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Nanocellulose as promising reinforcement materials for biopolymer nanocomposites: a review

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Abstract. Green growth and sustainable development are vital worldwide and need to be strengthened. In this aspect, biopolymers, biopolymer nanocomposites with biodegradable properties are the best way for this purpose. Nanocellulose (NC) is a biopolymer produced from natural resources like various plant species and agricultural waste products, including rice husk, tea leaves, sugarcane bagasse, etc. Due to their special properties such as biodegradability, renewability, biocompatibility, low cost, and outstanding mechanical capabilities, NC has gained growing research and application interests. This review provided detail information about production, structure and properties of NC. The usage of NC as reinforcement materials for different types of biopolymers is presented in the review. The surface modification of NC for better dispersion and better interaction of NCs in polymer matrices, the mechanical and thermal properties of the NC biopolymer nanocomposites are discussed.

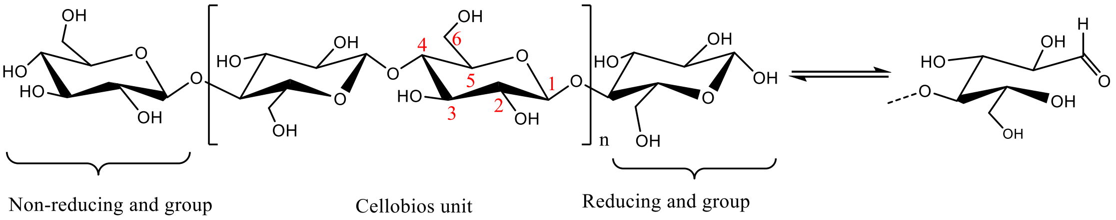
Keywords: nanocellulose, polymer nanocomposite, surface modification, mechanical properties, thermal properties.

Classification numbers: 2.4.2, 2.9.4.

1. INTRODUCTION

Polymer composites are widely used in various industrial sectors such as automobile industry, aerospace industry, home appliances, etc. [1, 2]. Since decade, polymer nanocomposites have attracted much research interest because nanomaterials with high specific areas could significantly improve some properties of the polymer matrices at relatively low content. Most petroleum-based polymers are not biodegradable and therefore they cause a growing concern in the world such as environmental pollution, and global warming. Thus, it needs to develop and apply a green polymer nanocomposite with full or partial biodegradability. In this aspect, biopolymers from renewable biological origin such as starch, chitosan, or synthetic biodegradable polymers as poly(lactic acid) (PLA), polycaprolactone (PCL) have gained increasing attraction [3 - 6].

Cellulose is the most common and sustainable natural polymer. It finds wide applications in numerous industrial sectors such as paper, textile, chemicals and material industries [7 - 9]. Chemically, cellulose is a high molecular weight polysaccharide composed of Danhydroglucopyranose (AGU) units linked together by β-1,4-glycosidic bonds. Each cellulose molecule has a free hemiacetal or aldehyde group at the C1 position, chemically reducing functionalities in one end. The other end of cellulose molecule has a free OH- group as non-reducing group at the C_4 position (Scheme 1) [10, 11].



Scheme 1. The molecular structure of cellulose polymer. The reducing end group can be either a free hemiacetal or an aldehyde, Reproduced from Ref. [10].

The cellulose unit has three hydroxyl groups at the C_2, C_3 positions (secondary alcohol) and C_6 position (primary alcohol). All three hydroxyl groups are possible sites for chemical modification of cellulose, where the OH group at the C_6 position is the most reactive. The polymerization degree of cellulose molecules varies from 10.000 to 15.000 depending on its origin. The cellulose monomer contains three OH-groups, which play an important role in fibrillar and semicrystalline structure as well as the physical properties [11]. With the explosive growth of nanotechnology, nanocellulose (NC) has gained increasing attention in the recent decades. NC with at least one dimension in nanoscale (less 100 nm) is classified in cellulose nanocrystal (CNC) with 4 - 70 nm in width, up to 500 in length, high crystallinity degree 54 - 88 %, and cellulose nanofibrils (CNF) with 20 - 100 nm in width and up to several microns in length and medium range of crystallinity degree (51 - 69 %) [8, 9, 12]. Besides the recyclable, reusable, compostable, biocompatible, and non-toxic properties, NC also possesses high strength and modulus, light weight, dimensional stability, thermal stability, and low oxygen permeability. CNC exhibits excellent mechanical properties because of its high crystallinity. The theoretical tensile strength is in the range from 7.5 - 7.7 GPa and its E-module is 150 GPa, respectively [13]. Depending on the average molecular weight, chemical and thermal treatment, the tensile strength of NC films varies in the range from 80 to 240 MPa, E-modulus from 3 to15 GPa, the elongation at break from 3 to 20 % [14 - 16]. These properties make NC a promising reinforcement for biopolymer materials to produce green polymer nanocomposites with high performances. However, NC also has some major drawbacks such as poor interfacial interaction, high water adsorption but can be solved by chemical modification [12].

The production of NC has been extensively reviewed in recent years, but its application as reinforcement materials for biopolymer matrices is relatively less reviewed. In this review, we comprehensively present various methods for preparation of NC as well as the surface modification of NC. Preparation and properties of some NC/biopolymer nanocomposites were also discussed.

2. PREPARATION OF NANOCELLULOSE

2.1. Material sources

The material sources for preparation of NC are plants or agro-industrial residuals. The majority of cell walls in plants consist of cellulose, hemi-cellulose and lignin. The chemical compositions of lignocellulosic materials are presented in Table 1 [17].

Table 1. Chemical compositions of some lignocellulose sources [17].

Lignocellulose sources	**Composition (%)**			
	Cellulose	Hemicellulose	Lignin	Extract, pectin and waxes
Hardwood	43 - 47	25 - 35	16 - 24	2 - 8
Softwood	40 - 44	25 - 29	25 - 31	1 - 5
Picone biomass	42 - 46	27	20 - 23	4 - 11
Coconut fiber	31 - 32	25 - 26	33 - 37	5 - 11
Cotton stalk	48 - 52	25 - 27	24 - 26	2 - 4
Sugarcane bagasse	45	30	20 - 22	3 - 5
Corncob	28 - 34	39 - 47	21 - 29	5 - 12
Jute	60	23	16	1
Pineapple leave	34 - 40	21 - 25	25 - 29	8 - 10
Wheat straw	37 - 43	31 - 37	18 - 22	2 - 14

Even though the lignocellulose sources with high cellulose content, such as wood pulps, could provide better yields of NC, the use of agro-industrial residuals is an attractive alternative source for the preparation of NC. These residuals can be treated and transformed into products with high-added value [17].

2.2. Preparation methods of nanocelluloses

The principle for preparation of NC is based on the structure of cellulose fibers. The structure of the cellulose fiber is shown in Figure 1 [10].

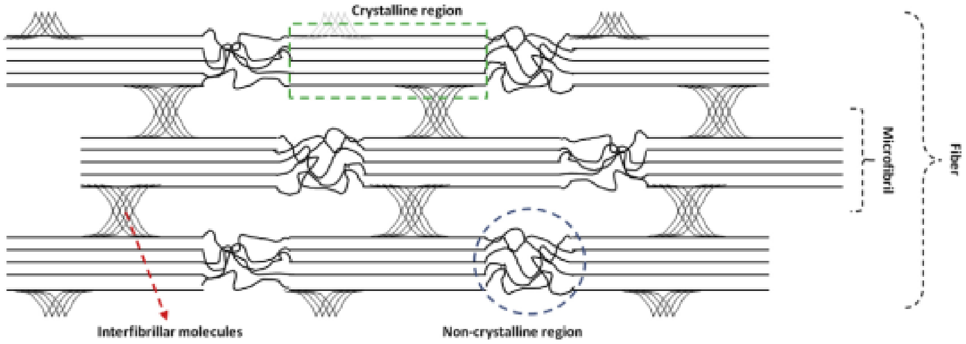


Figure 1. Structure of cellulose fiber Adapted with modification from [10].

