Review Article

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Overview of nanocellulose as additives in paper processing and paper products

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Abstract: The rapid economic growth and environmental concerns have led to high demands on paper and paper-based products in terms of variety, quantity, quality, and specialty. Enhancement and functionalization with additives are constantly required. Moving away from traditional petroleum-based additives, researchers have attempted to use "green" nanoadditives by introducing renewable environmentally friendly nanocellulose. This article studies the functions of nanocellulose as bio-additives (enhancer, retention and filtration reagent, and coating aid) in paper and paper products, and overviews the research development of nanocellulose-based additives and their applications in the paper industry for both efficient production and paper functionalization. The review shows that (1) a variety of nanocellulose-based bioadditives have been reported for various applications in paper and paper-based products, while commercially viable developments are to be advanced; (2) nanocellulose was mostly formulated with other polymer and particles as additives to achieve their synergistic effects; (3) major interests have concentrated on the nanocellulose in the specialty papers as representing more value added products and in the efficient utilization of recycled fibers, which remains most attractive and promising for future development. This report shall provide most useful database information for researchers and industries for paper recycling and enhancement, and paper-based products innovation and application.

Keywords: nanocellulose bio-additive, paper and paper-based product, specialty paper, recycle, functionalization

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1 Introduction

Nanocellulose (NC) is a nanoscale term used to refer to cellulosic materials, which are the most abundant, renewable, and biodegradable biopolymer on earth. Wood is currently the most extensive source of the industrialized cellulose, which is the orderly structure of the fiber elements that make up cells [1,2]. The hierarchical nature and complexity of biomass cellulose allow its structure to be analyzed at different levels, which is composed of growth ring, cell structure, cell wall, fiber matrix, microfibers, and cellulose molecules, being analyzed from the macroscopic, microscopic to nanoscale, as shown in Figure 1 [3–5].

Cellulose is a linear biopolymer, which occurs naturally in all plants. In the early nineteenth century, the chemical structure of cellulose was confirmed, followed by in-depth research activities. The linear polymer in cellulose is linked by D-glucopyranose with β-1,4-glycosidic bonds (Figure 2); two D-glucopyranoses compose cellobiose as the repeating unit of cellulose polymer. Each D-glucopyranose unit has six carbon atoms and three hydroxyl groups (respectively C2, C3, and C6 atoms). The degree of polymerization ranges between 10,000 and 15,000. Cellulose is hydrophilic because of its molecular structure, insoluble in water and most organic solvents, degradable, and chiral [6–10]. In addition, the cellulose is odorless and inexpensive, and has high crystallinity, excellent biocompatibility, low density, and robust strength [11]. The content and characteristics of cellulose may vary with the sources [12].

NC refers to a fibrous biomass-based material with a size less than 100 nm in at least one dimension, and

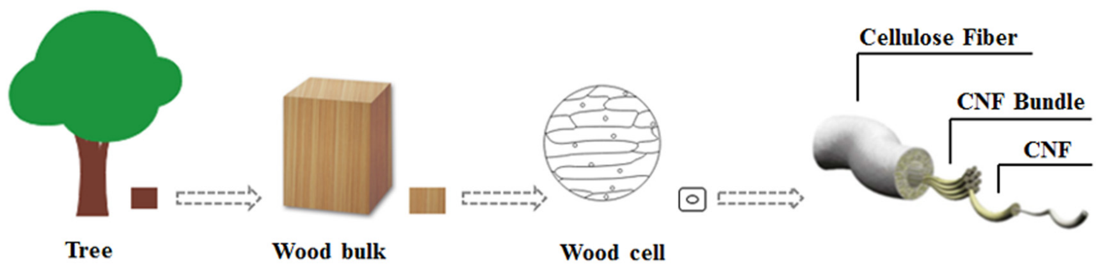

Figure 1: Hierarchical structure of cellulose.

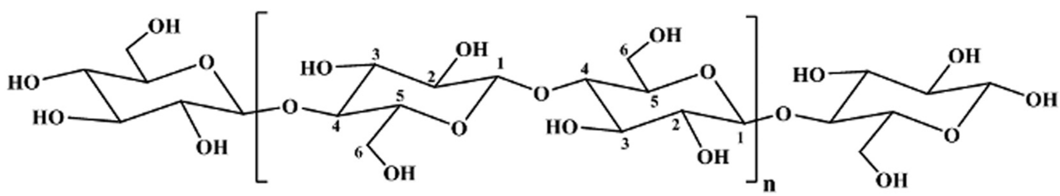

Figure 2: Molecular structure of cellulose polymer.

belongs to cellulose chain aggregates, including crystalline and amorphous regions [13–15]. Around the 1940s, some scholars began to get involved in the exploration of NC, and NC colloidal suspension by mixing acid hydrolyzed wood and cotton wool was obtained for the first time [16]. Ranby then used the concentrated sulfuric acid to degrade the amorphous region of cellulose to prepare rod-shaped rigid cellulose nanocrystals (CNC) with sulfate groups on the surface [17,18]. With the advances in theory and technology for decades, Turbak, Herrick, and their colleagues reported for the first time that high-pressure homogenization of softwood cellulose fiber slurry could lead to a translucent and highly consistent gel, which was called nanofibrillated cellulose (NFC) [19,20]. Since then, many scholars have opened the road of in-depth and promising research on NC-based materials [21–29], and gradually expanded its potential application in many industrial sectors. Till today, a relatively mature theoretical basis has been established and a solid foundation identified for the relevant research on NC materials. There are a variety of NCs and their derivatives in publications, which could nevertheless be grouped into two divisions: one is nanoparticles or cellulose nanofibers, including the nanocrystalline cellulose (NCC), CNC, cellulose nanowhiskers/NFC, and cellulose nanofibrils (CNF); the other is the micron-sized particles or cellulose nanostructured materials, including the microcrystalline cellulose (MCC), cellulose microcrystalline, microfiber cellulose (MFC), and cellulose microfiber (CMF) [3]. In principle, CNC are extracted from the fibers after the amorphous part is dissolved, while NFC is highly fibrillated because of the application of high shear force disintegration, resulting in highly interconnected fibers [30].

The application of nanoscale cellulose has attracted more and more attention, because of not only its biodegradability and richness, but also its unparalleled unique properties, such as barrier properties, mechanical and colloidal properties, low density, unique rheology, and many other excellent characteristics [31–43]. Its specific properties are summarized in Table 1.

The rapid economic development has led to high demands on paper-based products recently, especially in packaging industry. One of the major developments is to use "green" nanoadditives to enhance paper performance and functionalize papers with specific characteristics, by introducing renewable environmentally friendly NC to improve the properties, such as mechanical strength, gloss, writing and recyclability. This article overviews and presents the working principle of NC in paper and NC-based additives for paper products, including the NC as a paper enhancer on paper, a retention and filtration reagents to increase the retention rate of fine fibers and improve the filtration efficiency, and a coating aid to improve the barrier properties of paper. The application of NC in specialty papers has also been discussed, including the waterproof paper, fresh paper, insulation paper, blotting paper, and wrapping paper.

