Chapter 11
Nanocellulose in High-Value Applications for Reported Trial and Commercial Products

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Abstract Despite abundant academic studies reported their diverse applications (as discussed in previous chapters), the practical products of nanocellulose are launched only during recent five years by several companies. In view of most cases concerning nanocellulose-based products, this chapter first summarizes the scale-up production of two types nanocelluloses, cellulose nanofibrils and cellulose nanocrystals all over the world. The introduction of various nanocellulose commercial products is based on its properties and functions, including the high mechanical strength and rigidity for composite additives, water retention for personal care products, rheological modification for writing ink, adsorption and barrier for paper and packaging application. It is unfortunate that some critical information and parameters of processing techniques and products can't be obtained because of the confidential consideration of some companies. However, the commercial products of nanocellulose (particularly in the cases of cellulose nanofibrils) introduced in this chapter can inspire the future commercialization of these renewable nanomaterials for the development of competitive commodity in industry.

Keywords Cellulose nanocrystals · Cellulose nanofibrils · High-value application · Commercial products

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11.1 Scale-up Production of CNC and CNF

11.1.1 Worldwide Companies for CNC and CNF Production

Two important factors promote the commercial production of nanocellulose, concerning on non-renewable fossil resources and environment issues of synthesized polymers. With the global attention to the depletion of non-renewable resources such as oil, coal, natural gas and global environmental warming, nanocellulose as the renewable biomass resource, is expected to be transformed and utilized in our daily consumer good. In fact, plentiful academic research reported the remarkable advantages of nanocellulose in packaging barrier materials, high-performance composite materials, food and cosmetic additives, electronic products, biomedical materials, etc., which further drives the interest of global scale-up production of nanocellulose.

The reported commercial production of nanocellulose generally includes two types, viz. the rod-like cellulose nanocrystals (CNC) and semi-flexible cellulose nanofibrils (CNF). Despite the fact that numerous academic studies reported the preparation of CNC with the hydrolysis of inorganic acids [1], organic acids [2], enzymes [3] and deep eutectic solvents (DES) [4], the sulfuric acid hydrolysis to native cellulose is the prevailing method for CNC production in both laboratory and industry. In comparison with the other methods, the sulfuric acid hydrolysis is high efficiency (40–70% yield in 1–2 h), good reproductive, low-cost and can obtain the stable CNC product (surface negative charges) with a narrow size distribution and good dispersion stability. The preparation of CNF mainly adopts the methods of mechanical treatment such as high-pressure homogenization [5], ultrafine grinding [6] and microfluid method [7]. However, different conditions of mechanical treatments result in the wide scales of produced CNFs with 5–100 nm diameters and 1–100 μm lengths. It should be mentioned that the preparation of CNF generally includes a pretreatment process with the purpose of reducing the energy consumption, such as TEMPO oxidation [8], carboxymethylation [9] and enzymatic hydrolysis [10].

Since the first report on the commercial production of CNC by CelluForce company in 2011, the industrial technology on nanocellulose production was gradually advanced from laboratory to industrialization in order to obtain the high output at low cost. The scale-up production and pilot plants of CNC and CNF have been established in global companies, as summarized in Tables 11.1 and 11.2. Based on the traditional theory of strong acid hydrolysis to release CNCs, some companies invented the novel techniques to increase the yield and reduce the energy consumption. Canada's Blue Goose Biorefineries Inc. reported the transition metal catalyzed oxidation of lignocellulosic biomass to increase the CNC production. This technique is similar as pulp bleaching with material handling common in food production, taking the high quality and yield of the reported CNC production (10 kg/d). Compared with the traditional sulfuric acid hydrolysis, the reported CNC production by this process has no sulfonic group on CNC surface. Regarding the scale-up production

Table 11.1 Major industrial manufacturers of CNC in the world

Country	Region	Company	Reported capacity	Ref.
Canada	Windsor, Quebec	CelluForce	300 ton/y	[11]
	Calgary	Alberta Innovates (AITF)	100 kg/d	[12]
	Saskatoon	Blue Goose Biorefineries Inc.	10 ton/d	[13]
	Quebec	FPInnovations	10 kg/w	[14]
USA	–	American Process Inc.	–	[15]
	Madison	USDA-Forest Service-Forest Products Laboratory (FPL)	–	[16]
Sweden	Örnsköldsvik	MoRe Research	–	[17]
Israel	Rehovot	Melodea Ltd.	–	[18]

of CNF, Norwegian Borregaard reported the world's largest commercial-scale production facility for MFC (Exilva) production from Norwegian spruce in 2016, with a capacity of 10,000 tons suspension and 10% concentration (1000 tons dry weight). The commercial interest on CNF production is attracted by Japan's paper industry, including the Daio Paper, Sugino Machine, Chuetsu Pulp & Paper, Nippon Paper Industries, Oji Holdings and many other companies reported their pilot plants of CNF production. The Nippon Paper Industries is the largest paper company in Japan and reported the capacity of 500 tons/y of CNF production to meet the needs of research institutions and downstream companies.

