty fruit bunches	CNF	5–40	Jonoobi et al. [92]
Homogenization	Swede root	CMF	–	Bruce et al. [95]

(continued)

Table 1 (continued)

Methods for obtaining CNC	Cellulose source	Nanocellulose	Particle size (nm)	References
Substrate media	Bacterial cellulose	CNF	40–70	Castro et al. [96]
H_2SO_4 hydrolysis	Bacterial cellulose	CNC	50, 100–1000	Grunert and winter [97]
H_2SO_4 hydrolysis	Bacteria	CNC	10–50, 100–1000	George et al. [98]
HCl hydrolysis	Bacteria	CNC	15–25, 160–420	George and Siddaramaiah [99]
HCl hydrolysis	Cotton	CMC	5–10, 100–150	Araki et al. [100]
Steam explosion treatment and hydrolysis	Sunflower stalk	CNC and CNF	5–20, 150–200	Fortunati et al. [101]
Ultrafine grinding	Sludge (residue from dissolving cellulose production)	CNF	100	Jonoobi et al. [102]

Fatah et al. [59] reported a chemo-mechanical method to extract CNF from OPEFB and successfully achieved in attaining the CNF with a diameter ranging from 5 to 10 nm and observed a decrease in the crystallinity that is inclined by the pressure of mechanical method. The chemical ultrasonic technique was reported by Chen et al. [60] for the extraction of CNF from four different fibers such as wood, bamboo, wheat straw, and flax fibers. The authors successfully isolated the nanofibers with a diameter in the range of 10–40 nm from bamboo, wheat straw, and wood fibers; however, flax fibers with rich content of cellulose were not nanofibrillated evenly. Saito et al. [61] presented a pretreatment of cellulose by oxidation with 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated method. They extracted CNF in the range of 3–4 nm in width from hardwood celluloses. The defibrillation of nanofibrillated cellulose generally involves various mechanical techniques like cryocrushing, microfluidization, high-intensity ultrasonication, grinding, and high-pressure homogenization [62].

Kanoth et al. [87] synthesized nanofibrillated cellulose with the diameter of 18–20 nm from coir with the help of a commercial grinder to prepare the pulp followed by a chemical process. For the nanofibrillation of chemically pretreated and bleached pulp, an ultrahomogenizer was utilized.

5.4.1 Acid Hydrolysis

Sulfuric acid (H_2SO_4) is the most frequently used acids for the extraction of CNC. It is more stable than any other organic acids, and it can offer a better effect on hydrolysis. The CNC was evenly distributed during H_2SO_4 hydrolysis because its sulfate ion shows negative charges and could create an electrostatic repulsion between CNC particles [86]. However, H_2SO_4 is a strong oxidizing acid. The greater thermal degradation of cellulose generally happens when sulfates are introduced on the surfaces of cellulose during hydrolysis, mainly at maximum temperature, which leads to lesser yields of CNC, resulting in a negative impact on the manufacturing in the large-scale and CNC application. Due to these motives, growing efforts have been made to utilize other acids to substitute H_2SO_4 for the cellulose hydrolysis in recent periods. Hydrochloric acid (HCl) has the weak oxidizing capability and less thermal degradation of CNC leading to poor dispersal capability for CNC. The combination of H_2SO_4 and HCl may be a good option for the extraction of CNC. The HCl hydrolysis may improve the CNC dispersion property by the electrostatic repulsion of sulfate during the mixed acid hydrolysis.

Martins et al. [104] stated that the acidic hydrolysis is the common method used for the isolation of cellulose nanowhiskers (CNW), which could be performed using H_2SO_4 or HCl. In this method, the crystalline parts are insoluble in acid, under the conditions used for isolation. The isolation procedure and the source of cellulose are tremendously influent on the morphology and other properties of CNW; hence, selecting the hydrolysis method to be used becomes an important stage in the successful isolation of nanocrystals. It is well known that the utilization of different acidic solutions might cause variations in the stability of the colloidal suspension, because of the presence of different loads on the surface of fibers. The use of H_2SO_4 for isolation leads to the introduction of negative sulfate groups on the outer crystals surface during the hydrolysis process and considered that it is responsible for the stabilization of crystals in the resultant solution, although the presence of sulfate groups might cause the decrease in thermal stability, as a large amount of sulfate groups on the cellulose lead to decreased thermal degradation of the cellulose. If HCl is used instead of H_2SO_4 to hydrolyze the cellulose, the thermal stability of the obtained nanocrystals is enhanced; however, the nanocrystals are likely to aggregate due to the lack of electrostatic repulsion force between the particles, resulting in an unstable solution [104].

The isolation of CNW by acid hydrolysis might cause digestion of the pretreated fiber structure amorphous region, resulting in crystalline nanoparticles [105]. Siqueira et al. [106] explains the principle of the amorphous regions of cellulose disruption, to produce CNC. The hydronium ions can pierce into the amorphous domains which promote the hydrolytic cleavage of glycosidic bonds liberating individual crystallites [107].

Similarly, Siqueira et al. [106] studied the influence of the use of H_2SO_4 or HCl to extract stable suspensions of CNC. However, the H_2SO_4 might produce more stable suspensions when compared to the HCl because it results in CNC with marginal loading area and the CNC obtained by H_2SO_4 hydrolysis has a negatively charged surface due to esterifying the hydroxyl groups of the surface for generating the sulfate groups.

Johar et al. [43] mentioned in the reports that the process should ultimately decrease the size of the micro fibers to nanoscale level. The resulting nanoparticles are in the range of 15–20 nm in diameter and aspect ratio of 10–15 nm.

5.4.2 Ultrasound

The very simple and effective method for valuable recycling and degradation of cellulose wastes includes hydrolysis and ultrasonic degradation. Oksman et al. [108] compared the CNW obtained by ultrassonification, homogenization, and acid hydrolysis. The degree of crystallinity of the materials was 73% after ultrasonification, 77% after homogenization, and 75% after acid hydrolysis. This study concluded that the nanowhiskers produced by mechanical methods have good thermal stability compared to the chemical treatment. On the other hand, this stability is not greater than the thermal stability of native cellulose because the cellulose chains are shorter and might have a lower degree of polymerization. But, the dimensional of residues extracted by sonication and homogenization was 10 nm in sizes. Thus, the ultrasonification, homogenization, and grinding processes have gained more attention to the extraction of micro- and nanofibrils [109]. Additionally, the ultrasonic-assisted hydrolysis method has been confirmed to be more effective to enhance the productivity of CNC [110, 111].

5.4.3 Oxidation Mediated 2,2,6,6-Tetramethylpiperidine-1-Oxyl (TEMPO)

The nanofibrillated cellulose can be obtained through oxidation method using TEMPO and consequent mechanical dispersion in water. This technique has some important characteristics: The final material could be dispersed in water, with all individual fibrils having a uniform width of 3–4 nm. Also, there is plentiful presence of carboxylate groups on the surface of cellulose fibrils (~1.7 nm) by which the electrostatic repulsion or working of the osmotic behavior is efficient between the fibrils produced by this method anionically charged water [112–114]. Iwamoto et al. [114] described that the wood pulp oxidation by radical TEMPO which acts as a catalyst in an aqueous medium with sodium hypochlorite and sodium bromide at pH 10 might cause the development of C6 carboxylate groups on the surface of microfibrils, retaining the original crystallinity of cellulose I and the crystal width.

The films developed by TEMPO oxidation of CNF dispersed in water have better properties like good transparency and resistance to elasticity, low thermal expansion, and low oxygen permeability [114, 115]. Fukuzumi et al. [113] isolated CNF with an average width of ~4 nm, but with different lengths: 200, 680, and 1100 nm by TEMPO oxidation method. By examining the viscosity, average degree of polymerization (DPV) for individual CNF obtained was found to be 250, 350 and 400, respectively.

The nanofibrils having short length result in fewer DPV values; however, it has good light transmittance. In contrast, nanofibrils are in greater length and result in better tensile strength and elongation at break for the film. The barrier properties of all the films with different CNF lengths may differ, in which the nanofibrils with maximum length showed good oxygen barrier properties. However, in the case of water vapor permeability, the CNF length does not show any significant effect and mostly inclined by the water vapor transmission rates (WVTR) film.

Fukuzumi et al. [115], successfully isolated the nanofibrils from bleached kraft pulp prepared by TEMPO oxidation. The subsequent treatment with various calcium solutions was performed to exchange the ions by converting the carboxylate groups. The nanofibrils subjected to various treatments might improve the thermal behavior of CNF.

5.4.4 Mechanical

The CNF isolated by mechanical method provides some advantages than chemical treatment methods. The mechanical method being an environmentally friendly method does not involve the use of solvents or any other chemical reagents. Furthermore, the produced material can be used as reinforcement in polymer matrices [116, 117]. The mechanical methods utilize energy during its performance, however, make use of all wood materials for the production of CNF, whereas during the chemical method, almost half the wood becomes pulp and other half is dissolved [118].

Mtibe et al. [117] studied a comparison between two forms of isolation of corn stover CNF, by acid hydrolysis and mechanical method. Primarily, the waste was treated by basic procedure, then the pulp of cellulose was collected, and finally, it was subjected to these two methods. The mechanical method comprises of two steps: At first, the natural fiber was processed into a mechanic mixer and consequently passed through a mechanical grinder. By evaluating the results of both the nanofibers and nanowhiskers prepared by mechanical and chemical treatment respectively, it was noted that the dimensions of CNF were 4–10 nm in diameter and length in few microns, whereas chemically treated CNW had a dimension between 3–7 nm in diameter and 150–450 nm in length. Regarding the crystallinity data, the CNF exhibited 66.4% of crystallinity, but for the CNW, it was 72.6% of crystallinity. The degree of crystallinity is less because of the mechanical method used to break the crystalline domains of the cellulosic fibers. As for the mechanical behavior, the obtained CNF by mechanical technique indicates the enhancement of the stress transfer fiber to fiber that explains the increase in the mechanical and thermal behavior of the material, with better stability [117].

Ardanuy et al. [11] reported the elimination of amorphous phase of cellulose to form a crystalline CNC in the range of around 2–20 nm in diameter and 100–600 nm in length. The CNC might be utilized as reinforcing filler for the development of functional nanomaterials, antimicrobial films, protective coatings, polymeric nano-biocomposites, food packaging films, drug delivery, and membrane filters and substrates for flexible electronics [119–121].

Robles et al. [122] illustrated the variations of polylactic acid (PLA) behavior after the application of CNC obtained from blue agave. They observed that the different methods of producing the cellulose in nanoscale can provide various characteristics to the obtained composite, like enhanced mechanical behavior and hydrophobicity due to the non-polar covalent bond formation between the hydroxyl groups and free coupling which also improves the dispersion within the matrix that is important in producing the materials with good water barrier property.

5.4.5 Enzyme Hydrolysis

Enzyme hydrolysis is the new technology based on the use of hydrolytic enzymes alone or in combination with some other organic chelating compounds. This approach is now a very popular method to perform the pretreatment of the lignocellulosic materials. The aim is to purify the cellulose from other interfering compounds like lignin and hemicellulose, prior to its final acid hydrolysis which results in CNC [123]. The enzymatic pretreatments are more particular than the chemical treatment and have minimal effect on the surroundings. The use of enzymes like pectinases and cellulases has gained more attention for their capability in eliminating the water-soluble material, minerals, pectin, and amorphous hemicelluloses, etc. [106].

Fortunati et al. [70] explained that CNC was successfully isolated from both barley straw and husk by approaching two different methods: an alkaline and enzymatic pretreatment, followed by an acid hydrolysis. The results prove the efficacy of the enzymatic pretreatment on the value of resultant CNC. The outcomes showed that chitosan decreased the optical transmittance and the mechanical properties of PVA matrix, while its combination with CNC, particularly when isolated by enzymatic pretreatment and incorporated at a higher concentration, was capable to modify the optical transparency, and the mechanical and thermal behavior. In the case of enzymatically pretreated fibers, the defibrillation procedure appears to be more effective and certain coils, noticeable as vascular protoxylem arrangements were observed. They were visible because of the more efficient elimination of hemicellulose and lignin compounds.

Cellulases are complexes of endo-glucanases, exo-glucanases, and cellobiohydrolases. These enzymes act synergistically in the cellulose hydrolysis. Endo-glucanase enzymes randomly attack and hydrolyze the amorphous region of cellulose at the same time as exo-glucanase break down the polymer chain of cellulose either in the reducing ends or non-reducing ends. Cellobiohydrolases hydrolyze the cellulose chains either in the C1 or in the C4 ends by the utilization of protein in every case, into the cellobiose units.

Several enzymes, like hemicellulase, pectinase, xylanase, and cellulase, have been used to eliminate the non-cellulosic components. The proposed constituents of the enzyme are a mixture of various proportions of pectinase, hemicellulase, and cellulose [124]. It is well understood that the cellulase enzyme is used to hydrolyze the cellulose which leads to the removal of amorphous regions.