2 Working mechanisms of NC in paper matrix

It is well known that the strength of paper depends mainly on the strength of the fibers themselves, fiber

Table 1: Properties of NC

Nature	Specific performance	Application	Ref.
Mechanical properties	Young's modulus: 150 GPa; excellent network hydrogen bonding between celluloses	Reinforcement in polymer matrix	[41,55,56]
Rheology	Strong hydrogen bond and the ability to form a uniform layer on a hydrophilic substrate; suspension viscosity decreasing with increasing shear rate	Green adhesive; paint; paper coating; rheology modifier for food, coatings, cosmetics, and pharmaceutical products	[51–54]
Optical properties	Translucent, highly consistent gel	Transparent material; nano-paper	[49,50]
Thermal performance	Up to 350°C degradation temperature	Insulation material	[47,48]
Biodegradability	Hydrophilic surface; rapid degradation at ambient temperature	Films/membranes, beads/microspheres, hydrogels/aerogels, bioplastics	[44]
Oxygen barrier	Tight configuration between the fibers leads to reduced porosity	Liquid and gas material barrier	[45,46]

length, fiber orientation distribution, contact area between fibers, and the strength and number of hydrogen bonds in the matrix [57]. CNF generally achieves its function for the strength enhancement of paper by increasing the bonding area of the sheet. The reinforcement mechanism may be explained from two scenarios: (a) covering the fiber surface with a soft layer that helps to establish fiber-to-fiber contact at the molecular level, and (b) filling the voids and pores at the edge of each fiber bond, extending the possible bonding area [58]. CNF can be deposited on the fiber surface prior to sheet forming by selecting an appropriate retention aid, which makes the fiber surface softer and thus increases the bonding in a similar manner to dry strength polymers, as an example, using a cationic starch (CS) to act as a retention aid to help deposit anionic CNF on the fiber surface, rather than CNF filling the voids and pores between the fibers [59]. CNF also typically acts as a filler in the pores between fibers, filling the gaps and forming bridges between fibers, increasing the strength by increasing the bonding area of the sheet [60]. In the papermaking process, a network structure is formed between the fibers. As an important derivative of natural polymer cellulose, NC has broad application prospects in the pulp and paper industry because of its unique properties, such as paper reinforcement, retention of fine fillers and fine fibers, and as a coating aid to improve paper printing performance, mixed with other materials as a filter aid to improve paper performance, *etc*. [61]. The surface of NC is rich with free hydroxyl groups. When added to the pulp, it will be distributed in the gaps between the fibers or on the fiber surface and closely combined with the pulp fibers, which strengthen the adhesion between the fibers, fill the voids in the paper, and achieve the effect of improving the strength of the paper [62–66] (Figure 3).

As a natural polymer enhancer, NC is environmentally friendly and renewable, but its adsorption capacity on the fiber surface and the effect of a single use are limited, making it difficult to achieve high strength goals of modification. To address this insufficiency, some researchers have considered using NCs together with some cationic polymers as additives to achieve their synergistic effects and improve paper strength. For instance, CNF with cationic polyelectrolyte polyamide polyamine epichlorohydrin (PAE) have been attempted to enhance the wet and dry strength of paper [67]. The enhancement effect of the CNF/PAE system illustrated that PAE and CNF could be adsorbed on the pulp fiber in the form of a two-layer system, and the dry and wet tensile strength of the paper could be significantly improved. When the CNF and PAE are added in the form of nanoaggregates, the improvement of paper strength is moderate.

The potential of the functionalized NC as the whole additive seems very promising, which promotes sufficient bonding between fibers and filler aggregates. This may also lead to the reduced requirements for other paper additives. A study on making papers using the bleached eucalyptus kraft pulp with the addition of CNF-carboxymethylation (CNF-C) and CNF-TEMPO-mediated oxidation (CNF-T) additives showed that the retention rate of the mineral fillers in the paper and the effect on the paper properties substantially improved [68–70]. Adding carboxymethylated or TEMPO-oxidized CNF to the fiber matrix resulted in an increase in both the mechanical and optical properties of the paper.

Nanostructured cellulose-based additives can effectively bridge and network the long and short fibers because of many inherent merits, lending such additives with preference compatibility with cellulosic fibers, and therefore improve the mechanical, physical, and barrier

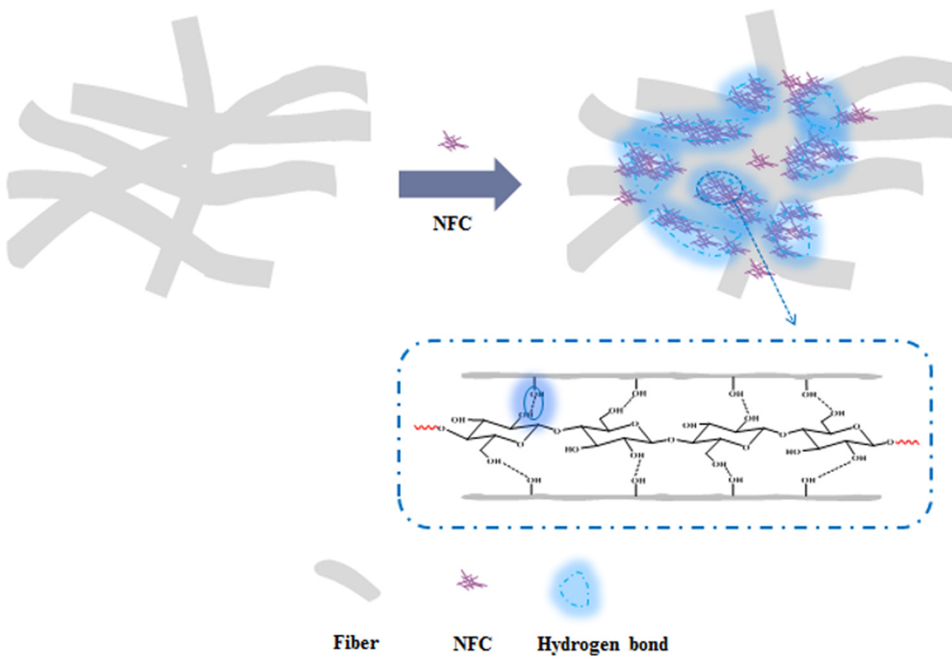

Figure 3: Combined effect of fiber entangling and NC reinforcement within paper.

properties of the resulted papers or paper products, extending the service life of paper products [71]. The shortage of forest resources makes this development more critical and important, as the proportion of non-wood fibers and secondary fibers, including waste paper pulp, continues to rise as raw materials in papermaking, the retention and enhancement of which require effective additives. NC-based additives could meet such requirements to increase the utilization rate of recycled paper. For instance, a research using mechanically treated NC to enhance the recycled eucalyptus pulp found that NC could make the recycled fibers more consistent within paper matrix, which had a positive effect on the properties of the produced paper [72].