According to the data listed in two tables, the number of CNC production companies worldwide is relatively small compared with CNF production companies. Furthermore, due to the relative high production cost and policy restrictions, the commercial production of CNC and CNF is mainly concentrated in North America, Europe and Japan. A possible reason for more popularity of CNF production than CNC production in industrial may be the different processing techniques. The relative complicated production process of CNC production and special production equipment (use of toxic and corrosive strong acid) may increase the cost and restrict the large-scale production of CNC. As a contrast, the mechanical treatment to produce CNF receives less pressure of environmental protection and equipment requirement than those of CNC production. It is worth noting that the advancement of scale-up production also promotes the commercialization of nanocellulose-based products in these regions, which will be discussed in the next section.

Table 11.2 Major industrial manufacturers of CNF and related products in the world

Country	Region	Company	Product (Brand)	Reported capacity	Ref.
Canada	–	Performance BioFilaments, Inc.	Cellulose filament	–	[19]
	Toronto	GreenCore Composites Inc.	CNF (NCell™)	–	[20]
USA	Atlanta	American Process Inc. (AVAPCO)	CNF	–	[15]
	Wisconsin	USDA-Forest Service-Forest Products Laboratory (FPL)	CNF	–	[16]
Norway	Sarpsborg	Borregaard	MFC (Exilva)	1000 ton/y	[21]
Sweden	Stockholm	InnventiaAB	Nanocellulose	100 kg/d	[22]
Finland	–	UPM-Kymmene Ltd.	Cellulose fibres	–	[23]
	Helsinki	Stora Enso Ltd.	MFC	–	[24]
	–	VTT	CNF	–	[25]
UK	–	ZelfoTechnology GmbH	NFC	–	[26]
	–	CelluComp	CNF (Curran)	–	[27]
France	–	InTechFibres	MFC	–	[28]
Germany	–	J. Rettenmaier & Söhne GmbH	CNF	–	[29]
Netherlands	Sittard-Geleen	Sappi	CNF	–	[30]
Japan	Tokyo	Dai-ichi Kogyo Seiyaku Co., Ltd	CNF	–	[31]
	Mishima	Daio Paper	CNF	100 ton/y	[32]
	Toyama	Sugino Machine	CNF (BiNFi-s)	1 ton/d	[33]
	Sendai	Chuetsu Pulp & Paper	CNF (nanoforest)	100 ton/y	[34]
	Ishinomaki	Nippon Paper Industries	CNF (cellenpia)	500 ton/y	[35]
	Tomioka	Oji Holdings	CNF	30 ton/y	[36]

11.1.2 Typical Cases of Scale-up Production for CNC and CNF

With the change from laboratory to commercial production of nanocellulose, the production condition and key equipment are important factors to affect the quality of products. In the CNC commercial production, the hydrolysis conditions need to be strictly controlled, including the factors of feedstock sources, hydrolysis duration and temperature, acid type and concentration, feedstock to acid ratio and mixing conditions. Optimizing the conditions can effectively increase the yield, reduce the cost, and obtain the products with the narrow size distribution and stable properties of CNC production. In the case of InnoTech Alberta's pilot plant (Canada), the acid hydrolysis is reported to occur in the reactor, where 110–155 kg of 63.5 or 64 wt% H_2SO_4 is pumped into the reactor from the acid storage tank. Sulfuric acid is then stirred at 200 rpm and heated up to 45 °C by low-pressure steam. Then, 10–13.5 kg of raw feedstock (bleached softwood or hardwood kraft pulps) is added into the reactor and reacts at this stirring speed for 2 h. After the reaction, 50 kg of water is pumped into the reactor to quench the acid hydrolysis reaction. The hydrolysate mixture is then transferred from the reactor to a 7500 L storage tank containing approximately 1200 kg of water to complete the reaction quenching, and finally neutralized by the slow addition of sodium hydroxide solution. In order to ensure the quality of CNC product, it is necessary to rapidly purify the hydrolyzed mixture, and the separation treatment (centrifugation) is the first step of the purification treatment. In this process, a centrifuge was reported to be used with a speed of 6500 rpm to separate the produced CNC from acid solution. After centrifugation, the CNC appears as a viscous paste-like solid, and the resulting centrifuge liquid (containing diluted H_2SO_4 solution) is sent to the spent acid treatment center for recycle. The paste-like CNC is sent to a storage tank, and diluted with 1500 L of water to produce the homogeneous and stable suspension. This CNC suspension is pumped back into the centrifuge for the water washing purification to remove high molecular weight cellulosic materials, large particles, dirt and unreacted materials. The purified CNC product is treated again as the aqueous suspension, and followed the second purification by ultrafiltration system to remove any sodium sulfate, glucose, oligomers and other impurities in the suspension. After the concentration to 3 wt%, the CNC suspension is dried into a powder. In this process, three key equipment viz. the reactor for hydrolysis reaction, the centrifuge for purification, and the dryer for CNC powders should be noted. In fact, the hydrolysis conditions and steps for the CNC production in industry is similar as those in the laboratory research. However, the equipment requirement is more rigid due to the large quantity of reactants. In the InnoTech Alberta's pilot plant for CNC production, the Pfaudler 50-gallon glass-lined reactor is used for the acid hydrolysis, and the GEA Westfalia SC-35 disk stack centrifuge is used for the solid-liquid separation. Regarding the last drying step, the spray drying (spx-anhydro ms-400 spray dryer) is used to remove water from some materials up to 37 kg per hour, which is one of the most widely used drying technologies in the food industry [37].