Cellulose fibers consist of crystalline regions, non-crystalline regions (amorphous regions), and interfibrillar molecules. For the preparation of cellulose nanocrystal (CNC) the amorphous region will be disrupted by hydrolysis methods, and the remaining crystals will be in nanometer size range. In contrast, by the preparation of cellulose nanofibrils (CNF), the interfibrillar hydrogen bonds will be broken and thus fibers with a few micrometers in length and nanometer size in width. Bacterial NC is prepared by special bacteria and grown as microfibrils in a culture medium. The as-prepared microfibrils can be hydrolyzed into CNC [10].

Figure 2 shows the general procedures of preparation of NC from lignocellulosic residuals 17**,** 18].

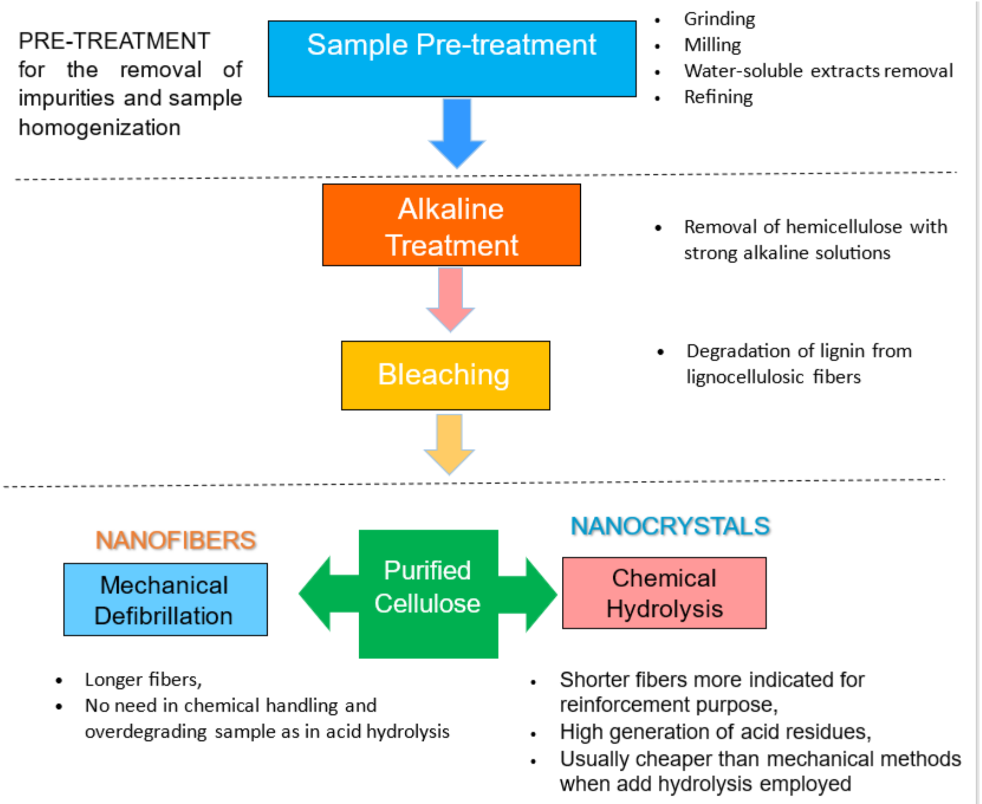


Figure 2. General procedures for preparation of NC from lignocellulosic residuals Adapted with modification from [17].

During the pre-treatment process, the cellulose fiber from different sources is milled or ground to small sizes, and afterwards washed in deionized water to remove impurities in the lignocellulosic residuals. Some studies conducted fiber de-waxing through treatment with a mixture of benzene/ethanol and toluene/ethanol as washing with deionized water may not be sufficient [17]. The next step is chemical treatment, including alkaline treatment and bleaching. The alkali treatment will partially remove the hemicellulose and also remove other compositions such as residual waxes at a pre-treatment stage, pectin, silica, or natural fats [19 - 21]. New approaches, such as steam explosions, have been used for efficient removal of lignin while leaving cellulose structure intact and therefore more pure [18, 22]. The bleaching process is necessary for the removal of lignin and residual hemicellulose after the alkali treatment [21]. The bleaching process is carried out by treatment with chlorine compounds under acidic conditions or with hydrogen peroxide under alkaline conditions. The chlorine route is more effective but harmful to environment [23, 24]. Purified cellulose is used for the preparation of CNC or CNF.

2.2.1 Preparation of CNC

Cellulose nanocrystals (CNC) are generally prepared by acid hydrolysis of cellulose fibers. In the early stage of acid hydrolysis, the acid molecules diffuse into the amorphous region of the cellulose fibers and hydrolyze the glycosidic bonds. Subsequently, more easily accessible glycosidic bonds in the cellulose structure are hydrolyzed. Finally, the hydrolysis process occurs at the reducing end group and at the surface of CNC, which will make the nanocrystal charge depending on what acid is used [10]. The cellulose sources, type of acid, acid hydrolysis conditions such as acid concentration, acid hydrolysis time, and temperature are some of the most important factors affecting the preparation of CNC. Table 2 summarizes dimensions of CNC prepared from different cellulose sources.

Table 2. Geometrical characteristics of CNCs prepared from different cellulose sources.

Cellulose source	Length, L (nm)	Cross section, D(nm)	References
Wood	100 - 300	3 - 5	[25]
Cotton	100 - 400	7 - 15	[25, 26]
Algae (Valonia)	100 nm to µm	10 - 20	[25, 27]
Bacterial cellulose	100 nm to µm	5 - 10	[28, 29]
Tunicate cellulose	100 nm to µm	10 - 20	[26]
Sugarcane bagasse	200 - 500	30 - 70	[30]
Wheat straw	220	5	[26]
Ramie	200 - 300	10 - 15	[31]

The rod-like nanocrystals produced from acid hydrolysis of native ramie cellulose fibers exhibited an average diameter of 6 - 8 nm and a length of about 150 - 250 nm as estimated by transmission electron micrographs [31]**.** Bacterial cellulose crystals obtained from acid hydrolysis were stiff, nearly straight rods and show some tendency to aggregate [29]**.**

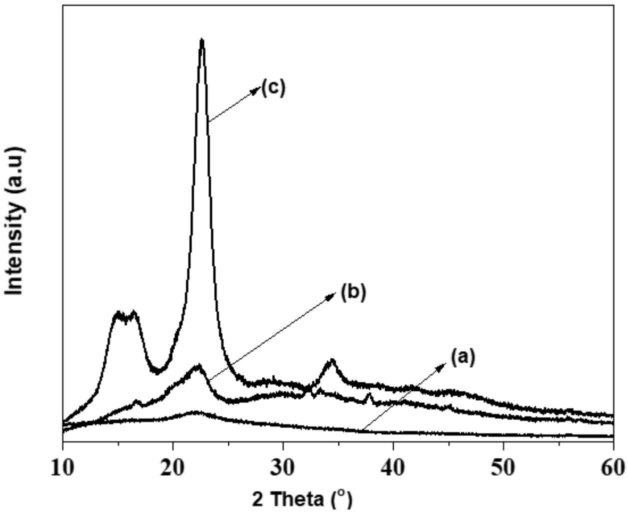


Figure 3. XRD pattern of (a): pristine sugarcane bagasse, (b): purified sugarcane bagasse and (c): CNC [30].