3 NCs as papermaking additives

Papermaking additives are also known as papermaking chemicals. Papermaking auxiliaries can impart various excellent properties to paper and are inseparable from the processes of pulping, papermaking, and paper processing. The addition of paper additives is very small, but could significantly improve the performance of papers. Common papermaking auxiliaries mainly include sizing agents, retention aids, filter aids, enhancers, defoamers, and dispersants as classified in Table 2.

NC is an important derivative of natural polymer cellulose, which has good swelling rate, biocompatibility, and degradability. The molecular structure characteristics indicate that it has naturally inherent advantages as a papermaking additive. Its structure is shown in Figure 2. The structural hydroxyl group (–OH) presented in the glucose unit is responsible for the hydrogen bonding ability of cellulose fibers, leading to a strong structure, and also contributes to the hygroscopicity of cellulose. NC has properties such as high specific surface area, aspect ratio, and tensile strength with Young's modulus of about 138 GPa, and the presence of a large number of hydroxyl groups on the surface that can form hydrogen bonds with the fibers [73]. An additive often

Table 2: Classification of papermaking auxiliaries

Collectively	Classification	The main purpose	Common additives
Papermaking additives	Functional additives	Improve paper performance	Sizing agent; dry and wet strengthening agent, *etc.*
	Process additives	Improve the performance of paper stock in the wet end	Retention aid; filter aid; defoamer; deinking agent, *etc.*

has multiple effects simultaneously and NC at least has a retention, drainage, and enhancement effects. The research, production, and use of papermaking additives have been the fundamental and crucial basis for the rapid progress and development of the papermaking and packaging industries, especially the research status as enhancers, retention aids, and filter aids, which are further discussed in the following sections.

3.1 NC-based paper enhancers

Paper strength is generally of dependence on three main parameters: (a) the strength of fibers themselves, (b) the bonding strength between and among fibers, and (c) the degree and characteristics of the entanglement of fibers within the matrix. The increase in paper strength caused by the addition of reinforcing agents is mainly reflected in the increase in fiber bonding strength, and the formation of hydrogen bonds is particularly important [74,75]. The diameter of CNF is very thin and the ratio of length to diameter is large. Therefore, the specific surface area is large, leading to a high hydrogen bonding potential. The hydroxyl groups on the NC can generate stronger hydrogen bonds with the hydroxyl groups on the fiber, so NC is considered an excellent paper enhancer to improve mechanical strength of the paper [75,76]. The perspective of chemical bonding of NC as an enhancer is illustrated in Figure 2 (magnified). As a promising bio-based material, NC has unique nano characteristics. A large number of hydroxyl groups on the surface may form hydrogen bonds with pulp fibers, cross-linking to fill the voids in the paper and improve the strength of the paper.

3.1.1 NC as a reinforcement of base papers

The enhancement effect of NC on base paper can be explained with the following two possible mechanisms: (1) NC acts as an adhesion promoter by bridging adjacent fibers together, which is conducive to fiber–fiber bonding and increases fiber contact and bonding areas; (2) NC could form network structures between relatively coarse fibers to improve the load bearing capacity of the papers [71].

The paper presents a layered structure. The fibers inside the paper are arranged randomly and interlaced with each other. The layers mainly rely on intermolecular bonding and hydrogen bonds. The molecular chains of cellulose are also bonded to each other through hydrogen bonds. NC is used as a reinforcing agent. The high polarity of the surface and the pulp fiber has a strong complementary effect, which increases the bonding points between the fibers, thereby enhancing the paper. The MFC and NFC isolated from cotton lint were used as strength additives in unbleached kraft paper, and it was found that the tensile strength of MFC- and NFC-enhanced kraft papers significantly increased compared with the unadded kraft papers [77]. González *et al.* compared some properties of bleached eucalyptus pulp before and after using CNF. The study proved that adding CNF to the bleached pulp made it suitable for the production of printing and writing papers [78].

Adding an appropriate amount of NC as an additive can achieve a reinforcing effect, but an excessive amount of the additive may lead to an adverse effect and reduce the fiber–fiber bonding force depending on the balance of the strength between NCs and fibers themselves. The modification of NC could improve the performance of paper as the mechanical properties and functionalities of NC may be enhanced. Hollertz and his colleagues compared the effects of four different NCs on paper properties, namely carboxymethylated CNF, periodate-oxidized carboxymethylated CNF, dopamine grafted carboxymethylated CNF, and microfibrillated cellulose made from unbleached kraft paper fibers [79]. The results showed that while an addition of NC can significantly increase the tensile strength, Young's modulus, and strain fracture of paper, the addition of CNF oxidized by periodic acid which was added together with polyvinylamine (PVAm) or poly-dimethyldiallylammonium chloride (pDADMAC) could significantly enhance the reinforcing effect.

3.1.2 NC composite as a reinforcement of base paper

The demand for paper enhancers increases in paper and paper-based packaging products, as the increase in the proportion of secondary fibers and the requirements of paper quality. The limitation of traditional single addition of NC is recognized, as the adsorption capacity of the additive on pulp fibers is limited and the reinforcement effect is moderate, which is often difficult to achieve the specific strength required. Scholars have proposed a NC composite reinforcement system, which could make better use of the synergistic effect between the constituents of an enhancer.

More effectiveness of NC composite reinforcement as a paper enhancer means less consumption of raw materials to achieve a similar outcome, which is beneficial to industries for possible cost reduction and less environmental impact. PAE has electrolyte properties and can ionize in aqueous solution to generate positive charges, adsorb negatively charged fibers, and form a relatively dense film on the fiber surface, thereby improving the wet strength of the paper. The working principle may be presented as in Figure 4. A composite system using food additive PAE with renewable biodegradable cellulose nanofibers (CNF) has been experimented to investigate the effect of the system on the performance of paper, and it was found that the CNF can partially replace the food additive PAE, such as reducing the amount of PAE used, while maintaining the same wet tensile strength [80].

CS introduces tertiary amine groups or quaternary ammonium groups on the basis of natural starch to make it positively charged in the solution. It may be adsorbed with negatively charged fibers through electrostatic interaction, and the hydroxyl groups on its skeleton may also interact with the hydroxyl groups on the fiber to form hydrogen bonds, thereby improving paper strength. Yousefhashemi and his colleagues used low cost recycled old corrugated box pulp as raw materials to produce new lignocellulose nanofibers (LCNF) through ultra-fine grinding technology, and then used nano-silica (NS)–CS system as a retention aid and LCNF as a paper enhancer to study the effect of LCNF/CS system on paper performance [81,82]. The results showed that the use of this composite system resulted in an increase in the stretch index of LCNF/CS paper by 32% compared to that of only LCNF modified paper, which was increased by 57% compared with the control hand-made paper. The function of the composite reinforcement within the matrix system is illustrated in Figure 5. Tajik and his colleagues used soda bagasse pulp to make handsheets mixed with CNF and highly substituted CS to enhance the structure of matrix and hence optical properties and strength properties. It was found that as the content of biological additives increased, the tensile strength and rupture strength continued to increase, reaching 33% and 23%, respectively [83]. The effect of various doses of PAE resin cross-linked TEMPO-oxidized cellulose nanofibrils (TOCNs) on the physical and chemical properties of paper films has also been investigated, and it was found that the paper with PAE-TOCNs added had high tensile strength, a wet strength of 95 MPa [84], and Young's modulus, possibly because of the close interconnected network structure (Figure 5).