Several industrial CNC products are shown in Fig. 11.1. Specifically, the CNC product from CelluForce company is obtained by H_2SO_4 hydrolysis of wood pulp, and exhibits a nominal average length of 150 nm and a nominal average diameter of 7.5 nm with the nominal aspect ratio of 20 (image A). Another industrial CNC product prepared by Blue Goose Biorefineries Inc. using the transition metal catalyzed oxidation of lignocellulosic biomass have the similar morphology and dimensions (100–150 nm length and 9–14 nm diameter) as that of H_2SO_4 hydrolysis (image B). The InnoTech Alberta company produced the spray-dried CNC powders with a good re-dispersion to save the storage and transportation costs (image C).

The commercial production of CNF is concerned with the strong mechanical treatment, with the equipment of high-pressure homogenization, mechanical grinding, water jet [38] or microfluid processing to treat the purified cellulose fibers. The basic mechanism during these treatments is the introduction of high-energy process to destroy the interaction between cellulose chains and peel off cellulose

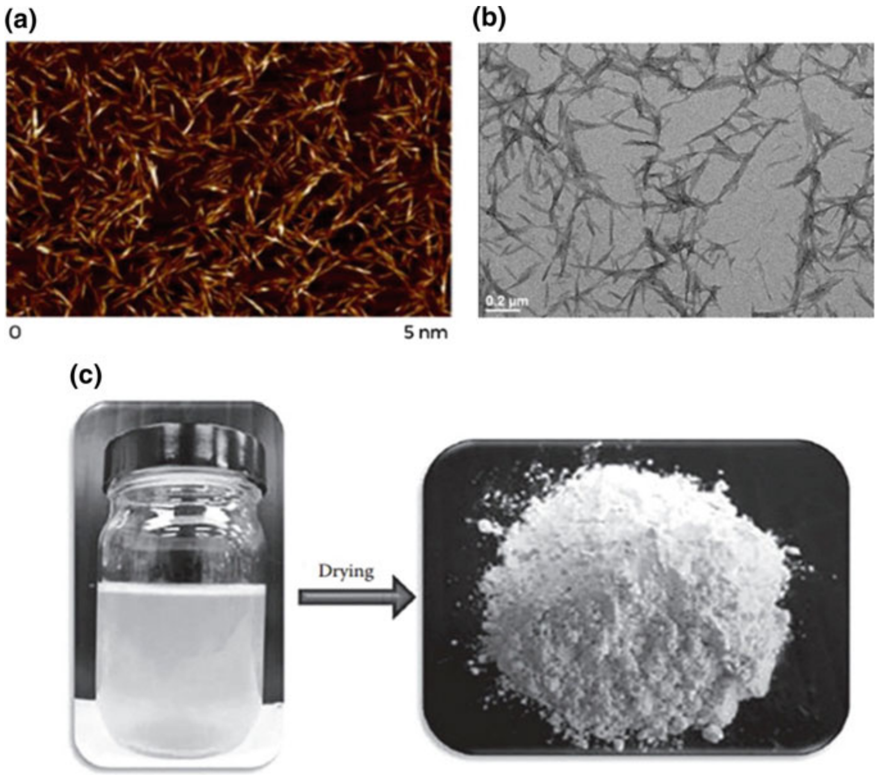

Fig. 11.1 **a** AFM image of CNC product from CelluForce company (reproduced from [11]); **b** TEM image of CNC product from Blue Goose Biorefineries Inc. (reproduced from [13]); **c** photos of CNC aqueous suspension and spray-dried powders from InnoTech Alberta company (reproduced from [37])