In recent times, Novozyme presented Scourzyme L to commercialize in the market for the application in textile industry. The enzyme, called pectate lyase, particularly catalyzes the breakdown of internal a-1,4-glycosidic linkages by β removal in pectic acid (pectate) at alkaline pH between 8 and 10. The specific attack on carboxylic acids decreases the acid constituent in the natural fibers, giving rise to low hydrophilic characteristics. Generally, this enzymatic method could be well fitted to the cellulosic fibers comprising of pectin.

Enzymatic pectin removal in the traditional softening procedure results in disassembly of fiber bundles in fibrous crops, like hemp and flax [125–127].

6 Biocomposites with Nanocellulose

6.1 Biocomposites Incorporated with Cellulose Nanocrystals

Chen et al. [128] produced nanocomposites with polylactide-grafted CNC (CNC-g-PLA) and poly(bhydroxybutyrate) (PHB) as a matrix. The results suggest that the nanocomposites with unmodified CNC exhibited a greater crystallization rate compared to neat PHB, whereas CNC-gPLA showed less crystallization degree. Additionally, several researchers illustrated that the CNC can also be able to act as nucleating agents, which affect the crystalline degree of the polymer [129, 130].

Fortunati et al. [131] developed poly(lactic acid) (PLA)-based nanocomposite films reinforced with modified CNC with an acid phosphate ester of ethoxylated nonylphenol (Beycostat A B09). The report suggests that the surfactant helps in NC distribution in the polymer composites, augmenting the nucleation effect of CNC and leading to plasticization.

The biocomposites prepared based on various polymers such as PLA [132, 133] and alginate [134] reinforced with CNC have been proven for the enhanced thermal properties of biocomposites. Starch biocomposite film with the addition of CNC content could increase the crystallinity up to 15% CNC [135].

Azeredo et al. [136] investigated the influence of CNC extracted from cotton or coconut husk fiber on alginate–acerola film. The biocomposite reinforced with CNC from both the fibers exhibited similar tensile and water vapor permeability. Similarly, Azeredo et al. [137] examined the effect of CNC isolated from coconut fiber on alginate-based film and compared with the nanoclay as a reinforcing agent. Both the biocomposite film showed better water vapor permeability than the pure matrix film.

A bio-nanocomposite film based on PLA reinforced with CNC at a concentration of 1wt% and 5 wt% results in improved tensile properties as well as transparency [138]. Likewise, the water vapor permeability was enhanced when the modified CNC and different concentrations of pristine were added to PLA [139]. A nanocomposite film prepared by using chitosan, CNC, glycerol, and olive oil exhibited enhanced water resistance and water vapor permeability [140].

6.2 Biocomposites Containing Cellulose Nanofibers

The chitosan [141] and PVA [142] film added with CNF were reported to have improved the thermal properties, water solubility, and water permeability. PLA reinforced with CNF obtained by Iwatake et al. [143] confirms the increased tensile strength and modulus. Similarly, Fernandes et al. [141] obtained the chitosan film with CNF reinforcement which results in the increment of tensile strength and modulus of the composite films. The xylan-rich hemicellulose film prepared with the addition of sorbitol as plasticizer improved the tensile strength and young modulus very effectively [144]. Bilbao-Sainz et al. [145] demonstrated the addition of CNF and TEMPO-CNF to HPMC films and compared it with the HPMC films reinforced with CNC. The results revealed that HPMC with CNC exhibited a better tensile and water vapor barrier properties and good transparency level of the film.

6.3 Biocomposites Reinforced with Bacterial Cellulose

George et al. [146] prepared the PVA-based film reinforced with the 4 wt% BCNC which improved the tensile and thermal properties of the films than the PVA matrix. Moreover, the starch film added with BCNF (50 wt%) exhibited a better tensile strength and modulus [147].

Barud et al. [148] studied the poly(3-hydroxybutyrate) film with bacterial cellulose which results in very good tensile and modulus properties because of its strong interfacial interactions between the BC and PHB networks. Conversely, the chitosan film was developed by Lin et al. [149] and reinforced with BC followed by comparison with the pure BC matrix which confirmed the enhancement of mechanical properties of the biocomposites. Likewise, the gelatin film combined with BC demonstrated the improvement of tensile behavior by interlinking the networks uniformly [55].

7 Development of Nanocellulose-Based Biocomposites

Nanocellulose materials can be produced by different methods which directly enhance the characteristics of final products. The important research efforts are focused on the production of NC-based biodegradable composites with enhanced properties [150].

The incorporation of CNC as reinforcing filler in polymer composites might lead to the formation of H-bonded three-dimensional network within the matrix [151]. This

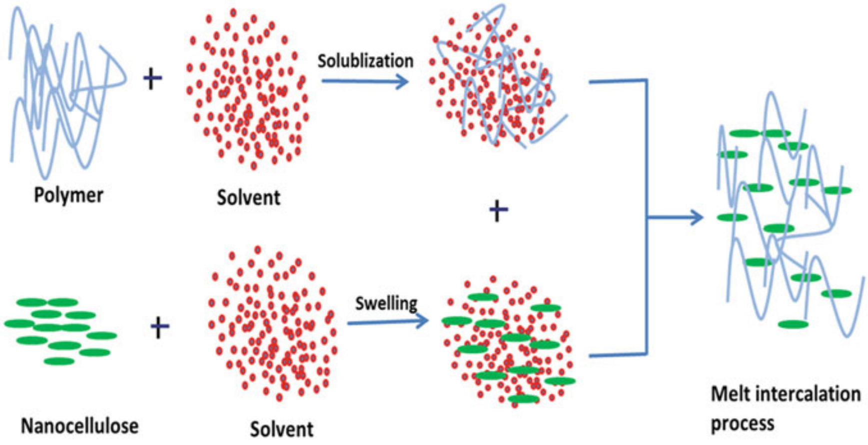

Fig. 5 Melt intercalation processing for the preparation of the bio-nanocomposite film [177]

network gives the energy to withstand the external strains, enhancing the mechanical behavior of nano-biocomposites. Furthermore, the CNC network had good oxygen permeability and improved the thermal behavior of nanocomposites [139]. CNC could also change the crystallization kinetics of the polymer matrices, and also, the surface modification has an important role in this process [152].

Petroleum-based polymers prevail in food packaging because of its simple handling, low cost, and good barrier behavior [153]. The utilization of nanocellulose might prolong the keeping quality of food and may also enhance the quality of food as they could aid as carriers for antimicrobial and antioxidants compounds.

Recently, the fast development of polymeric science and broad utilization of polymeric materials in technology have led to gaining interest in the development and characterization of polymer-based composite (Table 2).

7.1 *Melt Processing*

The knowledge of using heat to make soften and mold polymers has existed since 1868. John W. Hyatt manufactured a machine for the production of the billiard ball from plastics which can be utilized for the injection of the molten material into a mold form. More than 70 years later, a screw was added to a similar machine, permitting the mixing and recycling of polymers at high temperatures. Melt processing of biocomposites is an important method to market composite materials in large volume, and also, it is very cost-effective and quick progress method (Fig. 5).

Abundant progress has occurred in current techniques for preparing polymeric nanocomposites. The main part of these studies on cellulose nanocomposites is done in liquid media since the materials can reach good or reasonable suspension states

Table 2 Polymer matrix reinforced with nanocellulose to obtain bio-nanocomposite films

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Solvent casting	Kiwi pruning stalks	PVA_CH/CNC, carvacrol	CNC	3 wt%	Luzi et al. [72]
Solvent casting	Sugarcane bagasse	CMC/ST/CNC	CNC	0.5–5 wt%	Miri et al. [154]
Solvent casting	Barley straw and husk	PVA/CH/CNC	CNC	1–3 wt%	Fortunati et al. [70]
Solvent casting	Red algae	PVA/CNC	CNC	1–8 wt%	Achaby et al. [27]
Solvent casting	Industrial waste cotton	PVA/CNC	CNC	5 wt%	Thambiraj and Ravi Shankaran [69]
Solvent casting	Sugarcane bagasse	PVA/CMC/CNC	CNC	0.5–10 wt%	Achaby et al. [42]
Casting/evaporation technique	Sugarcane bagasse	PVA/CS/CNC	CNC	0.5–5 wt%	Miri et al. [23]
Casting technique	–	CS/CNF	CNF	0–20 wt%	Azeredo et al. [50]
Casting technique	–	CS/NFC	NFC	50%	Fernandes et al. [141]
Casting technique	–	CS/NFC	NFC	32 wt%	Wu et al. [155]
Solvent casting	Softwood kraft pulp	CS/CNW	CNW	5 wt%	Khan et al. [156]
Evaporation technique	Cotton linter	CS/CNW	CNW	0–20 wt%	Li et al. [157]
–	–	CS/CNW	CNW	0.18%	Dehnad et al. [158]
Solvent casting	Rice straw	PVA/CS/CNC	CNC	1–5 wt%	Anand babu et al. [88]
Solution casting	Cotton wool	PVA/CNC	CNC	5–15%	Popescu [89]
Solution casting	Kenaf fibers	TPCS/CNC	CNC	2–10 wt%	Zainuddin et al. [67]
Solution casting	MCC	Sodium caseinate films	CNC	1–3 wt%	Pereda et al. [159]
Solution casting	Wheat straw	Thermoplastic starch/CNF	CNF	–	Alemdar and Sain [57]
Twin-screw extrusion	Kenaf pulp	PLA/CNF	CNF	1–5 wt%	Jonoobi et al. [160]

(continued)

Table 2 (continued)

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Solution casting	–	NC-MC	NC	0.1–1%	Khan et al. [161]
Compression molding	–	Polycaprolactone + MC matrix/NCC	NCC	7.7%	Boumail et al. [162]
Melt extrusion method	–	PLA/CNW	CNW	–	Oksman et al. [132]
Solution casting	MCC	Alginate biopolymer	CNC	1–10 wt%	Abdollahi et al. [163]
Solution casting	Softwood kraft pulp	Alginate biocomposite	CNC	1–8 wt%	Huq et al. [134]
Compression molding	Needle-leaf bleached kraft pulp	PLA/CNF	CNF	10 wt%	Iwatake et al. [143]
Film casting	Jute and bacterial cellulose	ST/BCNF	BCNF	50 wt% BCNF	Soykeabkaew et al. [147]
Solution casting	Bleached sisal pulp	Xylan-rich hemicellulose films	CNF	20 wt% CNF	Peng et al. [144]
Solution casting	Bleached dry lap eucalyptus pulp	Polyethylene oxide matrix	CNF,CNC	10 wt%	Xu et al. [164]
Solution casting	Softwood pulp	Amylopectin films	CNF	0–10 wt%	López-Rubio et al. [165]
Film casting	–	HPMC films/MCC	CNF, TEMPO-oxidized CNF and CNC	0.08–0.8%	Bilbao-Sainz et al. [145]
Solution casting	*Gluconacetobacter xylinus*	Hydroxypropyl methylcellulose (HPMC)/CNC	BCNC	2 and 4 wt%	George et al. [166]
Heating	–	PVA/CNC	CNC	10%	Paralikar et al. [167]
Solution casting	*Gluconacetobacter xylinus*	Gelatin/BCNC	BCNC	1–5 wt%	George and Siddaramaiah [99]

(continued)

Table 2 (continued)

Preparation technique	Cellulose source	Biocomposite matrix	Nanocellulose form	CNC (wt%)	References
Film casting/evaporation technique	*Luffa cylindrica*	Poly(-caprolactone) (PCL)/CNC	CNC	0–12 wt%	Follain et al. [168]
Solvent exchange cum solution casting technique	Bamboo (Bambu sabalcooa)	Poly(3-hydroxybutyrate)/CNC	CNC	2 wt%	Dhar et al. [169]
Compression molding	Cotton linter pulp	Soy protein isolate	CNC	0–30 wt%	Wang et al. [170]
Solution casting	Pea hull fiber	Starch/CNC	CNC	30 wt%	Chen et al. [171]
Solution casting	Potato (*Solanum tuberosum* L.) tuber	Starch/CMF	CMF	3.3 wt%	Dufresne et al. [172]
Solution casting	*Acetobacter xylinum (G. xylinus)*	PVA/BCNC	BCNC	4 wt%	George et al. [146]
Sulfuric acid hydrolysis	Cotton fiber or coconut husk fiber	Alginate–acerola puree films	CNW	0–15%	Azeredo et al. [136]
Twin-screw microextruder	*Phormium tenax*leaves	PLA/CNC	CNC	1 and 3 wt%	Fortunati et al. [131, 138]
Casting technique	Commercial cotton paper	CS/CNC	CNC	1–12 wt%	Pereda et al. [140]
Solution casting	Eucalyptus wood pulp	CS/CNC	CNC	0–60 wt%	Mesquita et al. [173]
Film casting	–	Mango puree-based edible films	CNC	1–36 g/100 g	Azeredo et al. [174]
In situ chemical polymerization	Wood	TEMPO-oxidized CNF/PVA and PPy	CNF	2.5%	Bideau et al. [175]
Solution casting	Sunflower stalks	CNF and CNC/Gelatin biocomposite	CNF and CNC	0.47–1.46% v/v	Fortunati et al. [101]
Compression molding	Softwood kraft pulp	PCL/NCC	NCC	5 wt%	Khan et al. [176]

in aqueous media and some organic solvents. Nowadays, melt processing method is a greener approach because no solvents are used. Conversely, it involves some complications due to the inconsistencies between cellulose and polymeric matrices. In such cases, the auxiliary method could be followed to produce cellulose-based nanocomposites. Composites prepared by an extrusion technique, injection, in situ polymerization and resin transfer molding are generally found in the literature.