By the acid hydrolysis of cellulose fiber, sulfuric acid (H_2SO_4) is the most common acid for the preparation of CNC. Acid hydrolysis disrupt the amorphous region of cellulose fiber and thus increases the crystallinity of CNC. Figure 3 presents XRD pattern of pristine sugarcane bagasse, purified sugarcane bagasse cellulose, and CNC prepared from sugarcane bagasse using H_2SO_4 (64 wt.%) hydrolysis at temperature of 50 ^oC, hydrolysis time of 3 h [30].

The crystallinity of the materials could be determined according the equation 1.

$$Cr(\%) = \frac{I_{200} - I_{am}}{I_{200}} \text{ x } 100 \qquad (1)$$

where I_{200} is the XRD intensity of the crystal plane (200) at two theta angles of 22 - 23^o and I_{am} is the XRD intensity of the amorphous region at two theta angles of 18 - 20^o. The crystallinity of pristine sugarcane bagasse, purified sugarcane bagasse and CNCs are 28.5 %, 50.0 %, and 84.3 %, respectively [30]. The effect of H_2SO_4 concentration (16 wt.%, 40 wt.%, 64 wt.%), hydrolysis temperature (45 ^oC, 65 ^oC, 85 ^oC) and hydrolysis time of 25 min on the crystallinity size, crystallinity degree of CNC prepared from softwood pulp were investigated by Wadood Y. Hamad. The crystallinity of nanocellulose reached 65 to 90 % depended on reaction conditions [33]. Isolation of high crystalline CNCs (Cr was nearly 80 %) from Vietnamese agricultural wastes was also reported by V. Nang An *et al.* [34].

When H_2SO_4 concentrations increase, the degree of polymerization (DP) of CNC decreases. The highest crystallinity and smallest crystal size were obtained at the highest H_2SO_4 concentration. Depending on the hydrolysis conditions, the acid hydrolysis could also occur in the crystalline regions, resulting in degradation of cellulose structure. Therefore, the sulfuric acid hydrolysis process has been optimized by several researchers. The general optimal conditions for the preparation of CNC by H_2SO_4 hydrolysis are an acid concentration of 64 wt.%, a temperature of 45 ^oC, and time of 45 - 60 min with constant stirring, followed by quenching the suspension with 10-fold deionized (DI) water. After that, the CNC was washed, dialyzed with DI water several times until a neutral pH was achieved. The CNC suspension must be repeatedly sonicated to obtain a separate CNC [33, 34]. Some OH-groups of the CNC surface will be converted into sulfate groups ($-OSO_3^-$) by sulfuric acid hydrolysis, and thus a stable aqueous suspension is obtained [10, 32]. Beside sulfuric acid, other acids such as hydrochloric acid (HCl) [35 - 37] hydrobromic acid (HBr) [38], and phosphoric acid (H_3PO_4) have been used for CNC preparation. Using HCl and HBr to prepare CNC results in CNCs with no surface charge and tend to flocculate in organic solvent [39]. Tarchoun *et al.* [40] used different acid solutions (HCl, HNO_3, H_2SO_4, HCl/H_2SO_4 (2:1, v/v), HCl/HNO_3 (2:1, v/v) for preparation of CNC from giant reed. Combining treatment with hydrogen peroxide and dilute sulfuric acid solution, nanocellulose from rice straw and cassava bagasse was successfully prepared [41, 42]. The highest yield, highest crystallinity, and smallest dimension were obtained using mixed acid hydrolysis instead of single acid hydrolysis.

2.2.2 Preparation of cellulose nanofibril (CNF)

Unlike CNC, in the cellulose nanofibril (CNF) structure the non-crystalline parts are not disrupted and the length of the fibrils is preserved. Thus, CNF are commonly produced by mechanical treatment. Cellulose microfibrils are long, thread-like bundles of cellulose molecules that are connected together by hydrogen bonds between the -OH groups in the cellulose structure. A high shear force using mechanical treatment is applied to peel the fibers and break the interfibrillar bonds between the cellulose molecules. As a result, nanofibrils with nanoscale diameters and lengths ranging from nanometers to micrometers were obtained. The most common mechanical treatments for the preparation of CNF are the high-pressure homogenization process, ball milling, and ultrasonication [10, 18].

High-pressure homogenization is conducted by exposure of cellulose slurry to high pressure and high velocity [43]. The diluted suspension of cellulose fibers was pumped at high pressure and fed through a high-pressure spring-loaded valve assembly. The valve is opened and closed rapidly, which leads to significant pressure drops with shearing and impact forces affecting the fibers. The degree of micro and nanofibrillation depends on the number of pumped cycles and the starting materials.

Through the ball milling process, shear forces are produced between the balls and between the balls and the jar surface due to centrifugal force. The degree of fibrillation of cellulose fiber depends on the size and number of balls, milling speed, milling time, and milling state (dry or wet state). The main drawback of the ball milling process is the negative effect on the crystalline structure of cellulose fiber.

By ultrasonication, ultrasound waves in the frequency range of 10 - 20 MHz are used to disrupt the relatively weak bonding between cellulose fibrils, resulting in defibrillation of the aggregated fiber and finally CNF is obtained [44]. The major drawback of the mechanical treatment methods is their very high energy consumption, which is unsuitable for industrial production of CNF. Thus, chemical or enzymatic pretreatment is applied to ease cellulose fibers' micro and nano defibrillation. The CNF can be prepared from wood fiber by mechanical processing combined to enzymatic, TEMPO-oxidation, carboxylmethylation, and also extracted from *Opuntia ficusindica* [45].

The pretreatment will affect the cellulose fiber's surface, weakening the interaction between the cellulose fibers, thus reducing energy consumption. One of the well-known chemical pretreatment methods for cellulose fiber is 2,2,6,6-teytamethylpiperidine-1-oxyl radical (TEMPO) oxidation process [46, 47]. Figure 4 presents the reaction mechanism of TEMPO-oxidation process using TEMPO/NaBr/NaClO system in an aqueous solution at pH 10 [47].

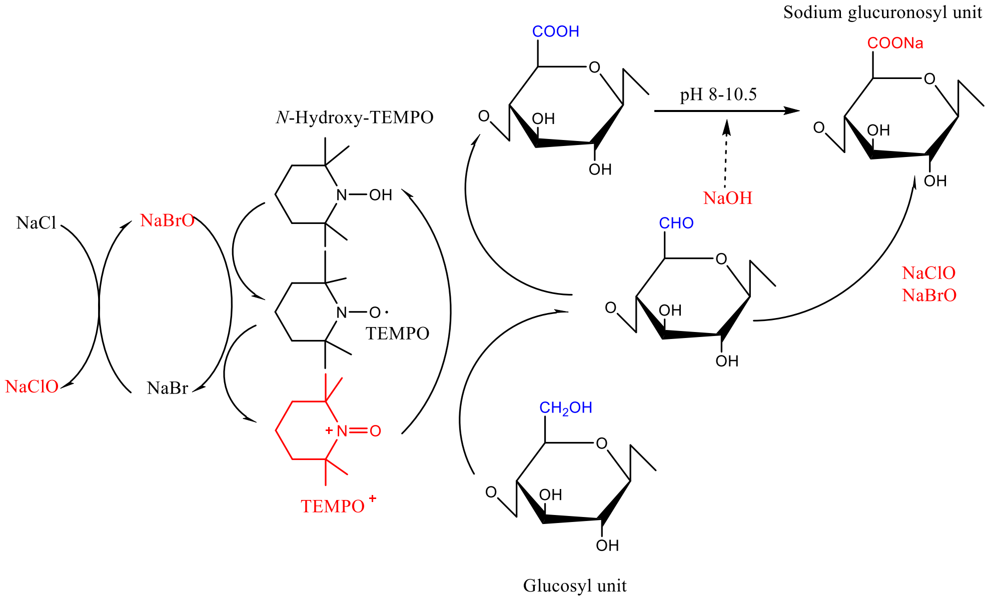


Figure 4. Reaction mechanism by TEMPO-oxidation of cellulose fiber, Reproduced from Ref. [47].