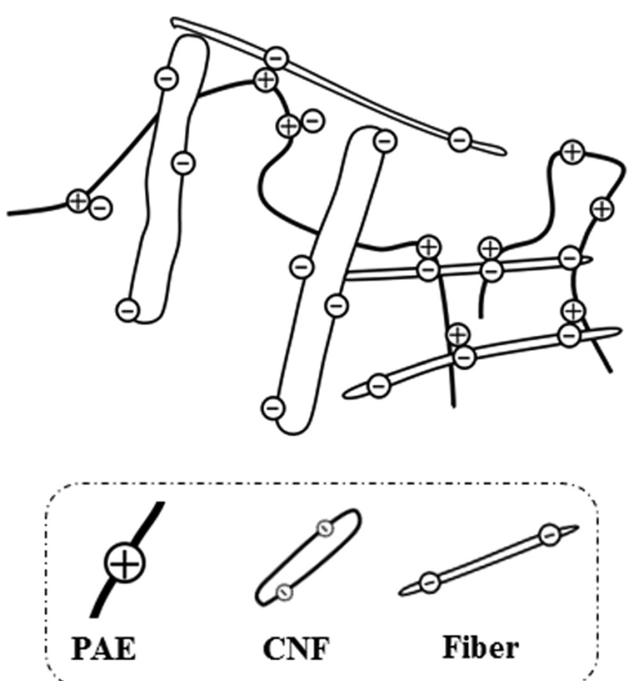

Figure 4: Charge angle and networking of paper matrix with NC composites.

3.2 NC-based retention and filtration reagents

Recycling papers or paper products has become common in current circular economy for all industrial sectors. However, a number of challenges still remain, such as the short fiber length and difficulty in removing some contaminants. Therefore, the number of recycling runs is limited and the performance of the paper made with the recycled fiber pulps may not meet the requirements of

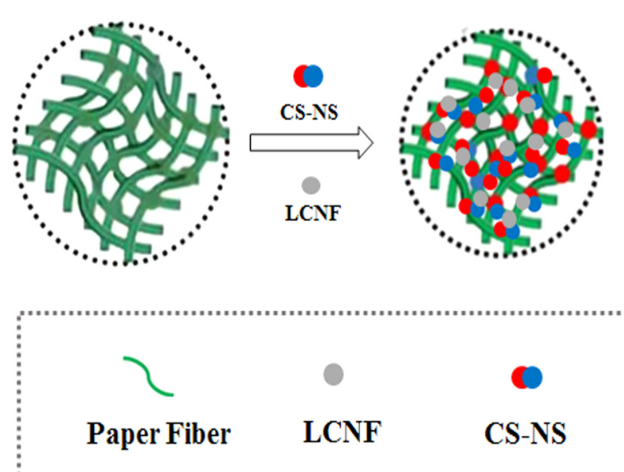

Figure 5: Schematic illustration on how CS–NS combination may interact with LCNF.

human needs. It is apparent that there is much need to develop suitable retention additives for the efficiency of pulp utilization and eliminating the environmental impact and costs for water treatment. On the contrary, both high concentration of short fibers and contaminants may result in reduction in water drainage performance of the pulp [85–89]. In recent years, to further improve the retention and filtration of fine fibers and fillers in the pulp, a dual retention system (RS) has been proposed. The main function of the filtration is to improve the drainage and dewatering speed of the wet paper. Often the water filtration and retention effects are similar in promoting the aggregation of fibers and fillers, and retention aids are also filter aids.

3.2.1 NC as a retention reagent

The use of appropriate retention aids may not only increase the retention rate of fine components in the pulp, saving resources, but also improve the recyclability of waste water. NC could change the physical properties of paper by either generating the surface contact bonding or improving the networking between fibers and the filler aggregates. This means that the addition of retention reagent could affect the process of paper production, especially in the drainage stage; therefore, a retention reagent is usually used at this stage to promote the interaction of cellulose fibers. Liu and his colleagues used a cationic NFC (CNFC) as a retention additive for the precipitated calcium carbonate (PCC) in the preparation of conventional handsheets of the reconstructed tobacco sheets/papers (RTS) [90]. Both the retention rate of PCC and the physical properties of the paper sheet are significantly improved. The PCC retention rate in RTS increased from about 33% to 45%. An enzymatic CMF has also been investigated to improve the filler flocculation and papermaking performance. It was found that the addition of CMF resulted in a better retention of fillers in the fiber matrix; therefore, the dry strength and wet strength of the paper were greatly improved [28].

As aforementioned, a single retention reagent may not be sufficiently effective. Where the dosage of the retention aid is small, the retention rate of fine fibers is greatly reduced; where the dosage of the retention aid is large, larger flocs will be formed, affecting the uniformity of the paper. The advance of papermaking technology has led to the development of two component reagents, which could achieve better results. A dual RS usually uses two different charged electrolytes to produce relatively high-strength flocs, for instance, the cationic polyelectrolyte could be added first, followed by the anionic polyelectrolyte for the best retention effect. The reinforcement mechanism can be proposed as in Figure 6. A number of dual retention reagent systems have been reported, for example, a CS-anionic nano-silica composition has been used as a drainage/retention aid to improve the retention of fine fibers and fillers [82], and a water-soluble cationic chitosan (C-Ch) and surface-modified microfibrillated cellulose (C-MFC) have been applied in cork and bagasse pulps. The study using the C-Ch and C-MFC together with bentonite showed that the influence of CMFC/bentonite and C-Ch/bentonite systems on filler retention was significant in the drainage and filler retention in handsheets made of cork and bagasse pulp, and compared with C-MFC, the use of C-Ch was more effective in improving filler retention [91]. Merayo and his colleagues examined the efficiency the retention aids of polyvinylamine, chitosan, CS, C-PAM, and C-PAM-B that were applied to the CNF made from eucalyptus kraft pulp and corn stover organic solvent pulp. It was found that the CNF containing C-PAM-B or chitosan significantly