Zhang et al. [178] developed CNC/PBAT nanocomposites with 0.5, 1.0, 1.5, and 2.0 wt% of sulfonated CNC by melt mixing methods and altered by acetic anhydride. They noted that the surface alteration leads to even diffusion and a better interfacial linkage between modified CNC and PBAT, augmenting the mechanical behavior of the nanocomposites. Morelli et al. [179] added CNC produced by acid hydrolysis and altered with phenylbutyl isocyanate in PBAT matrices by melt extrusion technique. The results revealed that the nanocomposites with modified NC exhibited a modulus which was smaller than the modulus of nanocomposites with unmodified NC with the same concentration of nanofillers. They ascribed this result to the greater crystallinity noted in the nanocomposites reinforced with unmodified CNC.

Habibi et al. [180] studied the CNC-g-PDLA added in PLLA matrix by melt processing. They described that the greater mechanical properties are possible because of the stereo complexion that hardens and stabilizes the percolation network.

Castro et al. [181] reported the reinforcement of high-density biopolyethylene with CNW isolated from curauá fiber and castor oil, soy, and linseed epoxidized as compatibilizers. The total process includes the extrusion and hot pressing, targeting to estimate the dispersal of CNW in the polymeric matrix. The TGA/DTG was performed to analyze the thermal degradation of the film incorporated with CNW. Menezes et al. [182] reported the reinforcement of polyethylene with CNW by extrusion technique to produce a nanocomposite film. This research suggests the possibility of CNC processing by a totally industrial procedure without affecting the characteristics desired for the material.

7.2 Injection Molding

It is a technique used to prepare a material with various structures and properties by the combination of different polymers and also by the addition of nanofillers. The injection molding process is well documented for the production of various composites reinforced with nanofibers. In this technique, the polymers are heated to prepare a composite in a definite shape using the mold which results in composites with better crystallization due to the heat transfer into the polymers. The polypropylene composite with CNC was developed by Yousefian and Rodrigue [183] by this injection molding which resulted in the composites with enhanced viscosity.

7.3 Extrusion

Extrusion method is the simplest technique used to prepare the composites based on various polymers including cellulose. This technique is used most commonly due to its easy procedure, and also, it can be useful in the industrial sector. In this method, the dispersion of the particles or agents in the polymer materials is achieved by imposing the mechanical stress through the screw. Alloin et al. [184] developed the nanocomposite films by various techniques including extrusion and casting evaporation for comparison which has proven the significant differences between similar composites. The mechanical properties of similar composites prepared using extrusion method are higher than the casting and evaporation technique at the same concentration of the materials.

Several researchers have reported that the twin-screw extrusion was used to combine the nanocellulose and different polymers such as PP [183], PE [185], and PVA [186]. Moreover, cellulose-based composites result in poor dispersion, while the extrusion method is performing due to the insufficient stress during this process to disperse the materials within the matrix. The dispersion capacity of CNF in the PE matrix was confirmed by using fluorescent marker by Zammarano et al. [187], who used the microscopic technique to identify the dispersion level. In this extrusion technique, the size of the nanofibers is decreased by the shear force which results in better reinforcement leading to strong mechanical properties.

7.4 Resin Transfer Molding

Resin transfer molding or liquid transfer molding is same like injection molding in few aspects. Nevertheless, the classical approach of this method needs prior placing of the filler within the mold in which resin is placed at a lower pressure. In addition, the resin is usually cured after settlement [188]. The process has several advantages like low cost and the possibility of controlling fiber orientation. The first attempt made to prepare nanocomposites by RTM was done by Lekakou et al. [189]. In this work, they suspended nanosilica materials in an appropriate solvent and formed a class of epoxy–silica masterbatch, which was used to produce solid layers. These layers were compacted into glass fabric–epoxy laminates with enhanced mechanical behavior. BC was used as auxiliary filler in thermoplastic composites prepared by liquid transfer molding where sisal fibers were used as continuous fibers [190]. Few researchers utilized NC itself as the mold for the resin. In this procedure, CNF was used as scaffolding for the resin by dipping the dry nanofibers into a resin bath under vacuum. The curing of the resin produced solid particles that were consequently molded by abrasion or pressure [191]. In recent times, Barari et al. [192] examined the influence of modified CNF as a scaffold for resin before curing. The utilization of non-modified cellulose could avoid the diffusion of resin to the middle of the specimen, forming dry spots within the fibrillar structure. The silylation of the CNF enhanced the spreading of the resin and improved the mechanical response of the post-cure structure than the pristine nanofibers. The alteration step also enhanced the curing of the resin by decreasing its activation energy [193].

7.5 In Situ Polymerization

In situ polymerization was the first technique used to develop nanocomposites. Recently, this method was used to prepare the thermoset composites. For thermosets like epoxies or unsaturated polyesters, a curing agent or peroxide is mixed to start the polymerization. For thermoplastics, the polymerization could be started either by the incorporation of a curing agent or by improving the temperature.

The monomer polymerization in the presence of nanofillers is an effective substitute for simply mixing to dispersing the particles in the matrix. The basic knowledge of using in situ polymerization has been applied to the development of cellulose-based nanocomposites (Fig. 6). Polymerization is usually achieved using a sufficient solvent in which the monomers are soluble and the cellulose nanoparticles are dispersible that can include a previous step of drying [194].

As discussed by Iyer and Torkelson [195], these necessities for the solvent could limit the industrial applications of in situ polymerization, as with casting and evaporation techniques. Certain limitations exist on the quantity of nanofiller which can be efficiently dispersed by this method. Auad et al. [196] observed that CNC materials altered by in situ polymerization exhibited higher percolation thresholds compared to non-modified CNC. A moderate addition of CNF could sustain good dispersion during polymerization. Concurrently, the existence of nanofiller altered the viscosity of the system, demanding increased reaction time to finish the polymerization [197]. The rise in viscosity might happen by the surface grafting of cellulose during polymerization method. Rueda et al. [198] explained the use of CNC as precursors of PU chains by grafting 1,6-hexamethylene diisocyanate onto CNC surfaces. The

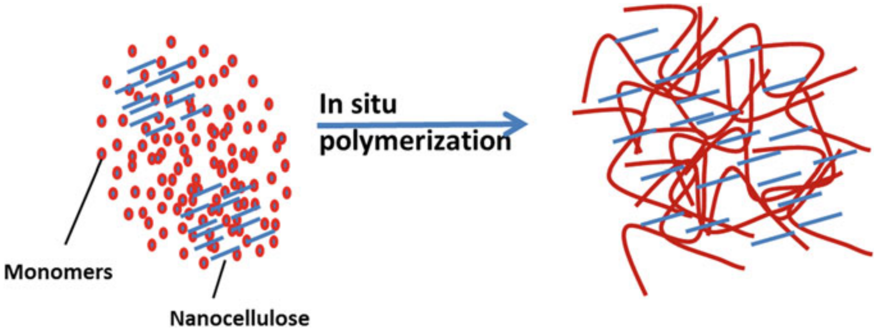

Fig. 6 In situ polymerization for the preparation of bio-nanocomposite film [177]

modified particles were used as templates to produce polymeric chains in a second reaction. A similar method was examined by Yu et al. [199]. The results enhanced the mechanical characteristics of methyl methacrylate (MMA) and butyl acrylate (BA) co-polymer P(MMA-co-BA) using a combination of grafted CNCs with the linear MMA-co-BA. The addition of CNC enhanced Young's modulus and tensile strength of the composite by augmenting the compatibility and entanglement of chain between grafted CNCs and co-polymer. Other properties might also be improved by in situ polymerizations. Müller et al. [200] revealed that the use of bacterial NC permitted the production of membranes with good flexibility for the application in organic electronics. Kaboorani et al. [201] added 1 and 3 wt% of CNC to develop a UV-curable coating for wood furniture. At higher content (e.g., >50%), the hydroxyl groups of NC could be used as crosslinkers for epoxy resins as the nanoparticles self-organize, which produces the iridescent colors and particles with exciting photonic applications [202]. Numerous reports using in situ radical polymerization have been reported previously for the development of nanocomposites based on NC with epoxy resin [203], enzymes [204], hydroxylbutyl acrylate [205], polyamide-6 (PA-6) [206], poly(3,4-ethylenedioxythiophene) [200], poly(n-butyl acrylate-co-methyl methacrylate) [194], poly(*N*-isopropylacrylamide) [207], and among others.

Morelli et al. [208] studied that the sulfonated CNC was grafted using a low molecular weight poly(butylene glutarate) by in situ polymerization method and added the modified nanocellulose into PBAT matrices by the technique of melt extrusion. The grafting improved the thermal behavior of the NC by 208 °C and lessens its hydrophilicity. The addition of 10 wt% of NC augments the tensile and elastic modulus of PBAT around 50%, without modifying its good extensibility and upsurges its storage modulus by almost 200%.

Biocomposite with bacterial cellulose (BC) and polypyrrole (PPy) was produced by Muller et al. [209] using an in situ oxidative polymerization of pyrrole (Py) in the presence of bacterial cellulose hydrogels with ammonium persulfate (APS) as an oxidant. The electrical conductivity, morphology, mechanical behavior, and thermal response of the nanocomposites achieved by ammonium persulfate (BC/PPy·APS) were examined and compared with BC/PPy composites obtained using as oxidant agent Iron III chloride hexahydrate. The morphology, electrical conductivity, and the thermal and mechanical response of/PPy·APS composites were studied and also compared with BC/PPy·$FeCl_3$ composites. The BC/PPy·$FeCl_3$ exhibits the electrical conductivity in the range of 0.01–1.2 S cm^{-1}, i.e., 100-fold higher than the BC/PPy APS composites.

7.6 Layer-by-Layer Lamination

Hand laminating, or layer-by-layer (LbL) laminating, is a simple and easy technique for molding the products by intercalating the layers, either by hand or by spray. The resultant materials are laminated, and the mixture of layer properties could provide the superior surface and mechanical behavior. It is well documented that the desired properties for various LbL systems are strongly reliant on the number of layers, pH, ionic strength, deposition conditions, and polymerization degree of the materials [210]. When the structure of the layered films of CNC and xyloglucan (XG) was compared to that of films prepared from a direct combination of CNC/XG in water, both resulted in similar thicknesses, however dissimilar in internal structures [211]. LbL normally uses aqueous media to dissolve the alternative layers of oppositely charged molecules.

The application of nanoparticle layers might be used to prepare materials with different characteristics. These layers might act as reinforcing agents or oxygen barriers, or develop materials with biomedical applications, like tablets with outstanding properties as drug carriers [212, 213].

The deposition of CNC from an anisotropic aqueous dispersion is entropy-driven. The materials produce layers with either random or aligned arrangements. The difference in arrangements is achieved by regulating the critical concentration that is dependent on the materials aspect ratio and dispersion of ionic strength [214].

Cranston et al. [215] studied Young's modulus of multilayer films of CNF and polyethyleneimine. The results confirmed that the humidity was vital to the film properties, as the presence of water altered the interlayer interactions, which leads to reductions in the modulus by more than 10 times. Furthermore, the introduction of charged particles like CNC looks like to make difficulties in the layer interactions more than it did for uncharged layered particles. Since layers are usually charged, the particle interface acts as a composite material and interacts particularly with the opposing layer.

Mesquita et al. [216] evaluated the charge properties to generate electrostatic interactions between negatively charged sulfate groups on CNC surfaces and the ammonium groups of chitosan. The prepared films exhibited thick and uniform dispersals of the CNC nanoparticles, with bilayer resulting in an average thickness of 7 nm. At the same time, the average thickness of collagen–CNC system determined was 8.6 nm for bilayers [217].