This method converted the primary hydroxyl group of cellulose to sodium C6-carboxylate groups. Along with mechanical treatment, CNF with 3 - 4 nm in width and a few microns in length could be obtained [47].

Besides mechanical treatments for the preparation of CNFs, in the past few years, the electrospinning method has been intensively investigated for preparation of CNFs. This simple and cost-effective process works on the principle that a cellulose solution is extruded-electrospun under a high electric field. At a sufficiently high voltage, a charged matter stream is ejected following a complicated loop and 3D spiral deployment trajectory. During the process, the solvent evaporates, and nanofibers are formed on the collector. Various parameters, including electric field strength, tip-to-collector distance, cellulose solution feed rate, and compositions are essential factors affecting the morphological features of the electrospun nanofiber [48].

2.2.3 Preparation of bacterial nanocellulose (NBC)

Unlike other cellulose sources, bacterial nanocellulose (BNC) is synthesized from special bacterial or microbial species such as *Acetobacter, Rhizobium, Agrobacterium, Pseudomonas* that build up cellulose nanofibers with widths of nanometers and lengths of up to micrometers [45, 46]. BNC possesses unique properties such as excellent and pure network structure, high degree of polymerization (up to 8.000), high mechanical strength, biocompatibility, and high water-holding capacity [49, 50]. The main applications of BNC are medical health and surgical applications such as bandages for wound healing, skin burn, etc. The BNC can also be used in other sectors like food, packaging industries. BNC’s drawbacks are the low availability of bacterial cellulose, the inefficient process of synthesizing bacterial cellulose, and the high costs, making BNC commercially unattractive [8].

3. SURFACE MODIFICATION OF NANOCELLULOSE

By preparing cellulose polymer nanocomposites, the dispersion of cellulose in the polymer matrix and the interphase interaction between the polymer phase and cellulose determine the physico-mechanical properties of the polymer nanocomposite. Therefore, surface modification of nanocellulose is the most critical step for improving the physico-mechanical properties of cellulose polymer nanocomposites. Some chemical methods for the surface modification of nanocellulose are described below in detail.

3.1. Polymer grafting

Polymer grafting brings an interesting and flexible way of incorporating various functional groups into nanocellulose. Generally, three main techniques have been reported on the synthesis of a grafted copolymer of cellulose, namely grafting to (polymer-to-polymer grafting), grafting from (monomer-to-polymer grafting), and grafting through (copolymerization). In the ‘‘grafting-to’’ approach, an end functional preformed polymer with its reactive end group is coupled with the functional groups located on the cellulose backbone. In the ‘‘grafting-from’’ approach, the growth of polymer chains occurs from initiating sites on the cellulose backbone. In the ‘‘grafting-through’’ approach, a macromonomer, usually a vinyl macromonomer of cellulose, is copolymerized with a low-molecular-weight co-monomer [1, 11].

The “grafting from” strategy was applied to synthesize poly(sodium acrylate) (PAANa)-modified TEMPO-oxidized cellulose nanofibril (TOCN) aerogel spheres. Free radical polymerization can also be performed with TEMPO-oxidized CNF by poly (sodium acrylate) to fabricated aerogels with the addition of cross-linker agents such as N,N′-methylenebisacrylamide [51]. First, the monomer, crosslinking agent N,N’-methylenebisacrylamide (BMA) and initiator potassium persulfate (KPS) were dissolved in distilled water (22 °C), and the concentration of AANa monomer was controlled at 5, 10, 15 and 20 % (w/v), respectively. The concentrations of BMA and KPS were controlled at 1 and 2 % based on the weight of monomer. After soaking in the mixed solution for 3 h with gentle stirring, the TOCN gel spheres saturated with AANa monomer aqueous solution were filtered out and transferred to a three-neck bottle, paraffin oil and the emulsifier span-85 were added almost at the same time in order to prevent the crosslinking between spheres. The TOCN gels saturated with the mixed aqueous solution were dispersed in paraffin oil by vigorous stirring and heated to 80 °C under the protection of nitrogen. After 2 h polymerization, the obtained composite spheres were washed to neutral by excessive acetone and distilled water several times. Then, the purified samples were frozen by liquid nitrogen and further dried by a freeze-dryer [51].

For controlled drug release purpose, Fang Zhang *et al.* [52] fabricated temperature-sensitive poly-NIPAm-modified cellulose nanofibril cryogel microspheres. First, pristine cryogel microspheres were prepared using a spray-freeze dry technique in the presence of a chemical crosslinker. Next, *in situ* free radical polymerization in the cryogel microreactor, NIPAm(N-iso-propylacrylamide) was polymerized and grafted onto the cellulose cryogel microspheres. The results demonstrated that porous CNF–PNIPAm hybrid microspheres could be a material for controlled drug release.

The structure of polymer-grafted CFN in colloidal dispersion was illustrated by Shuji Fujisawa *et al.* The amine-terminated PEG chain is attached to the CNF surface via a salt-bridge structure with carboxylate groups. The thickly grafted structure allowed the creation of a polymer brush layer on the CNF, explaining the good colloidal stability in solvents [53].

3.2. Silylation

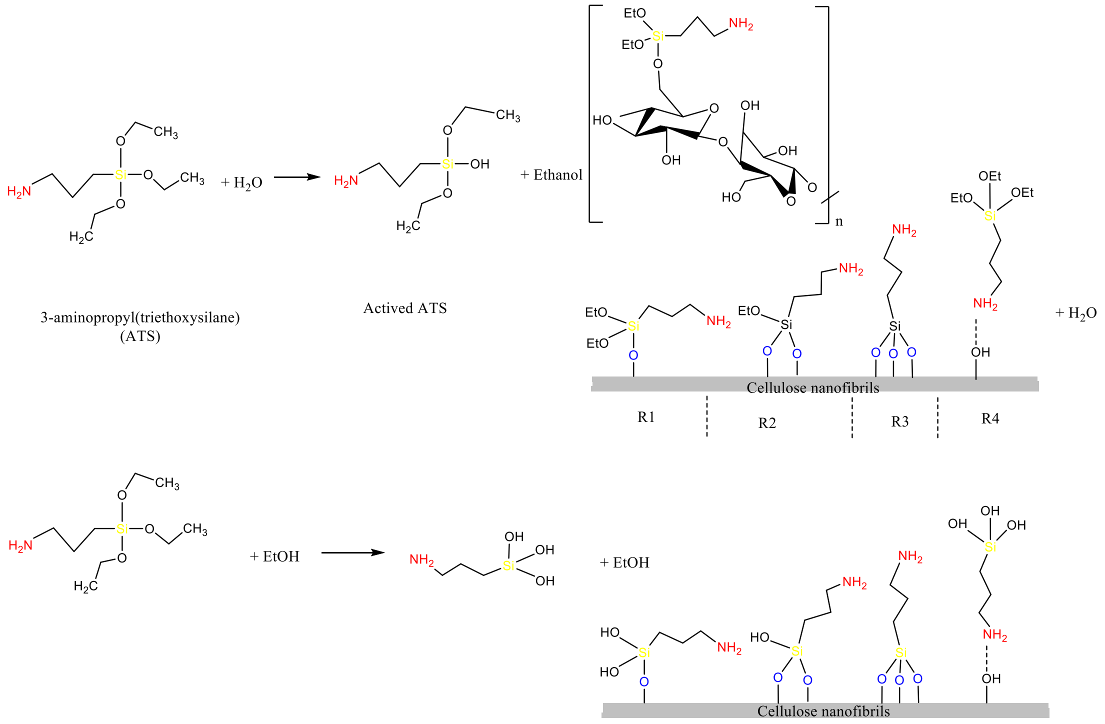
Silane coupling agents have a good affinity toward cellulosic substrates. The method of using organosilanes to prepare hydrophobic nanocellulose surfaces and to enhance matrix-filler incorporation for cellulose-reinforced composites has been confirmed to be a good way to give nanocellulose surface hydrophobicity by supplying as a coupling agent or even providing stability in nonpolar environments as well as hydrophobic functionality either as a suspension in different solvents or added as bulk into a polymeric matrix [54]. Functional alkoxysilanes are also widely used in many industrial applications as binding agents to improve the adhesion between the polymer matrix and the inorganic solid. The interest of these coupling reagents is the presence of two types of reactants in their structures. Indeed, the alkoxy groups, -OR, allow silanes to be fixed to surfaces carrying the hydroxyl group.