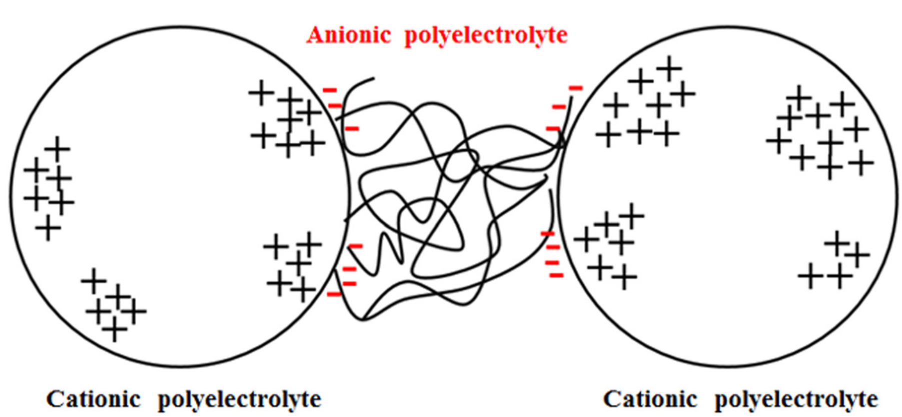

Figure 6: Reinforcement of dual retention reagent system.

reduced the drainage time, and gave rise to the best shape and high strength of handmade papers [92]. Balea and his colleagues used corn and rape straw pulp as raw materials to prepare CNF after bleaching, refining, and TEMPO-mediated oxidation, and used coagulants, cationic polyacrylamide (CPAM), and chitosan to investigate the two component retention reagents. The results showed that the CNF and chitosan combination gave the best outcomes as a retention reagent [93].

3.2.2 NC as a filtration reagent

The function of a filtration regent is to improve the drainage and dehydration speed of the wet paper. The positively charged filtration reagent can neutralize the charge on the surface of the fiber and filler. When the polarity is reduced, it is difficult for water molecules to wet or align on the surfaces of the fiber and filler. The dehydration process directly affects the effect of the formation of paper sheets; therefore, improving the slurry drainage performance is of great importance in the papermaking process. There are a number of filtration reagents used in pulp and paper industries, and main types of the reagents are grouped in Table 3. Filtration reagents also work as polymer surfactants, which have the effect of reducing surface tension. After being adsorbed or combined on the surface of fibers and fillers, the reagent can reduce surface tension and contact angles of the fiber, making it difficult for water molecules to wet the fiber surface. Fine fibers can create a strong grid structure leading to severe drainage problems. The drainage time could increase in proportion to the amount of CNF [59,94], as favoring the retention of CNF may clog the pores of paper sheets. Some researchers have addressed this issue by considering the complex interactions between cellulose pulp, CNF, mineral fillers, and commonly used additives. CNF can be added directly to pulp ingredients and potential problems related to dewatering can be avoided using relatively small amounts of CNF and appropriate retention aids [95–99]. Drainage can be maintained or even improved using the right combination of RSs and NC, and dual RSs based on a combination of polymers and microparticles can be used to control chemical flocculation and optimize retention, drainage, and formation [94,100].

NC is from natural fiber itself, having inherent characteristics of fibers compatible with pulp fibers, while in the papermaking process, the slender filaments can form a tightly entangled network structure, which may cause drainage problems [80,90]. The most intuitive manifestation of NC as a filtering agent is its ability to act as an adsorbent material. The viability of NC as a base material depends on its high specific surface area and the abundance of OH groups that have shown some attraction to contaminants carrying ionic structures or dyes, and can be easily modified to significantly increase the affinity of NC for a number of unique substances [109]. Appropriate modification of NC can improve its adsorption capacity for specific substances. Therefore, it is often used as a filtering agent. Taking advantages of both NC and traditional filtration reagents is considered a promising approach recently. PAE is a self-cross-linking polymer compound. By controlling the amount of epichlorohydrin added, the relative content of quaternary amine groups on the molecular chain can be controlled to further obtain different positive charges and a polymer compound with different chain structures. An investigation by embedding PAE and perlite particles into highly fibrillated NC has been carried out to manufacture filtration reagents, and the results showed that the combination of highly fibrillated NC fibers and cationic polyelectrolytes could customize the structure and performance of filters [90]. The investigation of combining NC, perlite, and a smaller amount of PAE for filters showed that the NC was able to replace PAE, reducing the dosage of PAE by 95%, while retaining the wet strength characteristics of the filters.

CPAM is a polyelectrolyte with medium relative molecular mass and medium charge density. It can be adsorbed on the surface of various particles and fibers, neutralize the charge on the surface of the fiber filler, and destroy the orientation arrangement in the fiber and the macromolecular structure of the substance in the fiber to facilitate water release. When corn stalks were used as

Table 3: Filtration reagents used in pulp and paper production

Species	Representative types	Ref.
Cationic	Polyvinylamine, cationic starch, polyethyleneimine (PEI), polyamide polyamine epichlorohydrin (PAE)	[101–103]
Zwitterionic	Amphoteric starch, amphoteric polyacrylamide	[104,105]
Anionic	Hydrolyzed polyacrylamide, carboxymethyl starch (CMS)	[106,107]
Nonionic	Polyacrylamide (PAM), polymannitol galactose, polyethylene oxide	[108]

raw materials to prepare NC, and compared the effects of CS, coagulant and cationic PAM binary system, and polyvinyl alcohol (PVA) polymer on the drainage performance of paper, the results showed that using a relatively low dose of NFC alone could increase the stretch index of the paper, but reduce the drainage rate. However, this effect could be overcome using the above-mentioned filtration reagents to form a combined system [110]. Citric acid has also been used as a filter aid to work with NC. It was found that compared with the control group or the NC added group alone, the filtration performance of the paper using the combined filtration system could be significantly improved [111].

3.3 NC-based coating agent for paper and paper products

The coating agent is used to enhance the surface of paper or paper product to improve certain properties of the product. The coating agent may penetrate into the paper fiber gaps to form a hydrophobic layer or film on its surface, which can improve the water resistance, surface strength and folding resistance of the paper, reduce air permeability, increase smoothness, and improve printability. High demands for paper or paper products, such as economy, biodegradability, recyclability, and mechanical flexibility, provide broad possibilities for its surface modification [112,113].

NC has a strong hydrogen bond and the ability to form a uniform coating on a hydrophilic substrate. Using it as a coating agent can improve the coating performance of paper and paper products [51,52,114]. Adding CNF to the paper coating can improve the printing resistance of the coating, increase the strength of the coating, and improve the rheology of the coating [42,115]. At present, the research of NC as a nano-coating agent is still in its infancy. The coating thickness and formula play a vital role in the performance of the coated paper [77]. A study on the effect of NC (CNF) coating on the physical, mechanical, and barrier properties of paper [116,117] showed that CNF concentration and number of coating layers were closely related to the quality of the coated products, with the surface porosity of the paper decreasing considerably. The air resistance, surface strength, stiffness, and tensile strength increased with increasing CNF concentration and coating layers. Starch can also be used as a coating agent, but most of the coating agents used are modified, as the fluidity, film-forming properties and coating effect are not sufficient. The blending of NC and modified starch can significantly improve the performance of the coating layer [52,117].