7.7 Solvent Casting Method

Solvent casting method is one of the easiest techniques for the development of polymer nanocomposites (Fig. 7) as it requires simple apparatus and is less time-consuming; however, in this technique, it is very difficult to manufacture films without sandwiching with another polymer film for support. Additionally, because of its rigidity, the film developed cracks easily, and this leads to easy peeling off into thin layers like mica. Films formed by the extrusion technique and tubular procedure, where the liquid-crystalline polymer (LCP) is considerably melted give rise to the problem of vertical anisotropy and interlayer peeling due to the peculiar alignment features. So, in such cases, if the solvent casting technique is used where, after dissolution in a solvent, the solvent is removed to obtain the product, a non-anisotropic film may be produced and the film could be prepared without melting the LCP. There-

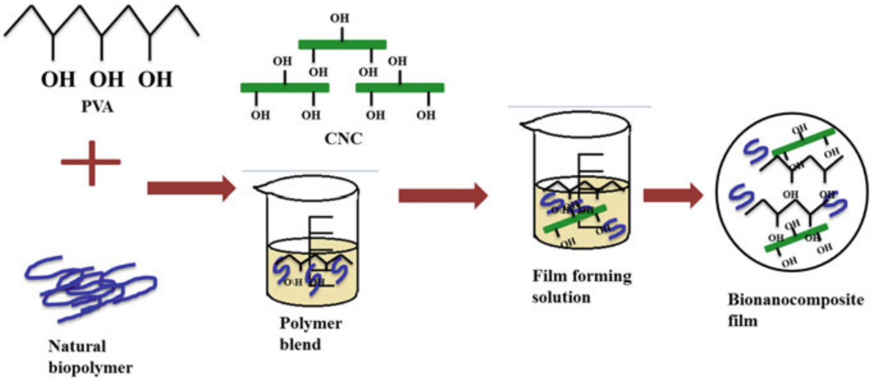

Fig. 7 Preparation of bio-nanocomposite film

fore, solvent-casted films from LCP transfer from an amorphous state to the film by treatment in such a way that the anisotropy in the processing of LCP films does not happen.

Composites produced by casting and evaporation technique result in the maximum mechanical reinforcement presented by CNCs. This is because sample preparation takes place over long time periods. During preparation, the materials have sufficient period to self-assemble into network systems. This method was widely examined in the last 20 years, leading to a well-developed theory and describing the complete potential of cellulose nanoparticles as agents of mechanical reinforcement [183, 218–220].

Nanocomposites might be produced by casting and evaporation technique with the help of polymers matrix which does not need to be water-soluble. A limited number of water-soluble polymers could be directly added with aqueous suspensions of cellulose nanoparticles. This confirms an optimal dispersal of nanoparticles after solvent evaporation technique, while the polymer is dried under controlled conditions. The preferred shape and thickness of the film might also be prepared. Conversely, as with masterbatch production, the use of high-speed homogenizer during polymer dispersion may cause chain scission. Bossard et al. [221] observed a decrease in poly(ethylene oxide) molecular weight led by chain scission during dissolution with stirring at high speed.

Even with these restrictions, the casting technique might be used to prepare very interesting composites. Recently, Cheng et al. [222] used (TEMPO)-oxidized CNF (TOCNF) to prepare waterborne polyurethane coatings (WPU) for the wood application. The addition of various fractions of TOCNF to the polymer–additive mixture intensely enhanced the mechanical behavior of the films. Young’s modulus of the film upsurged from 8.6 MPa (pristine WPU) to 440 MPa (5 wt% TOCNF). On the other hand, the inclusion of the nanoparticles also improved the surface roughness of the films from 3 to 27 nm and reduced the adhesive strength of the coating. This reduction was early described by Poaty et al. [223], who described the use of low molecular weight resins and various ratios of NC to regulate adhesiveness. Other features, like enhanced scratch behavior, have also been defined in the literature [224].

Morelli et al. [208] developed nanocomposites by solvent casting method from PBAT and CNC. Sulfonated CNCs were altered by 4-phenylbutyl isocyanate (5 and 10 wt% of CNC). The results suggest that augmented mechanical response of the nanocomposite with modified CNC to the p–p interfaces between the phenyl rings grafted onto the CNC particles and the aromatic rings of the polymeric chain. Furthermore, the DSC results confirmed that neither the NC incorporation nor their surface modification leads to the lessening of the PBAT amorphous region and in the entire crystallinity of the PBAT matrices.

Gardebjer et al. [225] prepared nanocomposite till 20 wt% of desulfated CNC and chemically altered with PLA. The modified CNC and unmodified CNC were added as nanofillers in three different biodegradable matrices: PLA (polylactide acid), PLGA (poly(lactide-coglycolide)), and PHB by solvent casting technique. The modified NC exhibited low agglomeration and improved interfaces with the polymers like PLA, PLGA, and PHB which are hydrophobic.

Bio-nanocomposites prepared using wheat straw nanofibers and thermoplastic starch (modified potato starch) by solution casting technique [57]. Tensile strength and Young's modulus of the biocomposite films were considerably improved that might be described by the even dispersion of CNF in the polymer matrices. Azeredo et al. [50] prepared chitosan films reinforced with NC and glycerol content as a plasticizer. Sodium caseinate-based films were produced by Pereda et al. [159] with the addition of NC by diffusing the fibers into the film forming solutions, casting, and drying. The composite films exhibited less transparency and more hydrophilic surface when compared to neat sodium caseinate films. Caseinate films developed showed an initial upsurge in the water vapor permeability and then reduced as the filler concentration improved.

7.8 Electrospinning

Electrospinning process produces a nanofiber of films with uniform diameters from the polymer solution with the help of high electric current. The fibers combined with the various polymers will stretch by the electrostatic repulsion between the solvent and surface area which results in nanofibers or films. Two different types of electrospinning methods are generally followed: (1) Two different polymer solution was injected simultaneously through the syringe needle for the formation of nanofibers or films; (2) initially, two polymers are mixed, and the blend was injected into the chamber for the formation of the films which is the most commonly used method for the better achievement of the products with good properties.

Several studies were reported on the electrospinning of the polymers with nanocellulose as reinforcing agents. Zhou et al. [226] stated the nanocellulose-based polyethylene oxide film by electrospinning technique. The rod-like CNC which was well dispersed in the composite nanofibers by this electrospinning results in the improved mechanical and thermal properties of the composites. The PVA-based nanocomposite films were obtained by Peresin et al. [227, 228] by using the electrospun method. The incorporation of CNC to the polymer composites enhanced the mechanical properties due to the formation of the percolation network by the strong bond fromations [227–229].

8 Nanocellulose-Reinforced Biocomposite in Food Packaging Applications

Chitosan-based films have been effectively used as a packaging material for the preservation of food quality [230]. NC-reinforced nanocomposite films might have a promising effect in food packaging applications in upcoming years because of its excellent mechanical and barrier response. Boumail et al. [162] prepared antimicrobial dispersed films for food applications. Antimicrobial dispersed films demonstrated the maximum tensile strength during storage. In addition, Savadekar et al. [90] productively isolated NFC from short cotton fibers by chemo-mechanical technique.

Abdollahi et al. [163] prepared a bio-based nanocomposite by the addition of cellulose nanoparticles extracted from sulfuric acid hydrolysis into alginate biopolymer by solution casting method. The tensile strength of the biocomposite films augmented with growing NC concentration from 0 to 5 wt%; then, it reduced with an additional upsurge of the filler concentration.

An innovative, technical, and economical process to mix the vermiculite nanoplatelets with NC fiber dispersals into functional biohybrid composites was obtained by Aulin et al. [231]. NC fibers of 20 nm in diameters and several micrometers in length were combined with high aspect ratio exfoliated vermiculite nanoplatelets by high-pressure homogenization.

The influence of CNF in the PLA matrix was demonstrated by Jonoobi et al. [160] in terms of mechanical and dynamic mechanical response in concern of the proposed application in food packaging. The upsurge in tensile strength, Young's modulus, and enhanced visco-elastic behavior were noted for nanocomposites films with 5 wt% of CNF. This highlights the success of the melt component process to produce the cellulose nanocomposites.

All cellulose nanocomposite films were prepared from sugarcane bagasse nanofibers using *N*,*N*-dimethylacetamide/lithium chloride solvent. The research investigated that a very less value agricultural residue could be changed into a high-performance nanocomposite. Cellulose nanocomposite films might be taken as a multiperformance particle with high potential in cellulose-based food packaging application due to its valuable properties such as toughness, bio-based, biodegradability, and acceptable levels of WVP. Thus, cellulose nanocomposite films have the potential for the production of the barrier and protective film in food packaging industries. The tensile behavior of cellulose nanocomposite films is at least similar to that of other biodegradable or non-biodegradable film [232].

Mechanical behavior of bio-nanocomposites films holding 6 wt% of CNC in thermoplastic cassava starch exhibited the maximum tensile strength of 8.2 MPa. This confirms the stress transfer and interfacial interactions between the matrix and the nanofiller that is associated with the great L/D and effectiveness of the fiber treatment. The kenaf fibers are also noted to be well suited with agar and starch prepared from potato, and the films were evaluated for their potential use in food packaging [233, 234].

An edible film based on alginate–acerola puree reinforced with CNW or MMT of coating application on fresh acerolas minimized fruit weight loss, reduced diseases incidence, and ripening behavior as well as enhanced the retention of ascorbic acid. Similarly, chitosan-based nanocellulose film studied by Dehnad et al. [158], to prolong the shelf life of meat results in reduced lactic acid bacteria than the nylon film packed samples after 6 days of storage at 25 °C.

PLA-CNC biocomposite film incorporated with oregano essential oil prepared by solvent casting was used for packaging to preserve the vegetables which revealed the retardation of *Listeria monocytogenes* during the storage at 4 °C for 14 days. Likewise, PLA-CNC nanocomposite film prepared with the addition of nisin by compression molding method that revealed the inhibition of *L. monocytogenes* for 14 days in cooked ham pack [235]

Cellulose nanofibrils with calcium carbonate were utilized by coating method for the preservation of blueberries [236]. The quality and shelf life of strawberries were enhanced by coating the fruits with chitosan and nanocellulose. It also helps to retain the bioactive compounds [237]. Similarly, Anand Babu et al. [44] reported that the biocomposite film (PVA-Mt/CNC) reinforced with CNC has prolonged the shelf life of mango cultivars till 19 ± 2 days by delaying the ripening behavior and also maintained the overall fruit quality.

Nanocellulose-based polymer composites also exhibit broad applications in various fields such as coatings for food packaging, water treatment, drug delivery, cosmetics, barrier films, and packaging bag for the preservation of food products. Nanocellulose also acts as natural emulsifying and stabilizing agent and might efficiently substitute the hydrophilic polysaccharides produced from seaweeds, microorganisms and carboxymethylcellulose and vegetable seeds. Nanocellulose exhibits great effects on various food products like salads, foams, soups, sauces, and puddings. Nanocellulose-based composites have wide applications in food packaging because of its competence with petroleum-based synthetic materials. CNC and CNF reinforced composites and its coating application, lessening the oxygen permeability that prolongs the keeping quality of the packaged food products as well as reducing the packaging waste of processed foods.

9 Conclusion

Biocomposites reinforced with CNC or CNF has very good potential to use in food packaging applications by substituting the petroleum-based conventional plastics. Some of the disadvantages of the polymer composites like poor mechanical and water vapor permeability limit their use in various applications specifically in food packaging industry. To improve the mechanical and barrier properties of the composites, the nanocellulose was generally used to reinforce with the polymer which may augment the composites behavior like antimicrobial, antioxidant, and mechanical characteristics. The composites with enhanced properties could be well suited for preserving the fruits, vegetables, and other foods in the food packaging applications. Thus, the nanocellulose-based polymer composites will provide the solution to overcome the problems mainly faced by the food industry.