The silane surface modification of CNF occurs in four steps that fundamentally involve a chemical grafting on the hydroxyl groups on the surface of cellulose via the reaction with silanol groups. Reaction 1: silicon units of the organosilane may bond uniquely by one to the cellulose surface; the two remaining silanol groups exist, either bonded to other silicon atoms or in free form. Reaction 2: two silyl ether bonds react with cellulose. Reaction 3: aminosilane reacts with cellulose via three silyl ether bonds. Reaction 4: aminosilane is polymerized. The first stage of the modification consists of solvolysis of the ethoxy groups, after which a reactive silanol group is formed [55 - 57].

After hydrolysis, the following reactions can occur either simultaneously or sequentially: condensation to oligomers with other silanol groups to form siloxane linkages; the oligomers then form hydrogen bonds with the –OH groups of the cellulose; stable condensation products are also formed with other oxides to form stable bonds with SiO; drying or curing at temperatures ranging between 80 °C and 110 °C, during which a covalent linkage is formed with the hydroxyl groups of cellulose with concomitant loss of water [50, 51].

At the interface, there is only one bond of the organosilane silicon on the cellulose surface. In any of the first three proposed reactions, the aminopropyl group remnant is available for covalent reactions or physical interactions with other phases. In the case of ethanol-based silanes, silanes were fully activated with hydroxyl groups but without hydrolyzable functional groups [50 - 52].

Eduardo Robles *et al.* investigated nine different surface modifications of cellulose nanofibrils (CNF) with 3-aminopropyl triethoxysilane (ATS) by varying the solvent systems. The effects of reaction conditions, such as solvent type and the amount of silane to cellulose, were assessed to evaluate their contribution to the degree of silane modification [54]. The presence or absence of ethoxy groups in the silane reflected the impact of the solvent on the solvolysis of the silane The impact of the solvent on the solvolysis of the silane was reflected by the presence or absence of ethoxy groups in the silane. Although the surface modification was directly proportional to the silane ratio in the reaction, the accumulation of nanofibrils was also increased, which can play a negative role in certain applications. Scheme 2 shows the reaction dynamics for the cellulose–silane interactions [54].



Scheme 2. Reaction dynamics for the cellulose–silane interactions, Reproduced from Ref. [54].

The hydrolysis of three alkoxysilane coupling agents, γ-methacryloxypropyltrimethoxysilane (MPS), γ-aminopropyltriethoxysilane was investigated by Marie-Christine Brochier Salon *et al.* [58]. ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy indicated that its rate increased in the order: MPS< APS<TAS. When TAS was hydrolyzed, colloidal particles precipitated in the medium, whereas APS and MPS only gave soluble products. Pristine and hydrolyzed MPS were then adsorbed onto a cellulose substrate. Thereafter, a thermal treatment at 110 – 120 ^{o}C under reduced pressure was applied to the modified fibers to create permanent bonding of the coupling agent at their surface (APS), and γ-diethylenetriamino-propyltrimethoxysilane (TAS), was applied in an ethanol/water (80/20) solution. During the hydrolysis and condensation, the structural changes occurring in the solution were investigated to select suitable conditions for the physical adsorption of silane compounds onto the organic substrates. This study paved the way for the rational use of silane-binding agents for the surface functionalization of organic materials.

Nhi *et al.* modified cellulose microfibrils (CMF) with (3-aminopropyl) trimethoxysilane (APTMS) to obtain hydrophobic CMF with a high water contact angle of 123.3^{o} [59].

3.3. Other chemical treatment

Acetylation/Esterification reactions using aromatics and aliphatic carboxylic reagents are promising reactions that expand the application of nanocellulose in a number of fields. Yonggui Wang *et al.* have reviewed the chemistry and application of functional nanocellulose materials through nanocellulose esterification reactions. Different esterification techniques and nanostructure manufacturing have been developed to confer specific properties on cellulose esters, expanding their feasibility for highly sophisticated applications [60].

Carbamylation is another method for surface modification of nanocellulose. Using this method the isocyanic acid was attached to the surface of nanocellulose [61].

The reaction between aliphatic and aromatic isocyanates with nanocellulose has been reported. Using the solvent casting method, a nanocomposite based on nanocellulose (with 5 - 10 % content) and poly (butylene adipate-coterephthalate) (PBAT) was successfully fabricated. In the case of CNC reacted with aromatic isocyanate, the PBAT chain was more anchored and the phenyl rings were grafted onto CNC. This rigid percolated network enhanced the elastic modulus and yield stress by up to 120 and 40 % of the composites compared to pure PBAT [62].

4. PREPARATION AND PROPERTIES OF NANOCELLULOSE BIOPOLYMER NANOCOMPOSITES

4.1. NC/starch nanocomposites

Starch is a polymer composed of morphology and longitudinal carbohydrates, amylopectin and amylose, derived from various agricultural sources such as corn, wheat, potatoes, and cassava [63]. Starch is biodegradable, environmentally friendly, low-cost, easily accessible, and semipermeable to water vapor, O_2, CO_2, and food components. It is a viable alternative to non-biodegradable plastics. Considerable interest researches have been given to the use of plant source-based stiflers as reinforcement in starch-based thermoplastics as a way to improve the mechanical properties and water sensitivity of starch biopolymers as well as to reduce the usage of non-degradable of water resistance and mechanical strength, fillers from plant sources have been reinforced into starch-based thermoplastics to produce green composites or biocomposites [6, 63, 64].

Nanocellulose possesses advanced characteristics such as high crystallinity, large surface area, good mechanical strength, and electrically active sites. The most favorable manufacturing technique for preparing nanocellulose-reinforced starch composites is solution casting method.

Generally, adding nanocellulose into starch-based composites not only permits the nanocomposite to gain the advantages of biomass but also gives the nanometer effect [59, 62, 63].

The shape, quantity, alignment of nanoparticles, and potential of the polymer matrix to transfer stress affected the mechanical properties of bio-composites [6]. Generally, the CNC can improve the tensile strength of films. However, the interaction between nanocellulose and polymer matrix is weak at higher concentrations, leading to a decrease in strength. Tensile strength is directly connected with compatibility, distribution, and hydrogen bonding between starch and nanocellulose [64 - 66].

