

# Chapter 9

## American Process: Production of Low Cost Nanocellulose for Renewable, Advanced Materials Applications

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**Abstract** Nanocellulose has proven to be a versatile material with a vast array of potential commercial applications including composites and foams for automotive, aerospace, and building construction, viscosity modifiers for cosmetics and oil drilling fluids, and high performance fillers for paper, packaging, paints, plastics, and cement. In addition to material performance properties like gelation, shear thinning, exceptionally high strength, and light weight, nanocellulose has a strong sustainability profile. Being made from biomass, it is renewable, biodegradable, compostable, and designed for the environment with a sustainable life cycle carbon footprint. American Process Inc.'s (API's) American Value Added Pulping (AVAP)<sup>®</sup> technology offers commercial-scale production of nanocellulose with flexibility in final product morphology (rod shaped nanocrystals and fiber shaped nanofibrils) and surface properties (hydrophilic or hydrophobic) to service the wide variety of emerging end-use market segments. The novel hydrophobic lignin-coated variety of AVAP nanocellulose can be incorporated into plastics. This achievement overcomes a well-known barrier to commercial utilization of nanocellulose. AVAP nanocellulose will also be low cost, with commercial selling prices anticipated to be comparable to competing petroleum-based polymers.

### 9.1 About American Process Inc.

American Process Inc. (API) focuses on pioneering renewable materials, fuels and chemicals from biomass and develops proprietary technologies and strategic alliances in this field to be scaled industrially throughout the world. The company was founded by Theodora Retsina in 1995, initially as an engineering consulting company specializing in energy use optimization for the forest products industry.

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Since then, API has completed over 500 energy integration and water reuse studies within the industry and identified annual energy savings opportunities of billions of dollars. API has worked with Pinch technology, a methodology for minimizing energy consumption of chemical processes by calculating thermodynamically feasible energy targets (or minimum energy consumption) and achieving them by optimizing heat recovery systems, energy supply methods and process operating conditions. API boasts the world's largest experience list for the application of Pinch technology to industry. In 2005, API began developing technologies for the conversion of biomass into cellulosic sugars to be used in the production of biofuels and biobased chemicals. American Process owns two distinct patented cellulosic technologies, Green Power+® and American Value Added Pulping (AVAP®) and operates demonstration plants for each within the US. The Green Power+ technology is demonstrated at the "Alpena Biorefinery" in Alpena, MI which can produce up to 1 million gallons per year of cellulosic ethanol along with a low carbon footprint, biobased potassium acetate deicer co-product. In April 2014, the Alpena Biorefinery sold the nation's first commercial quantities of cellulosic ethanol generated from woody biomass under the Environmental Protection Agency's Renewable Fuels Standard (RFS) program. Under the Energy Independence and Security Act of 2007 (EISA), the RFS program requires renewable fuel to be blended into transportation fuel in increasing amounts each year, where each renewable fuel must emit lower levels of greenhouse gases relative to the petroleum fuel it replaces. The Alpena Biorefinery was partially funded with a \$22 million grant from the Department of Energy and a \$4 million grant from the State of Michigan. API's AVAP technology is demonstrated at the "AVAP Biorefinery" in Thomaston, GA. The AVAP Biorefinery produces specialty cellulose products for advanced materials applications and exceptionally pure lignocellulosic sugars for on or off-site conversion into biobased fuels and chemicals. The plant can process three tons of biomass feedstock (dry basis) per day. Beginning in 2012, API has developed an innovative process based on the AVAP technology to produce commercially scalable, low cost nanocellulose. Nanocellulose is a material composed of high-strength nanosized cellulose crystalline rods known as cellulose nanocrystals (CNC) or longer crystalline and amorphous cellulose nanofibrils (CNF). API's nanocellulose has flexibility in final product morphology and surface properties (hydrophilic or hydrophobic) that can service the wide variety of emerging end-use market segments, including composites and foams for automotive, aerospace, and building construction, viscosity modifiers for cosmetics and oil drilling fluids, and high performance fillers for paper, packaging, paints, plastics, and cement. In addition to material performance properties like gelation, shear thinning, exceptionally high strength, and light weight, nanocellulose has a strong sustainability profile. Being made from biomass, it is renewable, biodegradable, compostable, and designed for the environment with a sustainable life cycle carbon footprint.