References

1. BCC Research (2013) BCC Research publishes a new report on global markets for biodegradable polymers. Available at http://www.bccresearch.com/pressroom/pls/global-volume-biodegradable-polymers-market-reach-3-billion-2019
2. Fischer HR, Gielgens LH, Koster TPM (1999) Nanocomposites from polymers and layered minerals. Acta Polym 50:122–126
3. Azeredo HMC, Rosa MF, Mattoso LHC (2017) Nanocellulose in bio-based food packaging applications. Ind Crops Prod 97:664–671
4. Croisier F, Jerome C (2013) Chitosan-based biomaterials for tissue engineering. Eur Polymer J 49:780–792
5. Bhatnagar A, Sillanpää M (2009) Applications of chitin- and chitosanderivatives for the detoxification of water and wastewater—a short review. Adv Coll Interface Sci 152:26–38
6. Harish Prashanth KV, Tharanathan RN (2007) Chitin/chitosan: modifications and their unlimited application potential—an overview. Trends Food Sci Technol 18:117–131
7. Kanatt SR, Rao MS, Chawla SP, Sharma A (2012) Active chitosanpolyvinyl alcohol films with natural extracts. Food Hydrocolloids 29:290–297
8. Costa-Júnior ES, Barbosa-Stancioli EF, Mansur AAP, Vasconcelos WL, Mansur HS (2009) Preparation and characterization of chitosan/ poly(vinyl alcohol) chemically crosslinked blends for biomedical applications. Carbohydr Polym 76:472–481
9. Abdelrazek EM, Abdelghany A, Tarabih A (2012) Characterization and physical properties of silver/PVA nanocomposite. Res J Pharm Biol Chem Sci 3:448–459
10. Chen Y, Cao X, Chang PR, Huneault MA (2008) Comparative study on the films of poly(vinyl alcohol)/pea starch nanocrystals and poly(vinyl alcohol)/native pea starch. Carbohydr Polym 73:8–17
11. Ardanuy M, Claramunt J, Garcia-Hortal JA, Barra M (2011) Fiber-matrix interactions in cement mortar composites reinforced with cellulosic fibers. Cellulose 18:281–289
12. Lu P, Hsieh YL (2012) Preparation and characterization of cellulose nanocrystals from rice straw. Carbohydr Polym 87:564–573
13. Morais JPS, Rosa MS, Filho MMS, Nascimento LD, Nascimento DM, Cassales AR (2013) Extraction and characterization of nanocellulose structures from raw cotton linter. Carbohydr Polym 91:229–235
14. Zhao X-B, Wang L, Liu D-H (2008) Peracetic acid pretreatment of sugarcane bagasse for enzymatic hydrolysis: a continued work. J Chem Technol Biotechnol 83:950–956

15. Abraham E, Deepa B, Pothen LA, Cintil J, Thomas S, John MJ, Anandjiwala R, Narine SS (2013) Environmentally-friendly method for the extraction of coir fibre and isolation of nanofibre. Carbohydr Polym 92:1477–1483
16. Mohanty AK, Misra M, Hinrichsen G (2000) Biofibres, biodegradable polymers and biocomposites: an overview. Macromol Mater Eng 276(277):1–24
17. Habibi Y, Lucia LA, Rojas OJ (2010) Cellulose nanocrystals: chemistry, self-assembly, and application. Chem Rev 110:3479–3500
18. Jeihanipour A, Taherzadeh MJ (2009) Ethanol production from cotton-based waste textiles. Biores Technol 100:1007–1010
19. Wang QQ, Zhu JY, Reiner RS, Verrill SP, Baxa U, MeNeil SE (2012) Approaching zero cellulose loss in cellulose nanocrystal (CNC) production: recovery and characterization of cellulosic solid residues (CSR) and CNC. Cellulose 19:2033–2047
20. Krishnan VN, Ramesh A (2013) Synthesis and characterisation of CNF from Coconut coir fibres. IOSR-J Appl Chem 6:18–23
21. Zhou Y, Canek FH, Talha MK, Liu JC, James H, Shim JW, Amir D, Youngblood PJ, Robert JM, Bernard K (2013) Recyclable organic solar cells on cellulose nanocrystal substrate. Sci Rep 3:1536
22. Zoppe JO, Habibi Y, Rojas OJ, Venditti RA, Johansson LS, Efimenko K, Osterberg M, Laine J (2010) Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: manufacture and characterization. Biomacromol 11:674–681
23. Miri N, Abdelouahdi K, Zahouily M, Fihri A, Barakat A, Solhy A, Achaby M (2015) Bionanocomposite films based on cellulose nanocrystals filled polyvinyl alcohol/chitosan polymer blend. J Appl Polym Sci. https://doi.org/10.1002/app.42004
24. Terech P, Chazeau L, Cavaille JY (1999) A small-angle scattering study of cellulose whiskers in aqueous suspensions. Macromolecules 32:1872–1875
25. Grishkewich N, Mohammed N, Tang J, Tam KC (2017) Recent advances in the application of cellulose nanocrystals. Curr Opin Colloid Interface Sci 29:32–45
26. Mujtaba M, Salaberria AM, Andres MA, Kayaa M, Gunyakti A, Labidi J (2017) Utilization of flax (*Linum usitatissimum*) cellulose nanocrystals as reinforcing material for chitosan films. Int J Biol Macromol 104:944–952
27. Achaby ME, Kassab Z, Aboulkas A, Gaillard C, Barakat A (2018) Reuse of red algae waste for the production of cellulose nanocrystals and its application in polymer nanocomposites. Int J Biol Macromol 106:681–691
28. Dufresne A (2012) Nanocellulose: from nature to high performance tailored materials. Walter de Gruyter
29. Klemm D, Kramer F, Moritz S, Lindström T, Ankerfors M, Gray D, Dorris A (2011) Nanocelluloses: a new family of nature based materials. Angew Chem Int Ed 50(24):5438–5466
30. Chandra CSJ, George N, Narayanankutty SK (2016) Isolation and characterization of cellulose nanofibrils from arecanut husk fibre. Carbohydr Polym 142:158–166
31. Jorfi M, Amiralian N, Biyani MV, Annamalai PK (2013) In: Thakur VK, Singha AS (eds) Biomass-based biocomposites, vol 14. Smithers Rapra Technology, pp 277–304
32. Sofla MRK, Brown RJ, Tsuzuki T, Rainey TJ (2016) A comparison of cellulose nanocrystals and cellulose nanofibres extracted from bagasse using acid and ball milling methods. Adv Nat Sci: Nanosci Nanotechnol 7. https://doi.org/10.1088/2043-6262/7/3/035004
33. Wang HD, Jessop PG, Bouchard J, Champagne P, Cunningham MF (2015) Cellulose nanocrystals with CO_2-switchable aggregation and redispersion properties. Cellulose 22:3105–3116
34. Bagheriasl D, Carreau PJ, Riedl B, Dubois C, Hamad WY (2016) Shear rheology of polylactide (PLA)-cellulose nanocrystal (CNC) nanocomposites. Cellulose 23:1885–1897
35. Song T, Tanpichai S, Oksman K (2016) Cross-linked polyvinyl alcohol (PVA) foams reinforced with cellulose nanocrystals (CNCs). Cellulose 23:1925–1938
36. Feng X, Meng XH, Zhao JP, Miao M, Shi LY, Zhang SP, Fang JH (2015) Extraction and preparation of cellulose nanocrystals from dealginate kelp residue: structures and morphological characterization. Cellulose 22:1763–1772

37. Lu QL, Lin WY, Tang LR, Wang SQ, Chen XR, Huang B (2015) A mechanochemical approach to manufacturing bamboo cellulose nanocrystals. J Mater Sci 50:611–619
38. Eichhorn SJ, Baillie CA, Zafeiropoulos N, Mwaikambo LY, Ansell MP, Dufresne A, Entwistle KM, Herrera-Franco PJ, Escamilla GC, Groom L, Hughes M, Hill C, Rials TG, Wild PM (2001) Review: current international research into cellulosic fibres and composites. J Mater Sci 36:2107–2131
39. Khandelwal M, Windle AH, Hessler N (2016) In situ tunability of bacteria produced cellulose by additives in the culture media. J Mater Sci 51:4839–4844
40. Santos SM, Carbajo JM, Gomez N, Quintana E, Ladero M, Sanchez A, Chinga-Carrasco G, Villar JC (2016) Use of bacterial cellulose in degraded paper restoration. Part I: application on model papers. J Mater Sci 51:1541–1552
41. Santos SM, Carbajo JM, Gomez N, Quintana E, Ladero M, Sanchez A, Chinga-Carrasco G, Villar JC (2016) Use of bacterial cellulose in degraded paper restoration. Part II: application on real samples. J Mater Sci 51:1553–1561
42. Achaby M, Miri N, Aboulkas A, Zahouily M, Essaid B, Barakat A, Solhy A (2017) Processing and properties of eco-friendly bio-nanocomposite films filled with cellulose nanocrystals from sugarcane bagasse. Int J Biol Macromol 96:340–352
43. Johar N, Ahmad I, Dufresne A (2012) Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk. Ind Crops Prod 37:93–99
44. Anand Babu P, Periyar Selvam S, Nambiar RB, Rotimi Sadiku E, Goitse P, Jayaramudu J (2018) Effects of multiscale rice straw (*Oryza sativa*) as reinforcing filler in montmorillonite-polyvinyl alcohol biocomposite packaging film for enhancing the storability of postharvest mango fruit (*Mangifera indica* L.). Appl Clay Sci 158:1–10
45. Danial WH, Majid ZA, Muhid MNM, Triwahyono S, Bakar MB, Ramli Z (2015) The reuse of wastepaper for the extraction of cellulose nanocrystals. Carbohydr Polym 118:165–169
46. Voon LK, Pang SC, Chin SF (2016) Regeneration of cello-oligomers via selective depolymerization of cellulose fibers derived from printed paper wastes. Carbohydr Polym 142:31–37
47. Khan A, Huq T, Khan RA, Riedl B, Lacroix M (2014) Nanocellulose-based composites and bioactive agents for food packaging. Crit Rev Food Sci Nutr 54:163–174
48. Dufresne A (1997) Mechanical behavior of films prepared from sugar beet cellulose microfibrils. J Appl Polym Sci 64:1185–1194
49. Beck-Candanedo S, Roman M, Gray DG (2005) Effect of reaction conditions on the properties and behavior of wood cellulose nanocrystal suspensions. Biomacromolecules 6:1048–1054
50. Azeredo HM, Mattoso LH, Avena-Bustillos RJA, Filho GC, Munford ML, Wood D, Mchugh TH (2010) Nanocellulose reinforced chitosan composite films as affected by nanofiller loading and plasticizer content. J Food Sci 75:N1–N7
51. Cao X, Chen Y, Chang PR, Muir AD, Falk G (2008) Starch based nanocomposites reinforced with flax cellulose nanocrystals. Polymer Lett 2:502–510
52. Dieter-Klemm D, Schumann D, Kramer F, Hessler N, Koth D, Sultanova B (2009) Nanocellulose materials: different cellulose, different functionality. Macromol Symp 280:60–71
53. Dieter-Klemm D, Schumann D, Kramer F, Hessler N, Hornung M, Schmauder HP, Marsch S (2006) Nanocelluloses as innovative polymers in research and application. Adv Polym Sci 205:49–96
54. Pecoraro E, Manzani D, Messaddeq Y, Ribeiro SJL (2008) Bacterial cellulose from Gluconacetobacter xylinus: preparation, properties and applications. In: Belgacem MN, Gandini A (eds) Monomers, polymers and composites from renewable resources. Elsevier, Oxford, pp 369–383
55. Chang S-T, Chen L-C, Lin S-B, Chen H-H (2012) Nano-biomaterials application: morphology and physical properties of bacterial cellulose/gelatin composites via crosslinking. Food Hydrocolloids 27:137–144
56. Duarte EB, Chagas BS, Andrade FK, Santa Brígida AI, Borges MF, Muniz CR, Souza Filho MSM, Morais JPS, Feitosa JPA, Rosa MF (2015) Production of hydroxyapatite–bacterial cellulose nanocomposites from agroindustrial wastes. Cellulose 22:3177–3187

57. Alemdar A, Sain M (2008) Isolation and characterization of nanofibers from agricultural residues—Wheat straw and soy hulls. Biores Technol 99:1664–1671
58. Fahma F, Iwamoto S, Hori N, Iwata T, Takemura A (2010) Isolation, preparation, and characterization of nanofibers from oil palm empty-fruit-bunch (OPEFB). Cellulose 17:977–985
59. Fatah IYA, Khalil HPS, Hossain MS, Aziz AA, Davoudpour Y, Dungani R, Bhat A (2014) Exploration of a chemo-mechanical technique for the isolation of nanofibrillated cellulosic fiber from oil palm empty fruit bunch as a reinforcing agent in composites materials. Polymers 6:2611–2624
60. Chen W, Yu H, Liu Y, Hai Y, Zhang M, Chen P (2011) Isolation and characterization of cellulose nanofibers from four plant cellulose fibers using a chemical-ultrasonic process. Cellulose 18:433–442
61. Saito T, Hirota M, Tamura N, Kimura S, Fukuzumi H, Heux L, Isogai A (2009) Individualization of nano-sized plant cellulose fibrils by direct surface carboxylation using TEMPO catalyst under neutral conditions. Biomacromolecules 10:1992–1996
62. Khalil HA, Davoudpour Y, Islam MN, Mustapha A, Sudesh K, Dungani R, Jawaid M (2014) Production and modification of nanofibrillated cellulose using various mechanical processes: a review. Carbohydr Polym 99:649–665
63. Camargo LA, Pereira SC, Correa AC, Farinas CS, Marconcini JM, Mattoso LHC (2016) Feasibility of manufacturing cellulose nanocrystals from the solid residues of second-generation ethanol production from sugarcane bagasse. Bioenergy Res 9:894–906
64. Teixeira EM, Pasquini D, Curvelo AAS, Corradini E, Belgacem A, Dufresne A (2009) Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. Carbohydr Polym 78:422–431
65. Oun AA, Rhim J-W (2016) Isolation of cellulose nanocrystals from grain straws and their use forthe preparation of carboxymethyl cellulose-based nanocomposite films. Carbohydr Polym 150:187–200
66. Kargarzadeh H, Ahmad I, Abdullah I, Dufresne A, Zainudin SY, Sheltami RM (2012) Effects of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. Cellulose 19:855–866
67. Zainuddin SYZ, Ahmad I, Kargarzadeh H, Abdullah I, Dufresne A (2013) Potential of using multiscale kenaf fibers as reinforcing filler in cassava starch-kenaf biocomposites. Carbohydr Polym 92:2299–2305
68. Wang Z, Yao Z, Zhou J, Zhang Y (2017) Reuse of waste cotton cloth for the extraction of cellulose nanocrystals. Carbohydr Polym 157:945–952
69. Thambiraj S, Ravi Shankaran D (2017) Preparation and physicochemical characterization of cellulose nanocrystals from industrial waste cotton. Appl Surf Sci 412:405–416
70. Fortunati E, Benincasa P, Balestra GM, Luzi F, Mazzaglia A, Del Buono D, Puglia D, Torre L (2016) Revalorization of barley straw and husk as precursors for cellulose nanocrystals extraction and their effect on PVA_CH nanocomposites. Ind Crops Prod 92:201–217
71. Fortunati E, Puglia D, Monti M, Santulli C, Maniruzzaman M, Kenny JM (2013) Cellulose nanocrystals extracted from okra fibers in PVA nanocomposites. J Appl Polym Sci 128:3220–3230
72. Luzi F, Fortunati E, Giovanale G, Mazzaglia A, Torre L, Balestra GM (2017) Cellulose nanocrystals from Actinidia deliciosa pruning residues combined with carvacrol in PVA_CH films with antioxidant/antimicrobial properties for packaging applications. Int J Biol Macromol 104:43–55
73. Shamskar KR, Heidari H, Rashidi A (2016) Preparation and evaluation of nanocrystalline cellulose aerogels from raw cotton and cotton stalk. Ind Crops Prod 93:203–211
74. Li Y, Liu Y, Chen W, Wang Q, Liu Y, Li J, Yu H (2016) Facile extraction of cellulose nanocrystals from wood using ethanol and peroxide solvothermal pretreatment followed by ultrasonic nanofibrillation. Green Chem 18:1010–1018
75. Luzi F, Fortunati E, Jiménez A, Puglia D, Pezzolla D, Gigliotti G, Kenny JM, Chiralt A, Torre L (2016) Production and characterization of PLA_PBS biodegradable blends reinforced with cellulose nanocrystals extracted from hemp fibres. Ind Crops Prod 93:276–289