The improvement in tensile strength of high amylose maize starch films might be due to linear amylose chains of starch enabling cooperation with hydrogen bonding, producing solid films. In contrast, amylopectin presented short and branched chains, weakening entanglement and making the films more brittle. In addition, a high content of nanocellulose resulted in agglomerate, leading to unequal stress distribution in the films. Biocomposite films produced using native wheat starch and oat CNC have the highest tensile strength (5.07 MPa), with an increase of 91.3 % compared with the film produced using natural starch [6, 67, 68].

Nanocellulose modification for reinforcing starch films was studied by Haoran Fan et al. The influence of introducing varied contents (0 %, 0.5 %, 1 %, 2 %, 5 % wt.%) of NC nanoparticles processed by the 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-mediated oxidation (TEMPO-SNPs) on the characteristics of maize starch film were evaluated. Elongation at break, tensile strength, and Young's modulus of the films increased as the TEMPO-SNPs content increased. At the TEMPO-SNPs content of 1 %, the elongation at break, the tensile strength, and Young's modulus of the films peaked. SEM indicated that the nanocomposite films had smoother surfaces and cross sections with no cracks or visible air pockets [69].

The addition of CNC from different sources (native starch and phosphorylated starch) did not influent the overall morphology of the NC/starch biocomposite films when observed by SEM. The original starch film displayed homogeneous morphology, while the films from phosphorylated starch showed a few cracks in their structure. The films from native starch presented fewer cracks than those from phosphorylated starch, regardless of the presence of CNC in their composition, as indicated by Graziella Pinheiro Bruni *et al.* [70]. The biocomposite films were smooth, homogeneous, and bubble-free surfaces with structural integrity, except for those from phosphorylated starch with eucalyptus CNC [70]. The biocomposite films' X-ray diffraction (XRD) exhibited peaks at 17.3°, 20.2°, and 22.4° as shown in Figure 8. Incorporating CNC into the origin starch films reduced their moisture content compared to films without CNC reinforcement. Additionally, the introduction of CNC did not influent the film's moisture content from phosphorylated starch [70].

Incorporating nanocellulose with a polymer substance for the expected mechanical properties of bio-nanocomposite films plays a key role in industrial applications. The degree of distribution of nanocellulose reinforcement in a polymer matrix is significant because the nanofiller content is low, nanocellulose gives a high surface area, and accumulation and agglomeration may occur rather than disperse in the polymer matrix. Two methods are usually adapted to prepare films of the nanocomposites: organic solvent or water evaporation via solvent casting and freeze-dried cellulose nanoparticles via extrusion method [68, 71].

Azeredo et al. prepared a nanocomposite from grain cellulose nanofiber-reinforced mango puree. The study indicated that the mechanical, vapor permeability, and thermal characteristics of the nanocomposite were considerably enhanced. The Young's modulus reached 322.05 MPa, the highest tensile strength of 38.0 MPa. The tensile strength and melting point of the films are also better [72]. A tensile strength of 38.0 MPa was also achieved when the bio-nanocomposites made from the reinforcement of kenaf cellulose nanofiber-reinforced corn starch, as indicated by Babaei *et al.* [73].

Lu et al. reported the incorporation of cotton CNC to enhance plasticized starch. The nanocomposites exhibited enhanced tensile strength (212 %) and Young's modulus (736 %), together with improved water resistance [74]. The addition of 10 wt.% CNC with the highest aspect ratio (L/D of 36) into the nanocomposite resulted in coincidental enhancement of the tensile strength, transparency, elongation at break, and water resistance [75].

The introduction of CNC to films makes homogeneous structures due to the strong force between cellulose and starch as their chemical similarity. During the fabrication of films, the plasticizer interrupts the intermolecular and intramolecular hydrogen bonds within the starch structure, which causes its morphology without accumulation of particles or swollen granules [76].

The reinforcement of nanocellulose for thermoplastic starch can replace synthetic plastic. It would be adapted in various fields such as packaging, agriculture, industrial, and medical applications.

4.2. NC/PLA bio-composite

Polylactic acid (PLA) is derived from renewable feedstock and is one of the most favorable biodegradable and recyclable thermoplastic biopolymers. PLA was progressively investigated as a packaging material. Nonetheless, inadequate thermal, mechanical, and barrier properties of PLA narrowed its application in different applications. One method for treating these shortcomings is applying nanocellulose as reinforcement fillers in the PLA matrix Researchers have paid increasing attention to nanocellulose-reinforced PLA biocomposites for academic and industrial applications [77, 78].

Nanocellulose-reinforced PLA biocomposites likely offer a bright future for PLA in packaging. Various strategies and reports on the surface modification of CNC in PLA-based composites. Normally, three surface modification strategies deal with nanocellulose to reinforce PLA-based composites: physical adsorption of a surfactant, chemical derivatization, and chemical grafting of PLA polymers [5, 77, 78].

Different nanocellulose including CNC, CNF, and BC has been employed to fabricate PLA-nanocellulose bicomposites. Due to the difference in the polarity, a good dispersibility of nanocellulose in the PLA matrix is difficult to obtain. In this case, modifications of CNC or PLA are necessary for the fabrication of PLA/nanocellulose biocomposites [79]. In comparison with CNC whiskers, CNF and BC exhibit longer and more flexible chains, which deal with credible entanglement with the PLA substance. So, most studies described pristine CNF as a direct nano-reinforcement in PLA-based composites. Efforts have also been made by selecting a miscible biopolymer to enhance the compatibility between nanocellulose and PLA [5, 79].

Physico-chemical characteristic of cellulose nanofibril-reinforced PLA biocomposite was investigated by Qianqian Wang *et al.* [77]. PLA was dissolved in dichloromethane, and then CNFs at 1, 2.5, and 5 % were added to the PLA solution. The biocomposite films were obtained after evaporation of dichloromethane in petri dishes. ATR-FTIR spectrum indicated that the PLA/CNFs biocomposite films displayed all characteristic bands of PLA, and no new band was observed (Figure 8). So, the authors suggested that interactions between PLA and CNFs were mainly physical. TGA analysis indicated that the thermal stability of the PLA/CNFs was enhanced when the content of CNFs was at 5 %. The tensile strength of the composite reached the maximum value of 52 MPa (8.5 % higher than that of the pristine PLA) when the CNF loading was 2.5 %. The improvement of the tensile strength was due to the good interfacial interactions and dispersity of CNF in the PLA matrix. However, the elongation at break of the composite was decreased when the CNF contents increased [77].

The acetylation reaction of surface nanocrystals with acetic anhydride was carried out. The product was coded as ACN. The results indicated that, after modification with acetic anhydride, the crystallite of the nanocellulose was unchanged. However, the substitution of hydroxyl groups by acetyl groups on the cellulose nanocrystals surface, acetylated cellulose nanocrystals (ACN) displayed enhanced dispersion in six common solvents, a reduction in surface polarity, and a higher decomposition temperature. When introducing 6 wt.% ACN filler into the PLA-based polymeric matrix, the tensile strength of the PLA/ACN-6 nanocomposite increased by 61.3 % and the Young's modulus reached 1.5-fold greater than those of the neat PLA sheet [80].