CNF and CNC have great potentials. Composite reagents containing NC fibers (CNF) have excellent oxygen and gas barrier properties. Composite reagents containing CNC are less likely to interact with hydrogen bonds, leading to higher gas permeability. An investigation on the barrier properties of composite reagents showed that, as proposed in Figure 7, the coatings with CNF and CNC exhibited a unique layering interface [118]. The air permeability of CNF/CNC double-coated paper was reduced by about 300 times, the oxygen transmission rate was reduced by about 260 times, and the water vapor transmission rate (WVTR) was reduced by 30%. It is apparent that the CNF/CNC double-layer coating system gave rise to optimum outcomes for the development of sustainable solutions for gas, oil, and grease resistant packaging, and these multilayer coatings may provide a new way for sustainable gas and oil resistant coatings [118].

4 Application of NC in specialty paper

Paper plays a pillar role, either as a product for direct uses or raw materials for paper products, *e.g.*, packaging materials. Advance in science and the requirements for higher living standard make the uses of paper materials expand and the requirements for paper performance more stringent. Natural plant fiber-based papers must be processed to improve their performance to obtain various special properties. Specialty paper is a paper with special functions through processing synthetic fibers, pulp or mixed wood pulp, and other raw materials, and adding special additives in papermaking process [119]. The definition of specialty paper is broad, and as long as it has a special purpose, it can be called a specialty paper. NC may play an important role in formulating specialty papers, *e.g.*, waterproof paper, cling paper, oil-absorbing paper, wrapping paper, insulating paper, and antibacterial paper, which are discussed in more detail in the following sections.

4.1 NC in waterproof paper

Some special additives have been attempted to make the paper hydrophobic and moisture-proof in addition to the ordinary writing function. At present, many natural

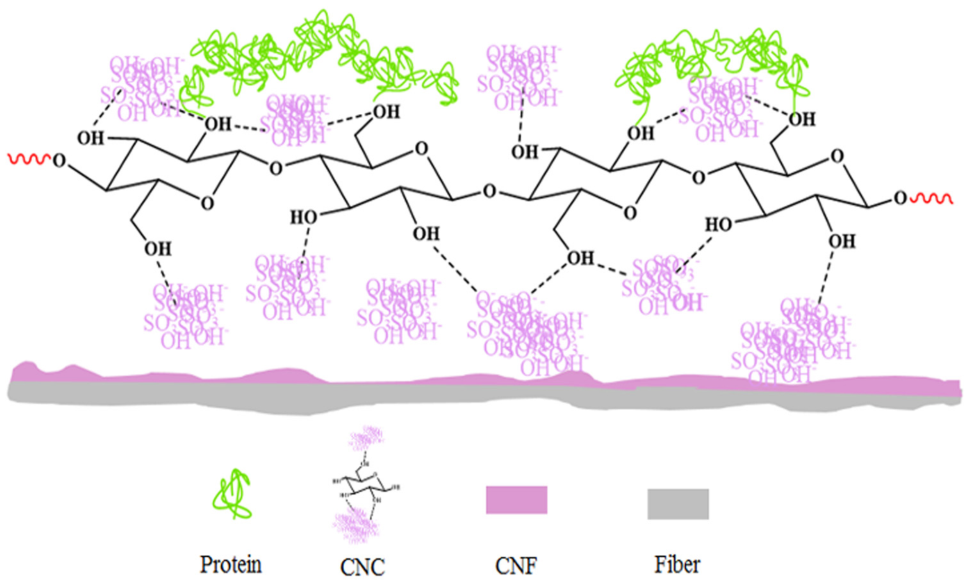

Figure 7: The enhanced adhesion of multilayered CNF and CNC coatings.

polymers have been reported for antibacterial and waterproof applications, including chitosan, whey protein isolate, starch, and its derivatives. Silver nanoparticles are often added to beeswax emulsions to prepare antibacterial and waterproof bifunctional paper. CNC has been attempted as a dispersant for Ag, where CNC worked as a stabilizer for Pickering emulsions, to make the silver-loaded CNC and beeswax more compatible [120]. Ag/CNC/beeswax composite material could then be used for paper coating to prepare multifunctional paper with antibacterial and waterproof properties. A simple dip coating method was used to assemble silver nanowires (AgNWs) and hydrophobic inorganic ceramics on pure NC paper to achieve an efficient electromagnetic interference shielding paper with water resistance and excellent mechanical flexibility [121]. The interaction of constituents of the composite paper is illustrated in Figure 8(a). Research showed that the prepared hydrophobic AgNW/cellulose (H-AgNW/CNF) composite paper still maintained good waterproof performance after dozens of bending tests and 1,000 peeling tests.

Lignin has also been attempted to work with CNF for the production of waterproof paper. Lignin is generally considered to be amphiphilic rather than truly hydrophobic, but it provides water resistance to the xylem in the vascular bundle. Colloidal lignin particles (CLPs) and cationized CLPs (c-CLPs) have such surface chemistry that are easy to disperse in aqueous media. There are also a large number of hydroxyl groups on the surface of CLP and c-CLPs, which could be embedded in the CNF fibril network, but not damage the distribution of hydrogen bonds in the CNF network. Farooq and his colleagues used a variety of cork kraft paper lignin (CLP and c-CLPs) to prepare strong and ductile CNF nanocomposite membranes with good water resistance. The results showed that the optimal 10 wt% content of CLPs could produce a film with almost twice the toughness compared with the CNF film without lignin. CLP and cationic CLPs (c-CLPs) made the film waterproof [122]. The mechanism diagram is illustrated in Figure 8(b). Compared with irregular lignin aggregates, the composite has better antioxidant activity, UV shielding, and visible light transmittance. This may bring new opportunities to the field of green bio-based nanocomposite materials and application in food packaging, water purification, and biomedical applications.

4.2 NC in fresh paper

Fresh paper is widely used in the food industry to inhibit bacterial and fungal growth as well as enzymes that cause over-ripening for a long-term storage. Some substances with special properties can be coated on the paper to make it have a fresh-keeping effect and extend the shelf time and quality of food. These materials need to withstand environmental factors, such as temperature and relative humidity, which may affect their properties, such as their barrier or permeability.