76. Cudjoe E, Hunsen M, Xue Z, Way AE, Barrios E, Olson RA, Hore MJA, Rowan SJ (2017) Miscanthus Giganteus: a commercially viable sustainable source of cellulose nanocrystals. Carbohydr Polym 155:230–241
77. Habibi Y, Goffin A-L, Schiltz N, Duquesne E, Dubois P, Dufresne A (2008) Bionanocomposites based on poly (3-caprolactone)-grafted cellulose nanocrystals by ringopening polymerization. J Mater Chem 18:5002–5010
78. Kumar A, Negi YS, Choudhary V, Bhardwaj NK (2014) Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. J Mater Phys Chem 2:1–8
79. Kaushik A, Singh M, Verma G (2010) Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw. Carbohydr Polym 82:337–345
80. Roman M, Gray DG (2005) Parabolic focal conics in self-assembled solid film of cellulose nanocrystals. Langmuir 21:5555–5561
81. Zhao Y, Zhang Y, Lindström ME, Li J (2015) Tunicate cellulose nanocrystals: preparation, neat films andnanocomposite films with glucomannans. Carbohydr Polym 117:286–296
82. Neto WPF, Mariano M, da Silva ISV, Silvério HA, Putaux JL, Otaguro H, Pasquini H (2016) Mechanical properties of natural rubber nanocomposites reinforced with high aspect ratio cellulose nanocrystals isolated from soy hulls. Carbohydr Polym 153:143–152
83. Sheltami RM, Abdullah I, Ahmad I, Dufresne A, Kargarzadeh H (2012) Extraction of cellulose nanocrystals from mengkuang leaves (*Pandanus tectorius*). Carbohydr Polym 88:772–779
84. Silvério HA, Neto WPF, Dantas NO, Pasquini D (2013) Extraction and characterization of cellulose nanocrystals from corncob for application as reinforcing agent in nanocomposites. Ind Crops Prod 44:427–436
85. Brito BSL, Pereira FV, Putaux J-L, Jean B (2012) Preparation, morphology and structure of cellulose nanocrystals from bamboo fibers. Cellulose 19:1527–1536
86. Pereira AL, do Nascimento DM, Souza Filho MDS, Morais JP, Vasconcelos NF, Feitosa JP, Brígidae AI, Rosac MF (2014) Improvement of polyvinyl alcohol properties by adding nanocrystalline cellulose isolated from banana pseudostems. Carbohydr Polym 112:165–172
87. Kanoth BP, Thomas T, Joseph JM, Kuthirummal N, Narayanankutty SK (2015) A cost-effective method to prepare cellulose nanofiber from coir. Adv Sci, Eng Med 7:492–497
88. Anand Babu P, Periyar Selvam S, Nambiar RB, Rotimi Sadiku E (2018) Development of polyvinyl alcohol/chitosan bio-nanocomposite films reinforced with cellulose nanocrystals isolated from rice straw. Appl Surf Sci. https://doi.org/10.1016/j.apsusc.2018.01.022
89. Popescu M-C (2017) Structure and sorption properties of CNC reinforced PVA films. Int J Biol Macromol 101:783–790
90. Savadekar NR, Karande VS, Vigneshwaran N, Bharimalla AK, Mhaske ST (2012) Preparation of nano cellulose fibers and its application in kappa-carrageenan based film. Int J Biol Macromol 51:1008–1013
91. Jonoobi M, Harun J, Shakeri A, Misra M, Oksman K (2009) Chemical composition, crystallinity, and thermal degradation of bleached and unbleached kenaf bast (*Hibiscus cannabinus*) pulp and nanofibers. BioResources 4:626–639
92. Jonoobi M, Khazaeian A, Tahir PM, Azry SS, Oksman K (2011) Characteristics of cellulose nanofibers isolated from rubber wood and empty fruit bunches of oil palm using chemo-mechanical process. Cellulose 18:1085–1095
93. Habibi Y, Vignon M (2008) Optimization of cellouronic acid synthesis by TEMPO-mediated oxidation of cellulose III from sugar beet pulp. Cellulose 15:177–185
94. Janardhnan S, Sain M (2006) Isolation of cellulose microfibrils—an enzymatic approach. BioResources 1:176–188
95. Bruce DM, Hobson RN, Farrent JW, Hepworth DG (2005) High-performance composites from low-cost plant primary cell walls. Compos A Appl Sci Manuf 36:1486–1493
96. Castro C, Zuluaga R, Álvarez C, Putaux JL, Caro G, Rojas OJ, Mondragon I, Gañán P (2012) Bacterial cellulose produced by a new acid-resistant strain of *Gluconacetobacter* genus. Carbohydr Polym 89:1033–1037

97. Grunert M, Winter WT (2002) Nanocomposites of cellulose acetate butyrate reinforced with cellulose nanocrystals. J Polym Environ 10:27–30
98. George J, Bawa AS, Siddaramaiah (2010) Synthesis and characterization of bacterial cellulose nanocrystals and their PVA nanocomposites. Adv Mater Res 123–125:383–386
99. George J, Siddaramaiah (2012) High performance edible nanocomposite films containing bacterial celulose nanocrystals. Carbohydr Polym 87:2031–2037
100. Araki J, Wada M, Kuga S (2001) Steric stabilization of a cellulose microcrystal suspension by poly(ethylene glycol)grafting. Langmuir 17:21–27
101. Fortunati E, Luzi F, Jiménez A, Gopakumar DA, Puglia D, Thomas S, Kenny JM, Chiralt A, Torre L (2016) Revalorization of sunflower stalks as novel sources of cellulose nanofibrils and nanocrystals and their effect on wheat gluten bionanocomposite properties. Carbohydr Polym 149:357–368
102. Jonoobi M, Mathew AP, Oksman K (2012) Producing low-cost cellulose nanofiber from sludge as new source of raw materials. Ind Crops Prod 40:232–238
103. Madhu K, Carole F, Grégory C, Jean-Luc P, Audrey M (2015) Transmission electron microscopy for the characterization of cellulose nanocrystals. Intech publisher. http://dx.doi.org/10.5772/60985
104. Martins DF, de Souza AB, Henrique MA, Silverio HA, Flauzino Neto WP, Pasquini D, Silvério HA, Flauzino Neto WP, Pasquini D (2015) The influence of the cellulose hydrolysis process on the structure of cellulose nanocrystals extracted from capim mombaça (*Panicum maximum*). Ind Crops Prod 65:496–505
105. Siqueira G, Bras J, Dufresne A (2009) Cellulose whiskers versus microfibrils: Influence of the nature of the nanoparticle and its surface functionalization on the thermal and mechanical properties of nanocomposites. Biomacromol 10:425–432
106. Siqueira G, Bras J, Dufresne A (2010) Cellulosic bionanocomposites: a review of preparation, properties and applications. Polymers 2:728–765
107. De Souze Lima M, Borsali R (2004) Rod like cellulose microcrystals: structure, properties, and applications. Macromol Rapid Commun 25:771–787
108. Oksman K, Etang J, Mathew AP, Jonoobi M (2011) Cellulose nanowhiskers separated from a bio-residue from wood bioethanol production. Biomass Bioenerg 35:146–152
109. Kalia S, Kaith BS, Kaur I (eds) (2011) Cellulose fibers: bio- and nano-polymer composites. Springer, Berlin, p 743
110. Guo J, Guo XX, Wang SQ, Yin YF (2016) Effects of ultrasonic treatment during acid hydrolysis on the yield, particle size and structure of cellulose nanocrystals. Carbohydr Polym 135:248–255
111. Jin Y, Hengl N, Baup S, Pignon F, Gondrexon N, Sztucki M, Romdhane A, Guillet A, Aurousseau M (2015) Ultrasonic assisted cross-flow ultrafiltration of starch and cellulose nanocrystals suspensions: characterization at multi-scales. Carbohydr Polym 124:66–76
112. Cao X, Ding B, Yu J, Al-Deyab SS (2012) Cellulose nanowhiskers extracted from TEMPO oxidized jute fibers. Carbohydr Polym 90:1075–1080
113. Fukuzumi H, Saito T, Isogai A (2013) Influence of TEMPO-oxidized cellulose nanofibril length on film properties. Carbohydr Polym 93:172–177
114. Iwamoto S, Kai W, Isogai T, Saito T, Isogai A, Iwata T (2010) Comparison study of TEMPO-analogous compounds on oxidation efficiency of wood cellulose for preparation of cellulose nanofibrils. Polym Degrad Stab 95:1394–1398
115. Fukuzumi H, Saito T, Okita Y, Isogai A (2010) Thermal stabilization of TEMPO-oxidized cellulose. Polym Degrad Stab 95:1502–1508
116. Herrera M, Mathew AP, Oksman K (2012) Comparison of cellulose nanowhiskers extracted from industrial bio-residue and commercial microcrystalline cellulose. Mater Lett 71:28–31
117. Mtibe A, Linganiso LZ, Mathew AP, Oksman K, John MJ, Anandjiwala RD (2015) A comparative study on properties of micro and nanopapers produced from cellulose and cellulose nanofibres. Carbohydr Polym 118:1–8
118. Abdul Khalil HPS, Bhat AH, Ireana Yusra AF (2012) Green composites from sustainable cellulose nanofibrils: a review. Carbohydr Polym 87:963–979