By solution casting method, Aihua Pei et al. fabricated nanocomposite films of poly(L-lactide) and silylated cellulose nanocrystals, concentrating on mechanical properties and crystalline assessment. Nanocrystals of 15 nm width and 200 - 300 nm length were functionalized by partial silylation (SCNC particles) using n-dodecyldimethylchlorosilane to improve their poly(L-lactide) dispersion. The unmodified CNC caused accumulation in the composites, while the SCNC was well-distributed in PLLA. The results indicated that due to crystallinity effects and fine distribution, introducing 1 % silylated cellulose nanocrystal led to an increase of 27 % in tensile modulus and a 21 % increase in tensile strength compared to the pristine PLA [81].

Philippe Tingaut *et al.* [82] prepared bionanocomposite based on PLA and acetylated microfibrillated cellulose (MFC). The grafted MFCs are easily dispersed in chloroform, a PLA solvent of low polarity. Figure 10 presents TGA thermograms of acetylated MFCs with acetyl contents of 0 (unmodified MFC), 1.5, 4.5, 8.5, 13, and 17 %)/PLA polymer nanocomposites. The results demonstrate the improvement of the polymer nanocomposites' thermal stability with increasing acetylation of MFC.

4.3. NC/chitosan nanocomposites

Chitin is a biopolymer composed of β-l,4 linked 2-acetamide-2-deoxy-D-glucose (N-acetylglucosamine, (GlcNAc) residues. It is the second most abundant biopolymer next to cellulose, widely found in nature, particularly in marine invertebrates, insects, fungi, and algae. Chitosan (CTS) is a linear copolymer of β-(1→4)-linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2- deoxy-β-D-glucopyranose being received by the partial deacetylation of chitin. The degree of deacetylation (DD) is determined by the proportion of D-glucosamine and N-acetyl-D-glucosamine. Depending on the degree of deacetylation, the bio-polymer is distinguished as either chitin or chitosan. Chitin/chitosan is biodegradable, biocompatible, hydrophilic, nontoxic, and highly bioavailable. Chitin/chitosan also possesses unique characteristics such as favorable selectivity of water, simplicity of modification, outstanding chemical resistance, and capability to form films, gels, nanoparticles, microparticles, beads, etc. [83, 84].

The idea for the combination of the two outstanding biopolymers was based on the fact that both chitin/chitosan and nanocellulose are similar in molecular structure. Both have linear molecular structures, highly functionalized and stiff-chain, but they have different properties that can be combined usefully. Chitosan contains amino groups that play electron donor roles and antibacterial characteristics. Otherwise, cellulose primarily offers hydrophilicity, structuring, and mechanical properties. In general, there are three groups of reported papers on nanocellulose-reinforced chitosan composites: the direct addition of nanocellulose into the chitosan matrix, the chemical or physical modification of nanocellulose to improve its incorporation with chitosan, and layer-by-layer processing for the preparation of the composites based on the cationic property of the chitosan. The addition of nanocellulose into chitosan-based composites usually improves the strength, modulus, thermal stability, and water resistance due to the good dispersion and interfacial interaction between chitosan and nanocellulose [85 - 89].

A direct mixture of them can be performed by solvent casting method in which nanocellulose is the filler and chitosan is the matrix in the composite system [81- 84, 90]. Chitosan films reinforced by CNC and CNF with different ratios (0 - 7 wt.%) were produced by solution casting. The physico-mechanical properties and water permeability of chitosan-cellulose composite were improved. The tensile strength, modulus, and elongation at break increased by 104, 28, 309, and 77 %, respectively. Morphological studies revealed the dispersion of CNC and CNF is in the contiguous matrix of chitosan with a homogeneous distribution without agglomeration [89]. Fernandes reported on the preparation and characterization of nanocomposite films based on different molecular weight chitosan and nanofibrillated cellulose to improve strength properties. The received films were highly transparent, flexible, and had better mechanical properties, with a maximum increment on Young’s modulus of 78 % and 150 % for high molecular weight and water-soluble high molecular weight filled chitosans, respectively, and of 200 % and 320 % for low molecular weight and water-soluble filled chitosans, respectively [88].

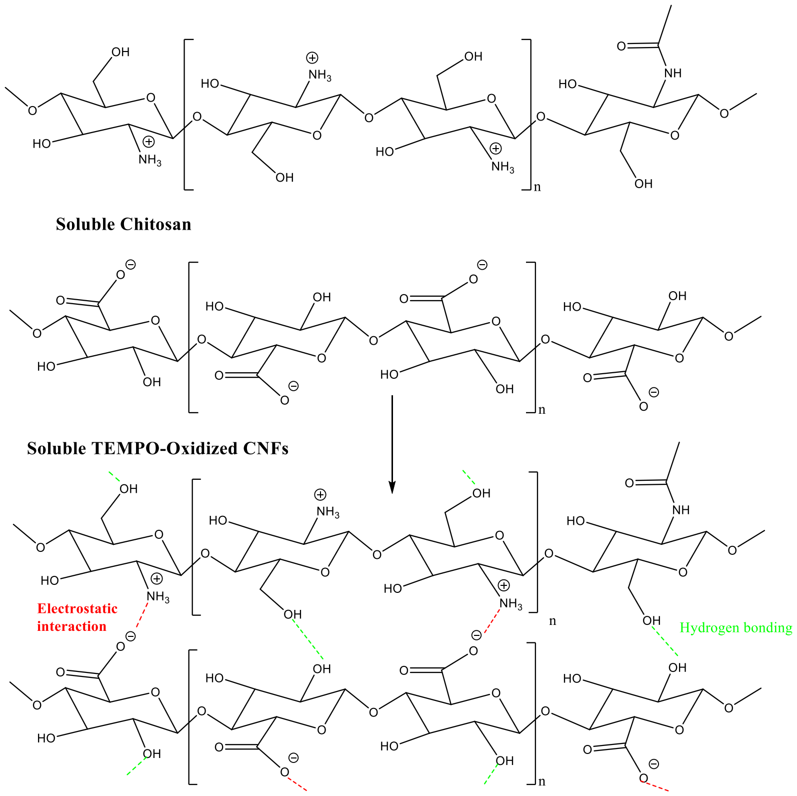


Figure 4. The schematic representation of intermolecular hydrogen bonds and electrostatic interactions in chitosan/TEMPO-CNF nanocomposite film, Reproduced from Ref. [93].

To enhance chitosan-nanocellulose interaction, the chemical and physical modification of nanocellulose was performed. Theoretically, the covalent linkage between nanofillers and the matrix should give better interfacial cooperation in the composites, resulting in better mechanical improvement of the nanofiller. The covalent linkage between CNC and chitosan should also be obtained by the addition of tannic acid [91] or genipin [92].

Oxidized nanocellulose containing -COOH groups (using TEMPO agent) or CHO groups (using periodate agent) can react with chitosan, forming stable carbodiimide or imine bonds without crosslinking agents. The transparent bio-nanocomposite film based on chitosan and TEMPO-nanocellulose with improved physico-mechanical properties was fabricated by Bhawna Soni et al. The surface morphology of the films observed by scanning electron microscopy (SEM) and atomic force microscopy (AFM) indicated that TEMPO-cellulose was well dispersed into the chitosan matrix. The composite film also had better thermal and mechanical properties than that of chitosan. Hydrogen bonds and electrostatic attraction between the negatively charged carboxylate groups ($-COO^{-}$) and the positively charged ammonium groups ($-NH3^{+}$) of chitosan (Figure 4) are the driving force for the best combination of both the polymers [93 - 95].

At room temperature, chitosan and TEMPO-cellulose are physically crosslinked through the formation of ionic bonds; after heating, the carboxyl group of TEMPO-cellulose and the amine group of chitosan react into amide covalent bond linkage -CONH- [96].