API's nanocellulose process and products are protected by granted patents (such as U.S. Patent Nos. 8,030,039, 8,038,842, 8,268,125, 8,585,863, and 8,685,167) and pending patents (such as U.S. Patent App. Pub. Nos. 2014/0154756, 2014/0154757, and 2014/0155301 and patent cooperation treaty (PCT) publications

WO 2014/085729 and WO 2014/085730) as well as proprietary know-how and trade secrets. In total, API has over 15 issued patents and over 130 patents pending in the biorefinery field. API is currently installing a nanocellulose pilot line at the AVAP Biorefinery for production of the full range of AVAP nanocellulose products by the second quarter of 2015. API has a research and development group composed of engineers and materials scientists that are dedicated to advancing nanocellulose processing and products. The company also partners internationally with industry, academia, and government for nano-scale characterization and development of commercial applications. University and government partners include the US Department of Agriculture's Forest Products Laboratory, the National Institute of Standards and Technology, Georgia Institute of Technology, the Renewable Bioproducts Institute, Clark Atlanta University, University of Maine, University of Alberta and Swinburne University. API's in-house expertise includes technology, product, and process development, engineering, procurement, plant installation, construction, operations, scale-up and commercialization.

In April 2013, the Brazilian company, GranBio, became a shareholder in API. GranBio is a 100% Brazilian-owned company, founded in June of 2011, and is known as an industrial pioneer in biomaterials, biofuels and biochemicals. The Brazilian National Development Bank (BNDESpar) is one of its shareholders.

## 9.2 About Nanocellulose

Cellulose ( $C_6H_{10}O_5$ )<sub>n</sub> is a polysaccharide consisting of a linear chain of several hundred to many thousands of D-glucose units. Cellulose is the most abundant natural organic compound on Earth, comprising at least one-third of all vegetable matter. It is tasteless, odorless, hydrophilic, insoluble in water and most organic solvents, and biodegradable. It's also renewable, non-toxic, carbon neutral, and exceptionally strong. The microfibrils in biomass have high tensile strength that support the cell walls. The microfibrils are composed of cellulose chains held firmly together in a side-by-side arrangement as multiple hydroxyl groups on glucose from one cellulose chain form hydrogen bonds with oxygen atoms on the same or on neighboring cellulose chains. As shown in Fig. 9.1, microfibrils can be broken down into smaller nano-scale particles including cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC). CNF and CNC can be extracted from biomass and utilized with existing technologies to create renewable-based materials that may compete in performance and price with petroleum-derived plastics and metals in various applications. CNCs are rod-shaped particles (3–5 nm wide, 50–500 nm in length) and highly crystalline. CNFs have a longer structure (5–50 nm wide, 500 to several microns in length) and contain both amorphous and crystalline regions.

Figure 9.2 shows that CNF and CNC have lengths similar in size to viruses and bacteria, respectively.