119. Asefa T (2012) Chiral nematic mesoporous carbons from self-assembled nanocrystalline cellulose. Angew Chem Int Ed 51:2008–2010
120. Cheung CCY, Giese M, Kelly JA, Hamad WY, McLachlan MJ (2013) Iridescent chiral nematic cellulose nanocrystal/polymer composites assembled in organic solvent. ACS Macro Lett 2:1016–1020
121. Lagerwall JPF, Schutz C, Salajkova M, Noh JH, Park JH, Scalia G, Bergstrom L (2014) Cellulose nanocrystal-based materials: from liquid crystal self-assembly and glass formation to multifunctional thin films. NPG Asia Mater 6:1–12
122. Robles E, Urruzola I, Labidi J, Serrano L (2015) Surface-modified nano-cellulose as reinforcement in poly(lactic acid) to conform new composites. Ind Crops Prod 71:44–53
123. Li Y, Pickering KL (2008) Hemp fibre reinforced composites using chelator and enzyme treatments. Compos Sci Technol 68:3293–3298
124. Van Sumere CF (1992) Retting of flax with special reference to enzyme retting. In: Sharma HSS, Van Sumere CF (eds) The biology and retting of flax, vol 157. Belfast, pp 153–193
125. Nykter M, Kymäläinen H-R, Thomsen AB, Lilholt H, Koponen H, Sjöberg AM, Thygesen A (2008) Effects of thermal and enzymatic treatments and harvesting time on the microbial quality and chemical composition of fibre hemp (*Cannabis sativa* L.). Biomass Bioenergy 32:392–399
126. Wang HM (2003) Removing pectin and lignin during chemical processing of hemp for textile applications. Text Res J 73:664–669
127. Zhang J, Henriksson G, Johansson G (2000) Polygalacturonase is the key component in enzymatic retting of flax. J Biotechnol 81:85–89
128. Chen J, Wu D, Tam KC, Pan K, Zheng Z (2017) Effect of surface modification of cellulose nanocrystal on nonisothermal crystallization of poly(β-hydroxybutyrate) composites. Carbohydr Polym 157:1821–1829
129. Morelli CL, Belgacem MN, Branciforti MC, Bretas RES, Crisci A, Bras J (2016) Supramolecular aromatic interactions to enhance biodegradable film properties through incorporation of functionalized cellulose nanocrystals. Compos A Appl Sci Manuf 83:80–88
130. Siqueira G, Fraschini C, Bras J, Dufresne A, Prud'homme R, Laborie MP (2011) Impact of the nature and shape of cellulosic nanoparticles on the isothermal crystallization kinetics of poly(ε caprolactone). Eur Polymer J 47:2216–2227
131. Fortunati E, Rinaldi S, Peltzer M, Bloise N, Visai L, Armentano I, Jiménez A, Latterini L, Kenny JM (2014) Nano-biocomposite films with modified cellulose nanocrystals and synthesized silver nanoparticles. Carbohydr Polym 101:1122–1133
132. Oksman K, Mathew AP, Bondeson D, Kvien I (2006) Manufacturing process of cellulose whiskers/polylactic acid nanocomposites. Compos Sci Technol 66:2776–2784
133. Petersson L, Kvien I, Oksman K (2007) Structure and thermal properties of poly(lactic acid)/cellulose whiskers nanocomposite materials. Compos Sci Technol 67:2535–2544
134. Huq T, Salmieri S, Khan A, Khan RA, Tien CL, Riedl B, Fraschini C, Bouchard J, Uribe-Calderon J, Kamal MR, Lacroix M (2012) Nanocrystalline cellulose (NCC) reinforced alginate based biodegradable nanocomposite film. Carbohydr Polym 90:1757–1763
135. Mathew AP, Dufresne A (2002) Morphological investigation of nanocomposites from sorbitol plasticized starch and tunicin whiskers. Biomacromol 3:609–617
136. Azeredo HMC, Miranda KWE, Rosa MF, Nascimento DM, De Moura MR (2012) Edible films from alginate-acerola puree reinforced with cellulose whiskers. LWT-Food Sci Technol 46:294–297
137. Azeredo HMC, Miranda KWE, Ribeiro HL, Rosa MF, Nascimento DM (2012) Nanoreinforced alginate–acerola puree coatings on acerola fruits. J Food Eng 113:505–510
138. Fortunati E, Luzi F, Puglia D, Dominici F, Santulli C, Kenny JM, Torre L (2014) Investigation of thermo-mechanical: chemical and degradative properties of PLA-limonene films reinforced with cellulose nanocrystals extracted from Phormium tenax leaves. Eur Polymer J 56:77–91
139. Fortunati E, Peltzer M, Armentano I, Torre L, Jiménez A, Kenny JM (2012) Effects of modified cellulose nanocrystals on the barrier and migration properties of PLA nano-biocomposites. Carbohydr Polym 90:948–956

140. Pereda M, Dufresne A, Aranguren MI, Marcovich NE (2014) Polyelectrolyte films based on chitosan/olive oil and reinforced with cellulose nanocrystals. Carbohydr Polym 101:1018–1026
141. Fernandes SCM, Freire CSR, Silvestre AJD, Pascoal Neto C, Gandini A, Berglund LA, Salmen L (2010) Transparent chitosan films reinforced with a high content of nanofibrillated cellulose. Carbohydr Polym 81:394–401
142. Jipa IM, Stoica-Guzun A, Stroescu M (2012) Controlled release of sorbic acid from bacterial cellulose based mono and multilayer antimicrobial films. LWT-Food Sci Technol 47:400–406
143. Iwatake A, Nogi M, Yano H (2008) Cellulose nanofiber-reinforced polylactic acid. Compos Sci Technol 68:2103–2106
144. Peng X-W, Ren J-L, Zhong L-X, Sun R-C (2011) Nanocomposite films based on xylan-rich hemicelluloses and cellulose nanofibers with enhanced mechanical properties. Biomacromol 12:3321–3329
145. Bilbao-Sainz C, Bras J, Williams T, Sénechal T, Orts W (2011) HPMC reinforced with different cellulose nano-particles. Carbohydr Polym 86:1549–1557
146. George J, Ramana KV, Bawa AS, Siddaramaiah (2011) Bacterial cellulose nanocrystals exhibiting high thermal stability and their polymer nanocomposites. Int J Biol Macromol 48:50–57
147. Soykeabkaew N, Laosat N, Ngaokla A, Yodsuwan N, Tunkasiri T (2012) Reinforcing potential of micro- and nano-sized fibers in the starch-based biocomposites. Compos Sci Technol 72:845–852
148. Barud HS, Souza JL, Santos DB, Crespi MS, Ribeiro CA, Messaddeq Y, Ribeiro SJL (2011) Bacterial celulose/poly(3-hydroxybutyrate) composite membranes. Carbohydr Polym 83:1279–1284
149. Lin W-C, Lien C-C, Yeh H-J, Yu C-M, Hsu S-H (2013) Bacterial cellulose and bacterial cellulose-chitosan membranes for wound dressing applications. Carbohydr Polym 94:603–611
150. Dufresne A (2017) Cellulose nanomaterial reinforced polymer nanocomposites. Curr Opin Colloid Interface Sci 29:1–8
151. Mariano M, Chirat C, El Kissi N, Dufresne A (2014) Impact of cellulose nanocrystal aspect ratio on crystallization and reinforcement of poly(butylene adipate-co-terephthalate). J Polym Sci, Part B: Polym Phys 52:791
152. Goffin A-L, Raquez J-M, Duquesne E, Siqueira G, Habibi Y, Dufresne A, Dubois P (2011) From interfacial ring-opening polymerization to melt processing of cellulose nanowhisker-filled polylactide-based nanocomposites. Biomacromol 12:2456–2465
153. García MA, Pinotti A, Martino MN, Zaritzky NE (2004) Characterization of composite hydrocolloid films. Carbohydr Polym 56:339–345
154. Miri NE, Abdelouahdi K, Barakat A, Zahouily M, Fihri A, Solhy A, Achaby ME (2015) Bio-nanocomposite films reinforced with cellulose nanocrystals: rheology of film-forming solutions, transparency, water vapor barrier and tensile properties of films. Carbohydr Polym 129:156–167
155. Wu T, Farnood R, O'Kelly K, Chen B (2014) Mechanical behavior of transparent nanofibrillar cellulose-chitosan nanocomposite films in dry and wet conditions. J Mech Behav Biomed Mater 32:279–286
156. Khan A, Khan RA, Salmieri S, Le Tien C, Riedl B, Bouchard J, Chauve G, Tan V, Kamal MR, Lacroix M (2012) Mechanical and barrier properties of nanocrystalline cellulose reinforced chitosan based nanocomposite films. Carbohydr Polym 90:1601–1608
157. Li Q, Zhou J, Zhang L (2009) Structure and properties of the nanocomposite films of chitosan reinforced with cellulose whiskers. J Polym Sci, Part B: Polym Phys 47:1069–1077
158. Dehnad D, Emam-Djomeh Z, Mirzaei H, Jafari SM, Dadashi S (2014) Optimization of physical and mechanical properties for chitosan nanocellulose biocomposites. Carbohydr Polym 105:222–228
159. Pereda M, Amica G, Rácz I, Marcovich NE (2011) Structure and properties of nanocomposite films based on sodium caseinate and nanocellulose fibers. J Food Eng 103:76–83

160. Jonoobi M, Harun J, Mathew AP, Oksman K (2010) Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. Compos Sci Technol 70:1742–1747
161. Khan RA, Salmieri S, Dussault D, Uribe-Calderon J, Kamal MR, Safrany A, Lacroix M (2010) Production and properties of nanocellulose-reinforced methylcellulose-based biodegradable films. J Agric Food Chem 58:7878–7885
162. Boumail A, Salmieri S, Klimas E, Tawema PO, Bouchard J, Lacroix M (2013) Characterization of trilayer antimicrobial diffusion films (ADFs) based on methylcellulose-polycaprolactone composites. J Agric Food Chem 61:811–821
163. Abdollahi M, Alboofetileh M, Behrooz R, Rezaei M, Miraki R (2013) Reducing water sensitivity of alginate bio-nanocomposite film using cellulose nanoparticles. Int J Biol Macromol 54:166–173
164. Xu X, Liu F, Jiang L, Zhu JY, Haagenson D, Wiesenborn DP (2013) Cellulose nanocrystals vs. cellulose nanofibrils: a comparative study on their microstructures and effects as polymer reinforcing agents. ACS Appl Mater Interfaces 5:2999–3009
165. López-Rubio A, Lagaron JM, Ankerfors M, Lindström T, Nordqvist D, Mattozzi A, Hedenqvist MS (2007) Enhanced film forming and film properties of amylopectin using micro-fibrillated cellulose. Carbohydr Polym 68:718–727
166. George J, Kumar R, Sajeevkumar VA, Ramana KV, Rajamanickam R, Abhishek V, Nadanasabapathy S, Siddaramaiah (2014) Hybrid HPMC nanocomposites containing bacterial celulose nanocrystals and silver nanoparticles. Carbohydr Polym 105:285–292
167. Paralikar SA, Simonsen J, Lombardi J (2008) Poly(vinyl alcohol)/cellulose nanocrystal barrier membranes. J Membr Sci 320:248–258
168. Follain N, Belbekhouche S, Bras J, Siqueira G, Marais S, Dufresne A (2013) Water transport properties of bio-nanocomposites reinforced by *Luffa cylindrica* cellulose nanocrystals. J Membr Sci 427:218–229
169. Dhar P, Bhardwaj U, Kumar A, Katiyar V (2015) Poly(3-hydroxybutyrate)/cellulose nanocrystal films for food packaging applications: barrier and migration studies. Polym Eng Sci 55:2388–2395
170. Wang Y, Cao X, Zhang L (2006) Effects of cellulose whiskers on properties of soy protein thermoplastics. Macromol Biosci 6:524–531
171. Chen Y, Liu C, Chang PR, Cao X, Anderson DP (2009) Bionanocomposites based on pea starch and cellulose nanowhiskers hydrolyzed from pea hull fibre: effect of hydrolysis time. Carbohydr Polym 76:607–615
172. Dufresne A, Dupeyre D, Vignon MR (2000) Cellulose microfibrils from potato tuber cells: processing and characterization of starch-cellulose microfibril composites. J Appl Polym Sci 76:2080–2092
173. Mesquita JP, Donnici CL, Teixeira IF, Pereira FV (2012) Bio-based nanocomposites obtained through covalent linkage between chitosan and cellulose nanocrystals. Carbohydr Polym 90:210–217
174. Azeredo HMC, Mattoso LHC, Wood D, Williams TG, Avena-Bustillos RJ, McHugh TH (2009) Nanocomposite edible films from mango puree reinforced with cellulose nanofibers. J Food Sci 74:N31–N35
175. Bideau B, Bras J, Saini S, Daneault C, Loranger E (2016) Mechanical and antibacterial properties of a nanocellulose-polypyrrole multilayer composite. Mater Sci Eng: C 69:977–984
176. Khan RA, Beck S, Dussault D, Salmieri S, Bouchard J, Lacroix M (2013) Mechanical and barrier properties of nanocrystalline cellulose reinforced poly(caprolactone) composites: effect of gamma radiation. J Appl Polym Sci. https://doi.org/10.1002/app.38896
177. Bharimalla AK, Deshmukh SP, Vigneshwaran N, Patil PG, Prasad V (2017) Nanocellulose based polymer composites for applications in food packaging: future prospects and challenges. Polym Plast Technol Eng 56:805–823
178. Zhang X, Ma P, Zhang Y (2016) Structure and properties of surface-acetylated cellulose nanocrystal/poly(butylene adipate-co-terephtalate) composites. Polym Bull 73:2073–2085