At present, cling paper in the food industry is a research hotspot and NC is of great significance in the field of cling paper [123,124]. NC can form a compact

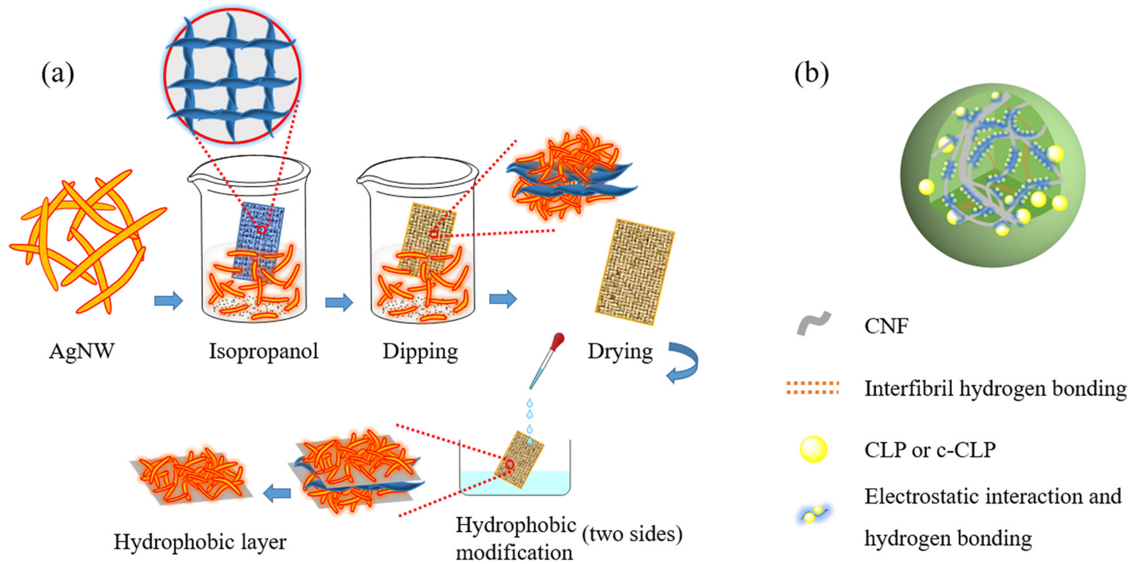

Figure 8: Interaction of constituents of composite papers (a) H-AgNW/CNF paper, (b) CNF and CLP or c-CLPs networks.

network structure, certain mechanical properties, and good oxidation resistance, but its high affinity is a major drawback. An addition of biopolymers or synthetic polymers could overcome this issue. Polypyrrole (PPy) is a common conductive polymer with certain hydrophobic properties. When combined with cellulose, it can reduce the WVTR. The bleached kraft pulp has been used as raw material together with 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) oxidation to obtain oxidized cellulose nanofibers (TOCN), which were then combined with PPy [125]. Coating the developed NC composite on paperboard resulted in dense network on the surface of paperboard. Both the mechanical properties and reduced air permeability of the coated paperboard have been significantly improved. It is apparent that such combination as a coating can perfectly combine the biodegradability, mechanical properties, and low air permeability of NC with the physical and chemical properties of PPy.

4.3 NC in blotting paper

Compared with ordinary paper, oil-absorbing paper contains more lipophilic substances. The most common is fiber-based oil-absorbing paper. Fiber-based oil-absorbing paper is made of natural fibers, has good toughness and softness, and can effectively absorb excess oil. However, one of its shortcomings is its limited oil absorption capacity. The surface of the absorbent paper is sometimes modified with porous sphere particles to improve its oil absorption capacity.

The molecular structure of NC contains a large number of active hydroxyl groups and their reaction characteristics. The chemical polarity and structure of NC molecules can be changed for a better interface compatibility between NC and polymer matrix. NC can also be polymerized with substances with a highly porous structure and used as an adsorption material. The presence of hydroxyl groups on its surface makes it hydrophilic. Therefore, hydrophobic chemical substance coating or long-chain fatty acid esterified hydroxyl were used to modify it, which can give cellulose-enhanced hydrophobicity and lipophilicity for blotting paper [126].

4.4 NC in wrapping paper

The use of bio-based and biodegradable materials for barrier packaging applications has always been a research focus. Recycled fiber has the feasibility of producing high value-added paper and is often used for packaging because of its excellent barrier properties and mechanical properties. PVA has received great attention because of its low price, stable chemical properties, low toxicity, and good film-forming properties. However, PVA is a water-soluble polymer with a large swelling coefficient and low mechanical strength. It is usually necessary to cross-link and modify PVA to form a stable three-dimensional network structure. The composite of NC (CNF) and PVA can significantly improve the tensile properties and oil resistance of paper, and reduce air permeability and moisture permeability [82,127].

Polylactic acid (PLA) is a polymer obtained by polymerization of lactic acid as the main raw material. Its raw materials have a wide range of sources and are renewable, and the synthesized products are biodegradable. PLA has relatively high tolerance to water vapor, but its barrier to oxygen is poor. Combining NC and PLA into a multilayer thin coating has been attempted on paperboard. Studies showed the potential to produce 100% biodegradable barrier packaging paper [128].

Polyhydroxybutyrate (PHB) has the advantages of non-toxicity, biocompatibility, biodegradability, and good mechanical properties. It is a high value-added biomass material and favored by the packaging industry. A biodegradable double-layer nanocomposite based on enhanced PHB, CNC, and cellulose paperboard was prepared to enhance the mechanical and barrier properties of the composite paperboard. It was found that PHB/CNC coating could overcome the water sensibility and resulted in an enhanced performance of the cellulose paperboard. This indicated the potential of replacing non-renewable polymers for the combined CNC-based full bio-based coating systems [129].

Chitosan has also been polymerized with NC (CNF) and used for paper coating. The blending of crystalline NC (CNC), chitosan (CS), and carboxymethyl cellulose has been found as an excellent barrier coating to prevent the penetration of liquids (grease, water, and oil) onto the cardboard substrate [130]. This again gives a potential for the production of an environmentally friendly green bio-based barrier film or coating in the field of packaging materials.

4.5 NC in electrical insulation paper

Insulating paper is mainly held together by hydrogen bonds between cellulose chains [131,132]. CNF are a promising renewable nano-component. The layer-by-layer technology that uses the charge of swollen wood fibers to physically adsorb polymers or particles is a promising way to introduce new functions to fiber-based insulation materials. A high-pressure homogenizer was used to produce kraft pulp NC (CNF) for traditional electrical insulation materials. A layer-by-layer method was used to incorporate oppositely charged polyelectrolytes and nanoparticles into kraft insulating paper. A durable, flexible paper with high strength and density was produced while the dielectric response in oil correlates with that of Kraft Paper with similar density [133].