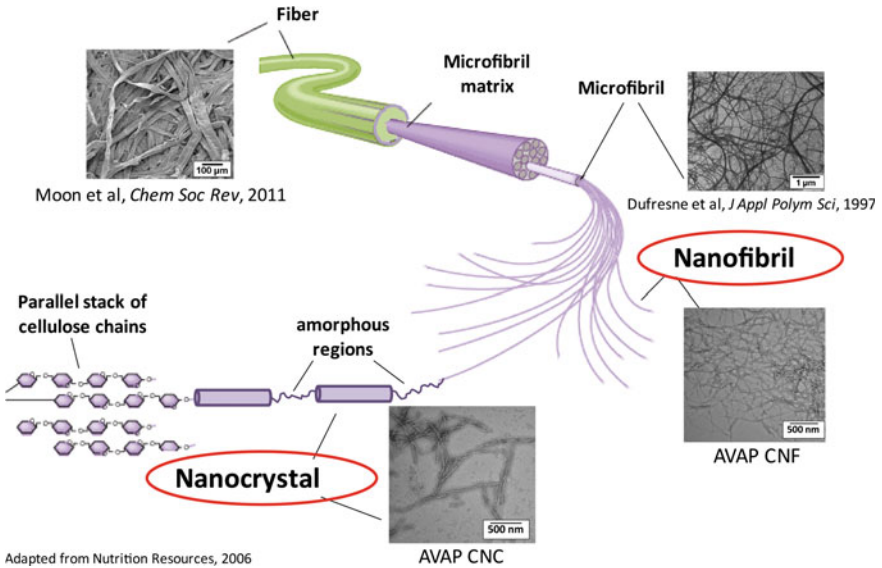


Fig. 9.1 Hierarchical structures in biomass

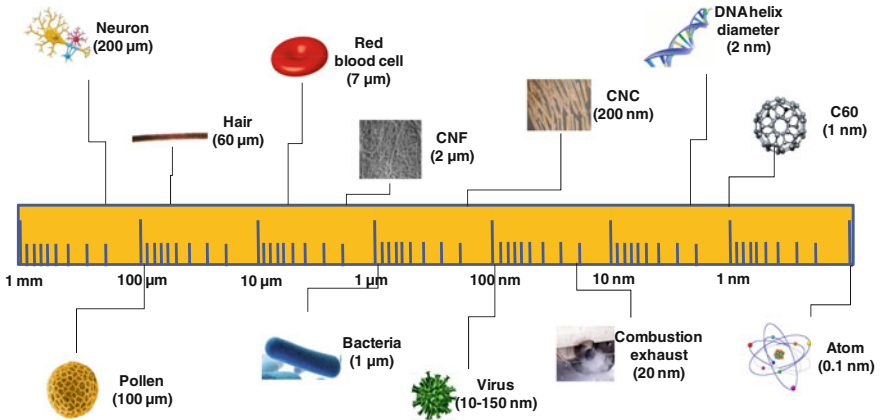


Fig. 9.2 Relative sizes of cellulose nanofibrils and nanocrystals

CNCs have high axial stiffness ( $\sim 150$  GPa), high tensile strength (estimated at 7.5 GPa), low coefficient of thermal expansion ( $\sim 1$  ppm/K), thermal stability up to  $\sim 300$  °C, high aspect ratio (10–100), low density ( $\sim 1.6$  g/cm<sup>3</sup>), lyotropic liquid crystalline behavior, and shear thinning rheology in aqueous suspensions. The exposed –OH groups on CNC surfaces can be readily modified to achieve different surface properties and have been used to adjust CNC self-assembly and dispersion for a wide range of suspensions and matrix polymers and to control interfacial

properties in composites. This unique set of characteristics results in new capabilities compared to more traditional cellulose based particles (pulp fibers, etc.) and the development of new composites that can take advantage of CNCs' enhanced mechanical properties, low defects, high surface area to volume ratio, and engineered surface chemistries [1].

CNFs have unique properties such as high aspect ratio (100–150), large specific surface area (100–200 g/m<sup>2</sup>), high strength and stiffness, good elastic properties, tendency for gel formation at low consistency, and shear thinning behavior. Potential applications include strength enhancement additives in packages and lightweight composites, rheology modifiers in coatings, paints, food, cosmetics barrier materials in food contact materials, and as porous and absorbent materials for various purposes [2].

### 9.3 Nanocellulose Commercial Applications

With its versatility, low toxicity, carbon-neutrality, biodegradability, and abundance (with an annual production in the biosphere of about 90 billion tons) cellulose is gaining significant global interest for the production of advanced materials, biofuels, and biochemicals. Increased concern about the environment and a consumer and market push for greater sustainability in the use of products and services are making the development and use of renewable materials and products one of the central priorities of this and coming decades. Resource constraints are driving a push toward bio-based products. Increased recognition of global climate change and its effects is behind a shift toward greater carbon neutrality associated with human economic endeavors, including manufacturing, transportation, and energy generation. In particular, concerns about the impacts of plastics and their additives have led to a search for safe and more sustainable alternatives. The use of woody biomass material contributes to a lower carbon economy because trees absorb carbon dioxide and become sinks for carbon. Managed forests, one of the largest sustainably-managed biomass sources in the United States, can reduce U.S. greenhouse gas emissions and foreign fossil fuel dependency by conversion of forest materials into novel materials and products [3].

A global research effort has shown that nanocellulose in particular can displace petroleum-based packaging, metallic components, and other non-renewable materials. For example, cellulosic nanomaterials have strong promise for use as reinforcements in polymer matrix composites due to their light weight, high tensile strength and modulus, and comparably low cost. As shown in Fig. 9.3, CNC potentially offers the lowest cost for specific strength and stiffness when compared to common polymer reinforcement materials [4]. Recent nanocellulose manufacturing advances by American Process Inc. have significantly lowered the production cost such that both CNF and CNC are anticipated to be cost competitive with petroleum based polymers and polymer additives.