179. Morelli CL, Belgacem N, Bretas RES, Bras J (2016) Melt extruded nanocomposites of polybutylene adipate-co-terephthalate (PBAT) with phenylbutyl isocyanate modified cellulose nanocrystals. J Appl Polym Sci 133:43678. https://doi.org/10.1002/app.43678
180. Habibi Y, Aouadi S, Raquez J-M, Dubois P (2013) Effects of interfacial stereocomplexation in cellulose nanocrystal-filled polylactide nanocomposites. Cellulose 20:2877–2885
181. Castro DO, Frollini E, Ruvolo-Filho A, Dufresne A (2015) Green polyethylene and curauá cellulose nanocrystal based nanocomposites: effect of vegetable oils as coupling agent and processing technique. J Polym Sci, Part B: Polym Phys 53. https://doi.org/10.1002/polb.23729
182. Menezes AJ, Siqueira G, Curvelo AAS, Dufresne A (2009) Extrusion and characterization of functionalized cellulose whiskers reinforced polyethylene nanocomposites. Polymer 50:4552–4563
183. Yousefian H, Rodrigue D (2015) Effect of nanocrystalline cellulose, chemical blowing agent and mold temperature on the morphological, physical and mechanical properties of polypropylene. J Appl Polym Sci 132:1–9
184. Alloin F, D'Aprea A, Dufresne A, El Kissi N, Bossard F (2011) Poly(oxyethylene) and ramie whiskers based nanocomposites: influence of processing: extrusion and casting/evaporation. Cellulose 18:957–973
185. Kiziltas A, Nazari B, Kiziltas EE, Gardner DJS, Han Y, Rushing TS (2016) Cellulose nanofiber-polyethylene nanocomposites modified by polyvinyl alcohol. J Appl Polym Sci 133:1–8
186. Sun X, Lu C, Liu Y, Zhang W, Zhang X (2014) Melt-processed poly(vinyl alcohol) composites filled with microcrystalline cellulose from waste cotton fabrics. Carbohydr Polym 101:642–649
187. Zammarano M, Maupin PH, Sung LP, Gilman JW, McCarthy ED, Kim YS, Fox DM (2011) Revealing the interface in polymer nanocomposites. ACS Nano 5:3391–3399
188. Kalia S, Dufresne A, Cherian BM, Kaith B, Avérous L, Njuguna J Nassiopoulos E (2011) Cellulose-based bio- and nanocomposites: a review. Int J Polym Sci
189. Lekakou C, Hearn A, Murugesh A, Le Page B (2007) Liquid composite moulding of fibre nanocomposites. Mater Sci Technol 23:487–491
190. Lee KY, Shamsuddin SR, Fortea-Verdejo M, Bismarck A (2014) Manufacturing of robust natural fiber preforms utilizing bacterial cellulose as binder. J Vis Exp 87. https://doi.org/10.3791/51432
191. Qamhia II, Sabo RC, Elhajjar RF (2013) Static and dynamic characterization of cellulose nanofibril scaffold-based composites. BioResources 9:381–392
192. Barari B, Ellingham TK, Ghamhia II, Pillai KM, El-Hajjar R, Turng LS, Sabo R (2016) Mechanical characterization of scalable cellulose nano-fiber based composites made using liquid composite molding process. Compos B Eng 84:277–284
193. Barari B, Omrani E, Moghadam AD, Menezes PL, Pillai KM, Rohatgi PK (2016) Mechanical, physical and tribological characterization of nano-cellulose fibers reinforced bio-epoxy composites: an attempt to fabricate and scale the 'Green' composite. Carbohydr Polym 147:282–293
194. Rahimi SK, Otaigbe JU (2016) Polyamide 6 nanocomposites incorporating cellulose nanocrystals prepared by In situ ring opening polymerization: viscoelasticity, creep behavior, and melt rheological properties. Polym Eng Sci 56:1045–1060
195. Iyer KA, Torkelson JM (2015) Importance of superior dispersion versus filler surface modification in producing robust polymer nanocomposites: the example of polypropylene/nanosilica hybrids. Polymer 68:147–157
196. Auad ML, Richardson T, Orts WJ, Medeiros ES, Mattoso LHC, Mosiewicki MA, Marcoviche NE, Arangurene MI (2011) Polyaniline-. modified cellulose nanofibrils as reinforcement of a smart poly-. urethane. Polym Int 60:743–750
197. Miao C, Hamad WY (2013) Cellulose reinforced polymer composites and nanocomposites: a critical review. Cellulose 20:2221–2262

198. Rueda L, Saralegi A, Fernández-d'Arlas B, Zhou Q, Alonso-Varona A, Berglund LA, Mondragon I, Corcuera MA, Eceiza A (2013) In situ polymerization and characterization of elastomeric polyurethane-cellulose nanocrystal nanocomposites.Cell response evaluation. Cellulose 20:1819–1828
199. Yu J, Wang C, Wang J, Chu F (2016) In situ development of self-reinforced cellulose nanocrystals based thermoplastic elastomers by atom transfer radical polymerization. Carbohydr Polym 141:143–150
200. Müller D, Cercená R, Aguayo AJG, Porto LM, Rambo CR, Barra GMO (2016) Flexible PEDOT-nanocellulose composites produced by in situ oxidative polymerization for passive components in frequency filters. J Mater Sci: Mater Electron 27:8062–8067
201. Kaboorani A, Auclair N, Riedl B, Landry V (2016) Physical and morphological properties of UV-cured cellulose nanocrystal (CNC) based nanocomposite coatings for wood furniture. Prog Org Coat 93:17–22
202. Khelifa F, Habibi Y, Bonnaud L, Dubois P (2016) Epoxy monomers cured by high cellulosic nanocrystal loading. ACS Appl Mater Interfaces 8:10535–10544
203. Herrera MA, Sirviö JA, Mathew AP, Oksman K (2016) Environmental friendly and sustainable gas barrier on porous materials: nanocellulose coatings prepared using spin-and dip-coating. Mater Des 93:19–25
204. Li Z, Renneckar S, Barone JR (2010) Nanocomposites prepared by in situ enzymatic polymerization of phenol with TEMPO-oxidized nanocellulose. Cellulose 17:57–68
205. Mabrouk AB, Ferraria AM, do Rego AMB, Boufi S (2013) Highly transparent nancomposite films based on polybutylmethacrylate and functionalized cellulose nanocrystals. Cellulose 20:1711–1723
206. Jiang F, Wang Z, Qiao Y, Wang Z, Tang C (2013) A novel architecture toward third-generation thermoplastic elastomers by a grafting strategy. Macromolecules 46:4772–4780
207. Zoppe JO, Habibi Y, Rojas OJ, Venditti RA, Johansson LS, Efimenko K, Osterberg M, Laine J (2010) Poly(*N*-isopropylacrylamide) brushes grafted from cellulose nanocrystals via surface-initiated single-electron transfer living radical polymerization. Biomacromol 11:2683–2691
208. Morelli CL, Belgacem MN, Branciforti MC, Salon MCB, Bras J, Bretas RES (2016) Nanocomposites of PBAT and cellulose nanocrystals modified by in situ polymerization and melt extrusion. Polym Eng Sci 56:1339–1348
209. Muller D, Rambo CR, Porto LM, Schreiner WH, Barraa GMO (2013) Structure and properties of polypyrrole/bacterial cellulose nanocomposites. Carbohydr Polym 94:655–662
210. Witt MA, Valenga F, Blell R, Dotto ME, Bechtold IH, Felix O, Pires ATN, Decher G (2012) Layer-by-layer assembled films composed of "charge matched" and "length matched" polysaccharides: self-patterning and unexpected effects of the degree of polymerization. Biointerphases 7:1–10
211. Cerclier C, Cousin F, Bizot H, Moreau C, Cathala B (2010) Elaboration of spin-coated cellulose-xyloglucan multilayered thin films. Langmuir 26:17248–17255
212. Li F, Biagioni P, Finazzi M, Tavazzi S, Piergiovanni L (2013) Tunable green oxygen barrier through layerby-layer self-assembly of chitosan and cellulose nanocrystals. Carbohydr Polym 92:2128–2134
213. Strydom SJ, Otto DP, Liebenberg W, Lvov YM, de Villiers MM (2011) Preparation and characterization of directly compactible layer-by-layer nanocoated cellulose. Int J Pharm 404:57–65
214. Jean B, Dubreuil F, Heux L, Cousin F (2008) Structural details of cellulose nanocrystals/polyelectrolytes multilayers probed by neutron reflectivity and AFM. Langmuir 24:3452–3458
215. Cranston ED, Gray DG, Rutland MW (2010) Direct surface force measurements of polyelectrolyte multilayer films containing nanocrystalline cellulose. Langmuir 26:17190–17197
216. Mesquita JP, Donnici CL, Pereira FV (2010) Biobased nanocomposites from layer-by-layer assembly of cellulose nanowhiskers with chitosan. Biomacromol 11:473–480
217. Mesquita JP, Patrício PS, Donnici CL, Petri DFS, de Oliveira LCA, Pereira FV (2011) Hybrid layer-by-layer assembly based on animal and vegetable structural materials: multilayered films of collagen and cellulose nanowhiskers. Soft Matter 7:4405–4413

218. Dubief D, Samain E, Dufresne A (1999) Polysaccharides microcrystals reinforced amorphous poly(b-hydroxyoctanoate) nanocomposite materials. Macromolecules 32:5765–5771
219. Dufresne A (2000) Dynamic mechanical analysis of the interphase in bacterial polyester/cellulose whiskers natural composites. Compos Interfaces 7:53–67
220. Dufresne A, Cavaille JY, Helbert W (1997) Thermoplastic nanocomposites filled with wheat straw cellulose whiskers. Part 2: effect of processing and modeling. Polym Compos 18:198–210
221. Bossard F, El Kissi N, D'Aprea A, Alloin F, Sanchez J-Y, Dufresne A (2010) Influence of dispersion procedure on rheological properties of aqueous solutions of high molecular weight PEO. Rheol Acta 49:529–540
222. Cheng D, Wen Y, An X, Zhu X, Ni Y (2016) TEMPO-oxidized cellulose nanofibers (TOCNs) as a green reinforcement for waterborne polyurethane coating (WPU) on wood. Carbohydr Polym 151:326–334
223. Poaty B, Vardanyan V, Wilczak L, Chauve G, Riedl B (2014) Modification of cellulose nanocrystals as reinforcement derivatives for wood coatings. Prog Org Coat 77:813–820
224. Vardanyan V, Poaty B, Chauve G, Landry V, Galstian T, Riedl B (2014) Mechanical properties of UV-waterborne varnishes reinforced by cellulose nanocrystals. J Coat Technol Res 11:841–852
225. Gardebjer S, Bergstrand A, Idstrom A, Borstell C, Naana S, Nordstierna L, Larsson A (2015) Solid-state NMR to quantify surface coverage and chain length of lactic acid modified cellulose nanocrystals, used as fillers in biodegradable composites. Compos Sci Technol 107:1–9
226. Zhou C, Chu R, Wu R, Wu Q (2011) Electrospun polyethylene oxide/cellulose nanocrystal composite nanofibrous mats with homogeneous and heterogeneous microstructures. Biomacromol 12:2617–2625
227. Peresin MS, Habibi Y, Vesterinen AH, Rojas OJ, Pawlak JJ, Seppälä JV (2010) Effect of moisture on electrospun nanofiber composites of poly(vinyl alcohol) and cellulose nanocrystals. Biomacromol 11:2471–2477
228. Peresin MS, Habibi Y, Zoppe JO, Pawlak JJ, Rojas OJ (2010) Nanofiber composites of polyvinyl alcohol and cellulose nanocrystals: manufacture and characterization. Biomacromol 11:674–681
229. Uddin AJ, Araki J, Gotoh Y (2011) Toward "strong" green nanocomposites: polyvinyl alcohol reinforced with extremely oriented cellulose whiskers. Biomacromolecules 12:617–624
230. Jo C, Lee JW, Lee KH, Byun MW (2001) Quality properties of pork sausage prepared with water-soluble chitosan oligomer. Meat Sci 59:369–375
231. Aulin C, Salazar-Alvarez G, Lindstrom T (2012) High strength, flexible and transparent nanofibrillated cellulose–nanoclay biohybrid films with tunable oxygen and water vapor permeability. Nanoscale 4:6622–6628
232. Ghaderi M, Mousavi M, Yoursefi H, Labbafi M (2014) All-cellulose nanocomposite film made from bagasse cellulose nanofibers for food packaging application. Carbohydr Polym 104:59–65
233. Piermaria JA, Pinotti A, Garcia MA, Abraham AG (2009) Films based on kefiran, an exopolysaccharide obtained from kefir grain: development and characterization. Food Hydrocolloids 2:684–690
234. Smith SA (1986) Polyethylene, low density. In: The Wiley encyclopedia of packaging technology. Wiley
235. Salmieri S, Islam F, Khan RA, Hossain FM, Ibrahim HMM, Miao C, Hamad WY, Lacroix M (2014) Antimicrobial nanocomposite films made of poly(lactic acid)-cellulose nanocrystals (PLA-CNC) in food applications: part A—effect of nisin release on the inactivation of *Listeria monocytogenes* in ham. Cellulose 21:1837–1850
236. Zhao Y, Simonsen J, Cavender G, Jung J, Fuchigami LH (2014) Nano-cellulose coatings to prevent damage in foodstuffs. US Patent 20140272013 A1
237. Dong F, Li S, Liu Z, Zhu K, Wang X, Jin C (2015) Improvement of quality and shelf life of strawberry with nanocellulose/chitosan composite coatings. Bangladesh J Bot 44:709–717