chains to obtain the nanoscale CNF products. In the case of MKZA10-15JIV supermasscolloider ultra-fine grinder produced from Masuko Sangyo co., Ltd. (Japan), the supermasscolloider ultra-fine grinders feature two ceramic nonporous grinders, which are adjustable at any clearance between the upper and lower grinder. Setting grinder clearance is important because it determines grain size, or the quality of products. The handle left and right rotation can be adjusted, with 1/100 mm gap up and down to adjust the clearance of the grinders. The porosity of traditional grinders is about 40%, and these pores will promote the growth of numerous bacteria, and may also cause cracks of grinder due to uneven heat distribution or thermal stress. The Supermasscolloider have nonporous grinders solves these problems completely, there is no growth of bacteria and no crack due to thermal stress. Meanwhile, the grinders have a 250 mm diameter and unique geometric geometry, which ensures an intensive dispersing effect and defibrillation of fibers by applying compression, circulation and abrasive shear forces. When using this equipment to prepare CNF, the fibers slurry (wood pulp, cotton, bamboo, etc.) was first soaked at 2% consistency and adequate mixing. The suspension was then fed into the supermasscolloider ultra-fine grinder, the feedstocks were passed 3–5 times through the grinder using gap width increasing operating power. The rotation speed was fixed at 1300 rpm in the first pass and at 1500 rpm in the following passes. The quality of the fibrillated cellulose was controlled by moving the lower grinder to set the clearance between the grinders. The fiber suspension was subjected to compression and shear forces between the grinders, which determined the particle size of the output material. The yield of the final product is 95% after the feedstock is treated by Masuko supermasscolloider ultra-fine grinder for 3–5 passes and the energy consumption during refining was 20.9 MWh/t [39–41].

Attributed to the strong hydrogen bonding interaction between cellulose chains, the scale-up CNF production by mechanical processes generally requires much energy and therefore results in the high costs. A high-efficiency approach to reduce the energy consumption during the industrial CNF production is the development of chemical pretreatment to the feedstock, and then followed by the mechanical treatments. Currently, the pretreatment methods of cellulose feedstock are reported to be the TEMPO oxidation, carboxymethylation, cationation, acetylation, phosphorylation, sulfonation, enzymatic hydrolysis, and the TEMPO oxidation pretreatment is widely used in both laboratory and industrial CNF production. In fact, performing the TEMPO oxidation pretreatment, the negative charges are introduced on the surface of cellulose fibers, and therefore the hydrogen bond interaction between cellulose chains can be reduced by repulsive effect from the introduced charges, which promotes the disintegration of aggregated nanofibrils. Furthermore, the pretreatment to the cellulose feedstock can make the cellulose less prone to flocculation, and more conducive to be peeled of chains, accompanied by the reduction of energy consumption and blockage risk for the equipment during the mechanical process. The UPM-Kymmene Ltd. (France) reported the different appearances and size distributions of prepared CNF by several techniques [42]. As shown in Fig. 11.2, the hardwood kraft pulp is treated by the supermasscolloider and microfluidizer with or without the TEMPO oxidation or carboxymethylation pretreatment to produce the CNF. It is apparent

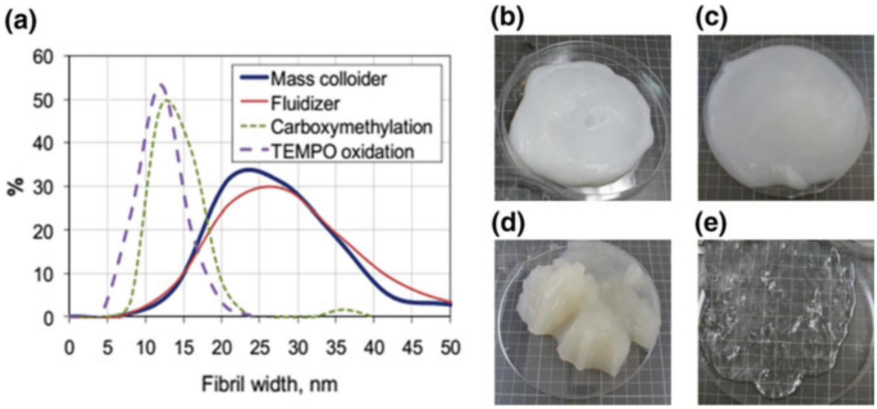

Fig. 11.2 The CNF fibril products from UPM-Kymmene Ltd. (France): width distribution (**a**) and appearances of products prepared by masscolloider (**b**), fluidizer (**c**), carboxymethylation pretreatment (**d**) and TEMPO oxidation pretreatment (**e**). Reproduced from [42]

that the CNF products prepared by the pretreatment have the smaller nanofibrils diameter (2.5–25 nm) and narrower diameter distribution than those CNFs produced only by mechanical processes (5–50 nm diameter). Furthermore, the CNF product prepared by the TEMPO oxidation pretreatment is more transparent than that of carboxymethylation pretreatment due to the additional surface charges.