NCs are more compatible with cellulose-based electrical insulating materials because of the same origin of the raw materials. The influence of four types of NCs as nano-additives on the insulation performance of power transformers was studied, namely unmodified NFC (UNFC), CNFC, anionic NFC (ANFC), and CNC. The tensile strength, DC volume resistivity, dielectric response, and breakdown behavior of nano-modified and conventional pressed paper were analyzed. The results showed that NFC could significantly increase the tensile strength of insulating paper and improve AC and DC breakdown performance [134]. The enhancement mechanism can be described as in Figure 9. The CNFC and ANFC surfaces have positive and negative charges respectively. The presence of a large

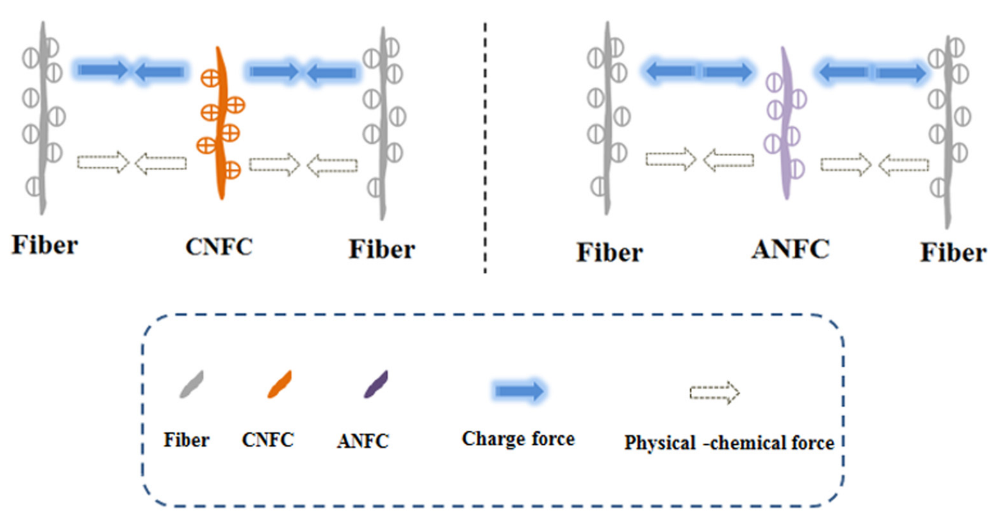

Figure 9: Reinforcement mechanism of CNFC/ANFC and cork fiber insulation material.

Table 4: Summary of cellulose functionalization for specialty papers

Specialty paper	NC types	NC modification	Function	Ref.
Waterproof paper	CNC	Ag/CNC/beeswax	Hydrophobic and moisture resistant	[120,121]
Fresh paper	CNF	TOCN-PPy	Freshness, long shelf-life, and improved quality of food	[125]
Blotting paper	CNF	Hydrophobic coating/long-chain fatty acid esterified hydroxyl	Ability to absorb oil	[126]
Wrapping paper	CNC/CNF	PVA/PLA/PHB/Chitosan	Superior barrier and mechanical properties	[128–130]
Electrical insulation paper	CNC/CNF	UCNF/CCNF/ACNF	High strength and high insulation	[134]
Antibacterial paper	NCC/CNF	Ag NPs	Antibacterial activity specific to bacteria	[135–137]

number of hydroxyl groups on the surface of pulp fibers with a negative charge leads to the physicochemical interaction and electrostatic attraction between CNFC and pulp fibers, which further increase the strength of the bond between fibers, while the electrostatic repulsion occurs between ANFC and pulp fibers because of their negative changes, resulting in a reduction in the bond strength between fibers. Therefore, CNFC-reinforced paper exhibits better tensile properties compared to ANFC-reinforced paper.

4.6 NC in antibacterial paper

The surface of NC is rich in hydroxyl groups, high aspect ratio, and other characteristics, which endow it with high water retention ability and stability, and can be well cross-linked with cellulose. NC can also be used as a carrier to adsorb antibacterial agents on the fiber to make antibacterial materials [135]. NCC prepared from bagasse pulp and antibacterial chitosan was used as a coating agent to coat the surface of the paper for the production of antibacterial papers. Polyelectrolytes have been used to electrostatically assemble Ag-NP onto NFC to prepare antibacterial NFC/Ag nanocomposites, which were then used for paper coating formulations to prepare paper with antibacterial properties. NC and zinc oxide were also attempted to compound the antibacterial paper, resulting in an improved air permeability and mechanical properties [135,136].

Incorporating nano-fillers, such as NC and silver nanoparticles, into biopolymers can not only improve mechanical properties and barrier properties, but also facilitate other functions, such as antibacterial activity, biosensing, and oxygen removal properties. PVA is a biodegradable biopolymer with chemical resistance, high crystallinity, and film-forming and hydrophilic properties [137]. A biodegradable nanocomposite film for antibacterial food packaging, consisting of PVA, NFC, starch-terminated silver nanoparticles (Ag NPs), and glycerin, has been proposed, and the study on its physical, mechanical, thermal, and antibacterial properties showed that the nanocomposite membrane had strong antibacterial activity against *Staphylococcus aureus* (MRSA) and *Escherichia coli* (DH5-alpha) [138].

4.7 Evaluation of materials for functionalized NC

In summary, NC plays an important role in the manufacturing of specialty papers. The NC could be functionalized to achieve various specific properties for various specialty papers depending on the modifications made (Table 4). The specialty paper industry has also been facing challenges in recent years, such as from the environment, energy, raw materials, markets, macroeconomics, the new economy and technology, and other aspects of the impact and challenges. Most of the specialist papers are facing an upward trend of prices. While it can be recognized that the demand for paper products is stringent, further enhanced functionalization is highly required.

5 Conclusion

NC and its derivatives have been widely studied as additives in papermaking with its superior performance. It has broad prospects in terms of strengthening the paper, increasing the retention rate of fine fibers, and improving the barrier properties of paper as a coating agent. Inherent hydroxyl groups make NC favorably combine and crosslink with pulp fibers, endowing paper and paper products with some superior properties. Addition of NC additives could significantly increase the tensile strength of paper; as a paper retention aid, reduce the loss of fine fibers; as a paper filter aid, improve the drainage performance of papermaking; and as a paper coating agent, provide barrier properties for paper products. NCs have also showed most promising functionalities in specialty papers, *e.g.*, the waterproof paper, fresh paper, insulation paper, blotting paper, and wrapping paper. While the efficiency of NC on its own was in some cases insufficient and the addition of NC could cause the water filtration performance of paper to deteriorate, complex interactions have been proposed between cellulose pulp, CNF, mineral fillers, and various additives to maintain or even improve the performance. Advances in NC additives have signified enormous potential for value added development in papermaking and specialty functionalities, and this review provides important database to serve further innovation and applications of paper and paper-based products.

Specialty paper is a high yield/low cost product that requires further innovation in specialty paper products, technologies, and models to improve the added value of products, thereby improving overall competitiveness and ultimately breaking the limitations of the specialty paper industry. With the development of economy and society, the performance and use of materials will continue to produce many new performance special paper needs. Papers, which are important materials for writing, printing, packaging, information, electrical and other high-tech industries, will certainly continue to innovate and expand. The price of CNF, which is not yet fully commercialized, will determine whether the prospect of its application on paper can be put into practice. The challenge in this case is the total production cost of CNF, including energy, chemical costs, and investment in production equipment as well as investment in paper machines. In addition, both CNF production and paper machine operability are a challenge and, at least in some cases, increased drying costs must be anticipated. Selecting the right CNF quality for the intended application is also important to optimize CNF functionality and production costs according to product requirements.

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