## Nanocellulose Has Interesting Properties

Material	Density	Tensile Strength	Tensile Modulus	Cost
	g/cc	MPa	GPa	\$/kg
Hi Strength Steel	7.9	600	210	~1
Aluminum 6061-T6	2.7	275	70	~2
E-glass fiber	2.5	3,500	80	~2
Carbon fiber	1.8	4,000	230	>20
Cellulosic Nanocrystals*	1.5	7,500	135	4-10

**Cellulosic nanomaterials are potentially useful as either primary or secondary reinforcements in polymer matrix composites**

\*Source: Ted Wegner, seminar at Oak Ridge National Laboratory, Nov 2012

**Fig. 9.3** Comparison between cellulose nanocrystals and common polymer reinforcement materials

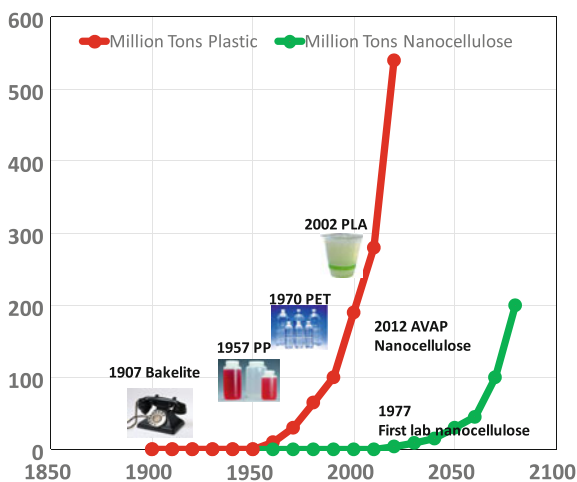
A recent exploration of potential applications for nanocellulose funded by the United State's Department of Agriculture's (USDA's) Forest Service estimated nanocellulose to have an annual U.S. market potential volume of 6.4 million metric tons and an estimated global market potential of 35 million metric tons [5]. As shown in Table 9.1, the applications identified as having the largest potential volume for nanocellulose include paper and paper packaging, textiles, cement, automotive polymer composite components, and hygiene and absorbent products like diapers. Smaller volume applications include rheology modifiers, cosmetics, construction materials, aerospace applications, pharmaceuticals, and paint additives. In the future, additive manufacturing (3D printing) may become a large volume user of cellulose nanomaterials for toys, architectural models, automobile parts, etc. Researchers at the US Department of Energy's (DOE's) Oak Ridge National Laboratory are currently evaluating nanocellulose as a 3D printing substrate.

API envisions the commercialization timeline for nanocellulose products to be similar to that of plastics. One hundred years after the development of the first fully synthetic plastic in 1907, plastics impact every aspect of our lives. Similarly, we expect nanocellulose materials to be fully integrated into society and commerce within one hundred years of the first nanocellulose gel developed in 1977. Figure 9.4 provides our estimated global production curve for nanocellulose assuming growth rates by decade to be similar to that of plastics [6]. This curve predicts that the USDA's global market size estimate for nanocellulose will be achieved around 2045. Commercial sustainability drivers and global environmental concerns may accelerate the production timeline beyond our conservative estimate.

**Table 9.1** Potential markets for nanocellulose

High volume applications	Low volume applications	Novel and emerging applications
Automotive body	Aerospace interiors	Sensors—medical, environmental, industrial
Automotive interior	Aerogels for the oil and gas industry	Reinforcement fiber—construction
Cement	Aerospace structure	Water filtration
Hygiene and absorbent products	Insulation	Air filtration
Packaging coatings	Paint-architectural	Viscosity modifiers-miscellaneous
Packaging filler	Paint-OEM applications	Purification
Paper coatings	Paint-special purpose	Cosmetics
Paper filler	Wallboard facing	Excipients
Plastic film replacement		Organic LED
Replacement-plastic packaging		Flexible electronics
Textiles for clothing		Photovoltaics
		Recyclable electronics
		3D printing
		Photonic films

**Fig. 9.4** Estimated nanocellulose global production curve



### 9.3.1 Nanocellulose Polymer Composites

The relatively low cost of cellulose nanomaterials creates an opportunity to use them as reinforcing fibers in composite materials with wide scale structural applications [7]. One auto manufacturer indicated it could create so many components