11.2 Reported Products of Nanocellulose as Mechanical Enhancement

Derived from its superior mechanical property with specific modulus 4–5 times higher than steel, nanocellulose has been proved the promising nanofiller for various matrices with the purpose of enhancing their mechanical performances. In fact, some research institutes and experts regard the mechanical enhancement of nanocellulose as its most potential property for the commercial applications. Many academic attempts and studies have reported the use of this light-weight and high-strength nanomaterial as reinforcing nanofiller, and proposed the critical factors of composition, processing, compatibility and interfacial adhesion to determine the resultant properties of nanocellulose-enhanced composites [43]. In most of cases a chemical modification on nanocellulose is necessary to regulate its surface properties for the improvement of compatibility with hydrophobic matrix. However, these chemical treatments are generally complicated and high-cost, and therefore only several commercial products on nanocellulose in this application are reported.

The ASICS company (Japan) released the first-ever shoe containing CNF as reinforcing fillers (GEL-KAYANO™) in 2018 for the improvement of long-distance running performance [44], as shown in Fig. 11.3. This new shoe is reported to

Fig. 11.3 The product of running shoe GEL-KAYANO™ 25 with the reinforcement of CNF in midsole from Japanese ASICS company. Reproduced from [44]

use a foamed material FlyteFoam™Lyte1 in the midsole containing the surface hydrophobized CNF to offer extra mechanical reinforcement. The introduction of modified CNF into the elastomer matrix can effectively improve the tensile strength and Young's modulus of the composite, and achieve a simultaneous strengthening and toughening effect for the foamed composite. In comparison with those of the unfilled FlyteFoam material developed by ASICS, the mechanical strength and durability of new FlyteFoam™Lyte material reinforced by modified CNF are reported to be enhanced by approximately 20 and 7%, while keeping the lightweight for the application in midsole.

Nanocellulose could potentially replace some of the synthetic fiber composites with a natural and renewable alternative. In 2018, the Ideas2cycles company (Finland) produced the world's first bicycle with the mechanical enhancement of CNF to fabricate the frame in order to partly replace the synthetic fiber and enhance the overall performance of the bicycle [45]. As shown in Fig. 11.4, this company develops a technology and process to build up the CNF layer on a mandrel and further used for the manufacture of tubes. The tubes are then cut and mitered to the desired

Fig. 11.4 The product of bonded joints containing CNF in the assembled bicycle from Finland Ideas2cycles company. Reproduced from [45]

length, and further adhesively bonding the tubes at correct angles with the help of 3D-printed fixtures. The bonded joints are reinforced by laminating carbon fiber on top (overmoulding). The laminate is cured in a vacuum bag and the smooth outer surface is achieved with the help of 3D-printed moulds. Finally, a clear coat was applied on the surface and the bicycle was assembled using standard components.

The Green Science Alliance Co., Ltd. (Japan) launched a nanocomposite called "Nano Sakura" for the purpose of ultimate environmentally friendly material [46]. The composite material is prepared from nanocellulose enhancement and various type of resins including biodegradable resins and thermoplastic plastics. This new generation of composites hold the necessary mechanical strength to meet the practical application and is reported as the truly sustainable and recyclable materials (Fig. 11.5). This company attempts to the combination of nanocellulose with four kinds of matrices to produce the novel composites. (i) Biodegradable materials. Based on its biodegradability, nanocellulose is used to enhance the biodegradable resins to make disposable products such as food tray, food containers, beverage container, straw, cutlery etc. (ii) Conventional synthetic materials. Molding products of mechanical strength will be stronger with lighter weight from nanocellulose enhancement so that application can expand to various type of purpose including automotive, construction material, film, container etc. In addition, gas barrier property, crystallinity, dimensional stability will be improved as well as low thermal expansion. (iii) Recycle materials. This category of material is made by mixing nanocellulose and thermoplastic waste with the applications of film, container, home electrics, automotive, construction. (iv) Hybrid materials. This material is composed of nanocellulose, biodegradable resins and inorganic materials such as calcium carbonate ($CaCO_3$).

The bottom plate of the table tennis racket is made of multi-layer plywood with adhesive to improve the softness and comprehensive performance of the racket. However, the addition of the traditional adhesive will make the feel of the racket hitting the ball hard, and the ball stretch will disappear after hitting the ball, that is the efficiency of the fly-in speed converted to the ball by the racket is reduced. In order to eliminate this shortcoming, Darker company (Japan) reported the "Sakura"

Fig. 11.5 The products of "Nano Sakura" polymeric masterbatch containing nanocellulose: CNF PLA composite (PLA + 23% of CNF, composite) (**a**), CNF color masterbatch (PLA + 23% of CNF + yellow pigment 25%, composite masterbatch) (**b**) and related commodities (mold product composed of PLA + 2% of CNF) (**c**) from Green Science Alliance Co., Ltd. Reproduced from [46]

Fig. 11.6 The product of table tennis bats with the "Sakura" containing nanocellulose as adhesive from Darker company. Reproduced from [47]

[47] as a binder for the racquet bottom plate, using the light weight and high strength of nanocellulose to eliminate the adverse effects of the adhesive on the table tennis racket (Fig. 11.6).