4.4. NC/alginate nanocomposite

Alginates are natural polysaccharides mainly extracted from bacteria or brown marine algae with a basic structure consisting of 1,4-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues. They are arranged into blocks of repeating M, G, or MG. Alginate is dissoluble in water. The stiffness of the three blocks decreases in the order GG > MM > MG. In nature, it exists in the form of alginic acid. A thermal stable and biocompatible hydrogel would be formed by the addition of di- or tri-cations. Being a naturally occurring polymer, alginate is a potential biomass-based matrix to fabricate nanocellulose-reinforced composites [97].

Tanzina Huq *et al.* reported on the preparation and characterization of cellulose nanocrystals (CNC) reinforced alginate-based nanocomposite film. The CNC content was varied from 1 to 8 %. The polymer nanocomposites containing 5 wt.% CNC content had the highest tensile strength, which was increased by 37 % in comparison to the pristine polymer. Molecular interaction between alginate and nanocellulose observed by the FTIR spectrum indicated an increase of hydrogen bonding between alginate and nanocellulose. With the incorporation of nanocellulose, the thermal stability of alginate-based nanocomposite films was also enhanced [98].

A nanocomposite based on nanocellulose and alginate was prepared for chlorhexidine digluconate carriers. Firstly, nanocellulose was produced by the acid hydrolysis method. Then 2 % NC was mixed with sodium alginate 1%; the mixture was stirred until the homogenous colloidal solution was created. The solution was sprayed, centrifugated, and freeze-dried overnight. TEM images indicated the presence of whisker and fiber nanocellulose with an average diameter of 20 nm. SEM image exhibited sphere and oval morphologies of microcapsules with a diameter of 500 nm [99].

Minsung Park *et al.* fabricated TEMPO-oxidized bacterial cellulose (TOBC)-sodium alginate (SA) composites to improve the properties of hydrogel for cell encapsulation. The TOBC fibers were received using a TEMPO/NaBr/NaClO design at pH 10, room temperature. The fibrillated TOBCs and sodium alginate mixture were cross-linked in the presence of Ca^{2+}

solution to form hydrogel composites. The compression strength and chemical stability of the TOBC/SA composites were better than that of sodium alginate hydrogel, which implied that TOBC played an important role in improving the composites' structural, mechanical and chemical stability. Cells were successfully entrapped in the TOBC/SA composites, and the viability of cells was examined. The results indicated that TOBC/SA composites should be a promising candidate for cell encapsulation engineering [100].

4.5. NC/protein and gelatine nanocomposite

Proteins, which are made up of 20 different amino acids, are key macromolecules for living organisms. It makes biological and organic systems to be alive and propagatable. Fibroin from silk and spider web, keratin from hair and wool, and all types of enzymes that stimulate bio–reactions in animal bodies are entirely proteins [101].

In comparison to starch, proteins are better matrices to make bionanocomposite because it possesses good gas barrier properties and low vapor permeability. As natural polymers, proteins also have been possibly used in edible packaging materials, such as soy protein sheets and collagen envelopes. Protein plastics were important in substituting for cellulose before synthetic polymers were found [102]. Various polymer blends based on protein and nanocellulose have been fabricated using different solvents and processing techniques. Depending on the method, starch and protein should be dissolved individually before combining their solutions at different compositions. Some systems needed pretreatment or chemical modification of the polymers [102].

Lina Zhang et al. demonstrated that the incorporation of 20 wt% nanocellulose crystals into soy protein-based composites improved tensile strength and Young’s modulus from 5.8 MPa to 8.1 MPa and 44 MPa to 133 MPa, respectively. SEM image indicated that the composite had a relatively smooth surface. This suggested that celluloses were distrusted uniformly in the soy protein matrix. Additionally, the crosslinking networks caused by intermolecular hydrogen bonds between the CNCs and the protein matrix made the composites displayed better water resistance and thermal stability than the pristine protein material [103].

A top-down approach produced biocompatible protein-functionalized cellulose membranes. The tensile mechanical properties, including stress, strain and Young’s modulus of the membranes are not significantly affected by the existent of residual proteins. SEM observation showed nanocellulose inhomogeneous width size randomly distributed in the matrices. The surface-charged assessment of the membranes was determined using streaming ζ-potential indicating that nonbleached cellulose membranes possessed highly negative surface charges at pH below 4 [104].

Gelatin is a type of protein received by denaturing triple-helix structure of protein into single-strain collagen. The mechanical behavior of gelatin gels and films is involved in reforming gelatin as crystalline triple helixes. Above 35^{o}C, the second bonding structure of gelatin was disrupted, leading to the materials’ poor mechanical and thermal properties. This protein is inexpensive, commercially available, and biodegradable. Additionally, gelatin presented good processability and film-forming properties [100, 101, 105, 106].

Julien Bras et al. reported on the preparation of nanocomposite based on gelatin (Gel) and nanocellulose for biodegradable packaging purposes. The interaction between CNC and gelatin was investigated by assessing the ζ-potential of Gel/CNC suspensions under acidic (pH 3), gel isoelectric point (pI) at pH 6 and alkaline (pH 8) conditions. The results indicated that the electrostatic attraction was promoted at pH 3; it was favorable for the electrostatic repulsion in the Gel- CNC pair at pH 8. In both cases, an increase in the suspension viscosity was observed. With the introduction of 5% nanocellulose, the water vapor permeability of the Gel/CNC films decreased by 68 % under electrostatic attractive forces and by 39 % at the gelatin pI. The addition of 0.5 wt.% CNC at pH 3 resulted in the formation of complex coacervates, which decreased the mechanical properties and increased the water vapor permeability of Gel/CNC films. When the pH increased above the Gel pI, it increases gelatine renaturation as triple helices. This phenomenon responded to the increase of Young's modulus and tensile strength by 152 % and 56 %, respectively. The drying temperature for film-forming had the opposite effect on the triple helix content and, as a result, on the physical properties of gelatin/nanocellulose films. All results implied that regulating the pH, nanocellulose content, and drying temperature is a proper strategy for improving the nanocellulose-reinforced gelatin film properties. The nanocomposite films may meet requirements for food packaging applications [107].

Bacterial cellulose nanocrystals with a 1 - 5 % loading content were used to reinforce gelatin nanocomposite films. Due to the presence of percolated networks of cellulose nanocrystals in the gelatin matrix, the mechanical properties of the nanocomposite significantly improved. The incorporation of 4 wt.% nanocrystals resulted in an increase in the tensile strength from 83 MPa to 108 MPa, while the elastic modulus increased from 2189 MPa to 2350 MPa [108].

W. Treesuppharat *et al.* prepared hydrogel composite materials using bacterial cellulose and gelatin. Glutaraldehyde was used as a crosslinking agent between the hydroxyl groups of nanocellulose and the amine groups of gelatins. The results indicated that the physico-mechanical properties and thermal stability of the hydrogel composite were considerably improved. An increase of 400 – 600 % in the swelling ratio of the hydrogel network in water was observed. Hydrogels are promising candidates for drug delivery systems [109].

5. CONCLUSIONS

Nanocellulose with unique properties such as biocompatible, biodegradable, renewable and highly mechanical properties have gained great attention for research and development of green materials for different applications. As reinforcement materials, nanocellulose can significantly improve biopolymer nanocomposites' physical and mechanical properties. Although there have been many achievements on a laboratory scale, there are still challenges to producing nanocellulose polymer nanocomposites in an industrial scale. One of the most problems is more research on environmentally friendly methods for producing and modifying nanocellulose as well as an understanding of interphase reaction between polymer matrix and nanocellulose is now required.

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