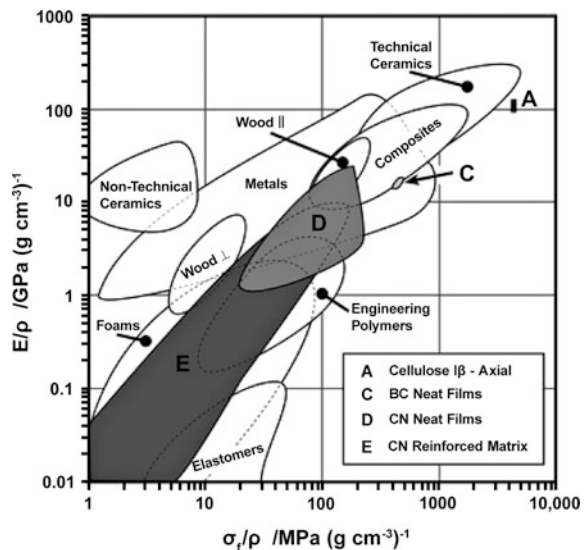
out of such materials—from body panels to interior trim—that it could shave 340 kg off the weight of its cars [8]. The demand for lightweight composite materials in vehicles is driven by fuel efficiency standards for vehicles. In the near term, adoption will most likely be in applications already using composite materials, while steel replacement is an additional, longer term potential application. Others are investigating the use of nanocellulose based polymers for fire retardant coatings [9].

Such applications include reinforcing (bio-) polymers to create promising, environmentally safe, lightweight construction materials for the car industry. CNC improves the prospects for using bio-plastics in interior automotive parts [10].

Although the mechanical properties of nanocellulose vary depending on the average molecular weight, chemical and thermal treatment, tensile strengths in the range of 80–240 MPa with 3–15 GPa elastic modulus and 3–20% strain-to-failure has been reported for neat nanocellulose films [11–14], as shown in Fig. 9.5 [13]. In addition, the crystalline region of nanocellulose is predicted to have a tensile strength and modulus in the range of 7.5–7.7 and 78–220 GPa [13, 15, 16], respectively.

As a filler reinforcement material, nanocellulose has shown to improve the overall mechanical properties of various hydrophilic polymeric matrices. Using a solution casting method, addition of 10 wt% CNF to a chitosan nanocomposite showed an increase in tensile strength and modulus of 20 and 25%, respectively [17]. Similarly, a 25% increase in strength and 18% increase in modulus were found when only 1 wt% of CNF was used in poly(ethylene oxide) matrices [18]. Poly(vinyl alcohol) reinforced with 6.6 wt% of CNF was also demonstrated to enhance tensile strength and modulus by 140% using the electrospinning process [19].

**Fig. 9.5** Ashby plot of specific modulus ( $E/\rho$ ) and specific strength ( $\sigma_t/\rho$ ) for various materials



Reproduced from Moon et. al., 2011



Incompatibility between the hydrophilic surface of nanocellulose and hydrophobic polymers has historically limited the performance of nanocellulose in a wide variety of polymers. Polycaprolactone (PCL) film reinforced CNF is an example that showed a decrease in tensile strength of 25 MPa as a neat PCL film to approximately 13–17 MPa after addition of 3 wt% nanocellulose [20, 21]. The hydroxyl groups on the surface of nanocellulose create high surface energy leading to insufficient wetting and weak interfacial adhesion with hydrophobic polymers [22–24]. Weak interfacial adhesion between CNF and a polymer matrix gives less effective stress transfer leading to low nanocomposite strength [25]. As discussed below, advances by API in creating hydrophobic, lignin-coated CNC and CNF appear to have overcome this well-known grand challenge.

### **9.3.2 Nanocellulose Concrete Composites**

Studies have shown that the high aspect ratio of nanocellulose may facilitate an increase in fracture toughness for cement composites. Preliminary results showed enhancement of fracture energy by up to 50% with the addition of 3 wt% of a mixture of cellulose micro- and nanofibers [26]. Recent work also demonstrated that an additional 20% flexural strength relative to the unreinforced cement paste could be achieved using 0.2 vol.% CNC [27]. The nanoscale fibers appear to fill small pores within concrete, thereby increasing its toughness and flexibility. Utilization of nanocellulose as a high-performance cement filler may reduce the volume of cement needed for a project, thereby lowering material and labor costs, and bringing the added benefit of reduction in associated greenhouse gas emissions.