As discussed before, the development of nanocellulose as the reinforcing filler to enhance the mechanical properties for the composites is widely expected to be the most prospective application in industry, particularly if only considering its superior mechanical properties. However, the practical application of nanocellulose as the mechanical reinforcing filler for the composites is not widely accepted by the industry like the commercial glass fiber, Kevlar fiber and inorganic additives. Several basic issues may restrict the practical enhancing effect of nanocellulose in the development of commercial products, involving the dispersibility and compatibility of nanocellulose with matrices, costs of processing and modification, and trade-off between different enhancing effects on strength, modulus and toughness.

11.3 Reported Products of Nanocellulose as High-Rigidity Component

Nanocellulose is a kind of typical rigid nanomaterial with the complete removal (CNC) or partial removal (CNF) of amorphous regions of cellulose chains, and therefore the high crystallinity and rigidity are their intrinsic features. Generally, the crystalline index and longitudinal modulus of CNF are reported as 60–80% and 100 GPa, which are even higher for CNC as 80–95% and 130 GPa [48]. This special physical property allows nanocellulose to be applied in the acoustic equipment, such as the diaphragm for headphone and audio speaker. As the sound unit of the headset, the diaphragm is very sensitive to the change of the magnetic field. When the electrical signal passes through the coil, the magnetic field changes, causing the diaphragm to deformation change under force. Meanwhile, the rapid change of electrical signal will cause the diaphragm to vibrate at high speed; thus, the vibration is transmitted to the air through the vibration of the diaphragm, and sound waves are generated. The quality of the diaphragm determines the overall quality of the headphone. Therefore, the design of the diaphragm is required to be lighter in weight and better in rigidity. Such a diaphragm can completely convert the kinetic energy of the coil into sound. Nanocellulose is an ideal material for the preparation of diaphragm due to its light weight and high rigidity. As shown in Fig. 11.7, the Onkyo company (Japan) invented the world's first audio speaker "SC-3(B)" using the CNF diaphragm [49]. "SC-3(B)" is reported to be equipped with the "non-press ONF (Onkyo Nano Fiber)" vibrator plate which is the rigid nanomaterial developed by CNF. With the addition of CNF, this CNF-based diaphragm is both powerful and low-gravity, to achieve good bass playback, reproduce the shock of live performance, with the sense of air for players and the venue.

Another Japanese corporation "Pioneer" launched a headphone "SE-MONITOR5", using the lightweight but high-strength CNF as the diaphragm component (Fig. 11.8) and edge free structure providing users with a better auditory experience. The CNF-based diaphragm headphones developed by "Pioneer" have independently developed a driver with a diameter of 50 mm that supports broadband

Fig. 11.7 The product of audio speaker "SC-3(B)" containing the CNF diaphragm from the Onkyo company (Japan). Reproduced from [49]

Fig. 11.8 The product of headphone "SE-MONITOR5" containing the CNF diaphragm from the Pioneer corporation (Japan). Reproduced from [50]

playback of high definition audio sources (5 Hz–85 kHz) and clear audio images, allowing the headphones to bring in fine and detailed sound quality [50].

11.4 Reported Products of Nanocellulose as Water Retention Additives

Nanocellulose is a type of nanoparticles derived from natural cellulose, possessing abundant hydroxyl groups in the structure, and therefore the water molecules can be locked inside the formed hydrogen-bonding network by nanocellulose. The good biocompatibility and low toxicity together with the super moisturizing property endow the nanocellulose with a potential moisturizing ingredient in cosmetics and skin care products. In 2017, the Asia NanoTech company (Korea) announced a new series of whitening cosmetic with the addition of the palm tree extracted CNF [51], as shown in Fig. 11.9. These products are reported to have a much more longer moisturizing effect, safer on skin and a competitive price than others. The CNF is regarded to be safe for human body, and easy to penetrate the skin with the excellent moisturizing performance. Furthermore, the introduction of 10 nm CNF in these cosmetics is reported to maintain the skin physiological activity for a long time, disperse moisture and nutrition composition equably at the same time, and therefore exhibit an excellent effect on skin protection. After the addition of CNF, the moisture content of these cosmetics can be kept at 30–40% for 24 h, in comparison with only 2–4% moisture retention for the traditional products made from collagen or hyaluronic acid.

The Japanese Koyo Kasei Co., Ltd. reported three styles of cosmetics (ingredient gel, cream and water) using rose essence and CNF (provided by the Nippon Paper company) as the moisturizing ingredient [52], as shown in Fig. 11.10. These products containing hydrophilic CNF components are reported to be effective to enhance the moisturizing property easily absorbed by the skin to lock the water molecules.

The FABULA company (Taiwan) released their latest facial mask product—"Bio Fiber Nanocellulose Mask" (Fig. 11.11), which was made from nanocellulose with a diameter of about 20 nm, a hundred times smaller than the fiber of traditional nonwoven fabric. This mask was reported to be composed of nanocellulose fermented

Fig. 11.9 The series cosmetics products using CNF as the moisturizing ingredient from the Asia NanoTech company (Korea). Reproduced from [51]

Fig. 11.10 The three cosmetics products of "rose fragrance gel", "rose body & hand cream", and "rose skin water" using CNF as the moisturizing ingredient from the Koyo Kasei Co., Ltd. (Japan). Reproduced from [52]

Fig. 11.11 The product of "Bio Fiber Nanocellulose Mask" from the FABULA company (Taiwan). Reproduced from [53]

by microorganisms containing various face essence with the function to bleach, tranquilize the skin and eliminate wrinkles. The good hydrophilic and water retention of nanocellulose endow this mask with 200 times more moisture retaining than typical nonwoven mask. Attributed to the nanosized fiber and large specific surface area, it was reported that this nanocellulose-based mask can infuse 50% more nutrition essence, and deeply penetrate to skin's pore, grasp skin and moisture and not drop off. The three-dimensional network formed by the hydrogen bonds from nanocellulose can provide the extra tiny aperture for holding the water molecules and slowly evaporation of the essence. Moreover, the FABULA nanocellulose-based mask was reported to remove 49% of sebum (skin's natural oil) after applying the mask for 20 min, and also possess good air permeability to provide the protection for injured skin [53].

11.5 Reported Products of Nanocellulose as Rheological Modifier

Cellulose and its derivatives are widely used as rheological thickeners with regulating thixotropy behaviors in many applications. Different from the native cellulose, nanocellulose have some unique rheological properties, which can be used as a novel rheology modifier to regulate the rheological behaviors of fluids by the change of its loading level, size distribution and temperature [54]. Typically, with the increase of the concentration, the nanocellulose suspension exhibits varied rheological behaviors as the liquid crystal polymer solution. Moreover, the shear rate significantly affects the viscosity of the nanocellulose suspension. It has been reported that at low shear rates, the viscosity of the nanocellulose suspension decreases with the increase of shear rate, indicating its shear thinned behavior at this stage. However, at high shear rates (above the critical shear rate), the viscosity of the nanocellulose suspension increases with the increase of shear rates.

A novel gel ink ballpoint pens using the oxidized CNF as the ink tackifier is released by the Mitsubishi Pencil Co., Ltd. (Japan) [55]. The viscosity of composite ink is reported to be reduced by about 50% compared with the traditional products, and even if writing quickly there will be no instability problem (as shown in Fig. 11.12). In the developed aqueous ink composition, the introduced oxidized CNF provides a high viscosity even at a low viscosity of 0.05–1.5 wt% and the composite inks show the high thixotropy index. The introduction of oxidized CNF exerts a rheology controlling effect as a thickener and gelling agent for the aqueous ink compositions in a smaller amount than those of a conventional fine cellulose (carboxymethyl cellulose) and xanthan gum.

In the aqueous ink composition, the content (solid content) of the oxidized CNF is optimized as 0.05–1.5 wt%, preferably 0.1–1.0 wt% based on the total amount of ink. If the content of CNF is less than 0.05 wt%, the satisfactory thickening action cannot be obtained, and meanwhile the solid matters such as the pigment will settle down in some cases. On the other hand, if the content of CNF exceeds 1.5 wt%, the viscosity of composite ink grows much high, and therefore a splitting phenomenon of the drawn lines and inferior discharge of the ink will appear. Another important component for this composite ink is the sugar's additive. The sugars (non-reducing sugars, particularly sugar alcohols) having an average molecular weight of 5000 or less used in the aqueous ink composition are a component which inhibits time-dependent heterogeneity (difference in viscosity between up- and down-sides) in viscosity distribution. The content of sugar should be ranged from 0.001 to 30 wt%, preferably 0.01–10 wt% based on the total amount of the aqueous ink. From the

Fig. 11.12 Gel ink ballpoint pen uni-ball "Signo 307" developed by the Mitsubishi Pencil Co., Ltd. (Japan) using CNF as the ink tackifier; and the pictures of lines drawn by the conventional product and uni-ball Signo 307. Reproduced from [55]

viewpoint of dispersion stability, the oxidized CNF has more preferably a number average fiber diameter of 3–80 nm. Controlling a number average fiber diameter of the oxidized CNF to 2 nm or more makes it possible to allow the oxidized CNF to exert a function of a dispersion medium, and on the contrary, controlling the number average fiber diameter to 150 nm or less makes it possible to further enhance dispersion stability of the cellulose fibers themselves [56, 57].