### **9.3.3 Nanocellulose Aerogels**

Aerogels are extremely low density solid materials with a highly porous surface area composed of up to 99.98% air by volume. As a result of good dimensional stability and mechanical properties, Nanocellulose-based aerogels have been considered for packaging applications to substitute polystyrene-based foam and thermal insulation. There is also strong interest in using nanocellulose-based aerogels as porous templates for advanced materials, because of specific properties like water absorbency, selective separation of oils and organic solvents, CO<sub>2</sub> capture, heavy metal removal, and electrical conductivity. Superior water absorbency of 104 g water per g of dried mass with reusability for at least 20 times has been demonstrated for TEMPO-oxidized CNF aerogels [28]. In recent works, selective separation of oils and organic solvents such as dodecane from contaminated water can be effectively achieved using silane modified nanocellulose aerogels [29–31] or titanium dioxide modified nanocellulose aerogels [32]. Similarly, using aminosilane treatment, modified CNF aerogels have been developed for the capture of carbon

dioxide from air [33]. Rapid and effective removal of hexavalent chromium has also been developed using CNF aerogels functionalized with quaternary ammonium [34]. Controlled drug delivery was reported using nanocellulose aerogels from CNF and bacterial cellulose, as carriers [35]. Both CNF and bacterial cellulose aerogels have also been engineered to achieve flexible and highly conductive material for electronic products [36, 37].

Aerogels also offer advantages for insulation materials. Recent advancements have been made towards creating cheaper, thinner, more breathable insulating materials with higher R-values [38]. This novel material has the lowest bulk density of any known porous solid, as well as significant insulating qualities. Cellulose nanomaterials can create insulating materials using little material and low energy inputs, offering advantages in the fast growing green building sector [5].

Aerogels prepared from 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) cellulose nanofibrils (discussed in more detail below) gave low densities in the range of 0.01–0.26 g cm<sup>-3</sup> with surface areas up to 485 m<sup>2</sup> g<sup>-1</sup> [13]. High Brunauer–Emmett–Teller (BET) surface areas have also been reported for CNC aerogels with densities in the range of 0.078–0.155 g cm<sup>-3</sup> [13]. Specific surface areas as high as 605 m<sup>2</sup> g<sup>-1</sup> and a density of 0.078 g cm<sup>-3</sup> have been achieved with CNC using supercritical CO<sub>2</sub> drying [39].

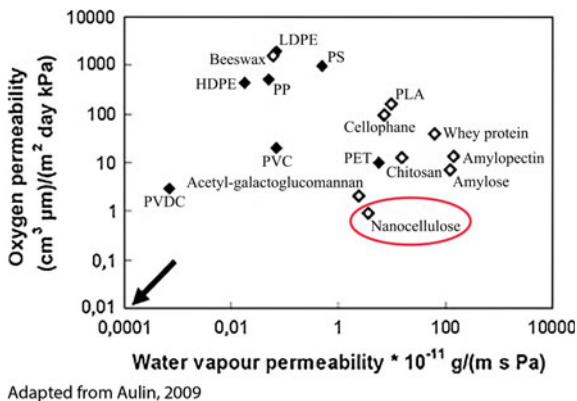
### 9.3.4 Nanocellulose Barrier Films and Packaging

Neat nanocellulose films have been demonstrated to have high water vapor absorption with low oxygen permeability [13, 40]. Several factors, such as the type of nanocellulose, degree of crystallinity, film entanglement and porosity, as well as physical and chemical treatment, play a major role in determining water vapor transmittance rate (WVRT) and oxygen transfer rate (OTR) [40]. As shown in Fig. 9.6, OTR values in the range of 4–18 mL m<sup>-2</sup> day<sup>-1</sup> have been reported for nanocellulose [40, 41]. Given that the recommended OTR value for modified atmosphere packaging (i.e. food storage and distribution) is in the range of less than 10–20 mL m<sup>-2</sup> day<sup>-1</sup> [40, 42], nanocellulose films show promise for use in oxygen barrier applications within the packaging industry.

In addition to superior oxygen barrier properties, preliminary work indicates that the dense structure of nanocellulose films has certain oil resistance capabilities [43]. CNF-coated paper reduces ink absorption levels into paper as CNF acts as an inkjet pigment binder at the surface [44]. In another work, reinforcing poly(vinyl alcohol) with carboxylated CNC shows an improvement in trichloroethylene resistance [13].