11.6 Reported Products of Nanocellulose as Adsorption Materials

The features of high aspect ratio and specific surface area of nanocellulose endow its good air permeability and strong adsorption performance based on the formed three-dimensional and porous network structure by the intertwining of nanofibers, which can be applied to the functional paper, disposable diapers and other daily necessities. In 2015, the Nippon Paper Industries Co., Ltd. (Japan) developed the "Hada Care Acty" series of adult diapers containing CNF (Fig. 11.13), exhibiting some functions of absorbing metal ions, deodorizing and sterilizing properties. It was reported that this kind of CNF-based diaper held three times of deodorizing effect in comparison with the traditional adult diapers [58]. Meanwhile, this diaper has the antibacterial performance, superior water absorption and good air permeability, which provides the better user experience than the traditional products.

Fig. 11.13 The product of adult diapers containing CNF from the Nippon Paper Industries Co., Ltd. (Japan). Reproduced from [58]

Another Japanese company Daio Paper Corp. reported the combination of CNF with pulp fibers to produce the functional paper toilet cleaner [59]. The CNF prepared from wood are tightly entangled with the pulp fibers, and provides two times mechanical enhancement to this paper toilet cleaner than that of the ordinary paper. Furthermore, this new CNF-based toilet paper also exhibits the deodorization and bacteriostasis under the premise of meeting basic cleaning requirements (Fig. 11.14). It was reported that one such paper toilet cleaner can make the whole toilet clean. In order to meet the various needs of consumers, the company recently launched some

Fig. 11.14 The product of functional paper toilet cleaner containing CNF from the Daio Paper Corp. (Japan). Reproduced from [59]

advanced products with the pure fragrance, rose, perilla, lemon and other fragrance paper toilet cleaner.

11.7 Reported Products of Nanocellulose as Packaging and Barrier Materials

With the advantages of lightweight, high-strength and nontoxicity, nanocellulose is a promising candidate for the preparation of lighter and stronger packaging materials. In order to replace the non-renewable materials, the Stora Enso company (Finland) launched its new packaging product prepared by microfibrillated cellulose (MFC) reinforced cardboard, which was reported to be widely used in fast-food packaging, liquid packaging (milk cartons, as shown in Fig. 11.15), barrier coating films etc. The Stora Enso company is supporting Canadian Elopak with renewable innovations on the New Natura Concept (NNC) mainly based on MFC, aiming to make packaging as light as possible [60]. By converting a small portion of wood pulp to MFC and mixing it into the composite, it can make paperboard with the same strength, opacity and brightness but use less original fibers. Therefore, the introduction of MFC allows for the stronger composites, weight saving and renewability. In addition, the introduction of MFC as the enhancing fillers for the folding box board can increase its bending strength, which can make a stronger board or reduce the package's total weight. According to the report of this company, the MFC can also create coatings and films featuring excellent barrier properties to preserve aromas and to protect against gases like oxygen, and even grease and oil. Besides the mechanical enhancement of MFC,

Fig. 11.15 The lightweight packaging product containing MFC for the storing of milk and beverage from the Stora Enso company (Finland). Reproduced from [61]

the barrier films fabricated by this nanomaterial exhibited the remarkable reduction of metals, CO_2 footprint and bacterial in stores of food and beverage products [61].

11.8 Concluding Remarks

The inherent properties of a substance determine its potential applications. The numerous advantages of renewability, nontoxicity, good biocompatibility and biodegradability together with the lightweight, high modulus and specific surface area make nanocellulose as a type of promising nanomaterial to replace traditional inorganic and metal particles in various applications, particularly with the requirement of environmental protection. Despite the fact that abundant academic studies reported diverse potential applications during last twenty years, the commercial products of nanocellulose were really developed until recent five years. As discussed in this chapter, some companies are very interested in these natural nanomaterials, and have attempted various applications based on the properties of nanocellulose as the mechanical and rigid enhancing fillers, water retention additives, liquid rheological modifier, adsorption and barrier components. Regarding the family of nanocellulose, the industrial interests on cellulose nanofibrils (CNF) are much higher than cellulose nanocrystals (CNC), which may be resulted from the relative low-cost and green preparation techniques of CNF than the strong acid hydrolysis for the preparation of CNC. Although several practical products on nanocellulose have been launched by some companies, the challenges still remain until the wide applications of these renewable nanomaterials in the development of competitive commodity. (i) A more high-efficiency, economical and "green" production technique of nanocellulose is required by the industry, which is strongly associated with the cost of prepared nanocellulose and price competition of the resultant products. One theory from the nanocellulose industry is the cost of commercial CNF should be controlled as 2–3 and 8–10 $/ton for commercial CNC, which can be competitive as other similar products. (ii) The exploration of new functional properties of nanocellulose is demanded to create the high added-value for the related products. In comparison with the traditional polysaccharide-based commercial derivatives and synthesized polymers, the new functional properties of nanocellulose may be the solution for its irreplaceability on the road of commercialization.

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