Nanocellulose films may also offer novel alternative filtration technologies. They have also been shown to have barrier properties that control the permeability of other gases, solvents, and charged species. Preliminary results suggest that the membrane performance of CNF films for organic solvent filtration can be tailored by simply controlling the concentration and dimensions of nanofibrils [45]. TEMPO-oxidized CNF films also have excellent hydrogen gas permeation selectivity [46], while films

**Fig. 9.6** Oxygen and water vapor permeability of various materials



formed using negatively charged CNC are shown to exclusively adsorb positively charged species [47].

### 9.3.5 Nanocellulose Viscosity Modifiers

Nanocellulose suspensions form thixotropic, or shear thinning, gels [48, 49] that can be used as thickeners and suspension stabilizers for both solid and oil-water emulsions [48–51]. Nanocellulose has been tested as a rheology modifier in food products, cosmetics, paints, aircraft anti-icing fluid and oil recovery [49, 52]. In food products, the addition of flavoring ingredients for salad dressing into 2 wt% CNF suspensions in water showed a stable suspension for more than 6 months [48, 49]. For oil recovery, fracturing fluids from CNF suspensions were shown to generate a stable suspension of 10 wt% fine sand in 2 wt% CNF at elevated temperature of 100 °C for 3 months [48, 49]. The water solubility of nanocellulose allows easy addition for modifying the viscosity of water-based paints and coatings, [49, 53] and has been demonstrated to improve the durability of water-based polyurethane varnishes and paints, reportedly improving finish durability, and protecting paints and varnishes from wear caused by UV radiation [54].

## 9.4 Nanocellulose Manufacturing Challenge: Production Cost

While cellulose nanocrystals and nanofibrils have strong commercial promise, their commercialization has been limited to date due to material availability and estimated commercial sales price. As discussed below, start-up of API's 0.5 ton per day (dry basis) nanocellulose production line in the first quarter of 2015 at our existing Biorefinery in Thomaston, Georgia will overcome these challenges.

### 9.4.1 Conventional Cellulose Nanocrystals Production

While CNC has been produced in lab quantities since the 1950s, it first became commercially available in 2012 when CelluForce started up a 1 ton per day demonstration plant in Windsor, Québec. However, as of September 2014, the plant has been idle [55]. In March 2015, CelluForce announced an investment into the company by Schlumberger, the world's leading supplier of technology, integrated project management and information solutions for the global oil and gas industry. Otherwise, CNCs are produced at pilot scale at the U.S. Forest Service's Nanocellulose Facility located at the Forest Products Laboratory (FPL) in Madison, Wisconsin. The pilot plant started in 2012 and can produce up to 50 kg CNC aqueous suspension per week as a 5–10% solids suspension.

The preparation of CNCs from biomass generally occurs in two primary stages. The first stage is a purification of the biomass to remove most of the non-cellulose components in the biomass such as lignin, hemicelluloses, extractives, and inorganic contaminants. This is typically done by conventional pulping and bleaching. The second stage uses an acid hydrolysis process to deconstruct the "purified" cellulose material into its crystalline components. This is accomplished by removing the amorphous regions of the cellulose microfibrils. The resulting rod-shaped particles (3–20 nm wide, 50–2000 nm long) are ~100% cellulose, and are highly crystalline (62–90%, depending on cellulose source material and measurement method). The variations in CNC characteristics (e.g., particle morphology, surface chemistry, percent crystallinity, etc.) are strongly linked to the cellulose source material and the acid hydrolysis processing conditions [1].

FPL's CNC production process is based on the nonproprietary concentrated sulfuric acid hydrolysis method published by Grey et al. [56]. Typically, machine-dried prehydrolysis Kraft rayon-grade dissolving wood pulp is shredded, placed under nitrogen atmosphere, and heated to 45 °C. Sulfuric acid (64 wt%) at 45 °C is sprayed over the top of the shredded pulp strips and the mixture is stirred at 45 °C for 90 min. The reaction is quenched by diluting ~10-fold with water and hypochlorite solution (household Clorox) is added to remove color formed during the reaction. The use of dissolving pulp as a starting material gives less color than with bleached Kraft pulp. The CNC suspension is then neutralized by slow addition of 5–8% wt% NaOH, diluted ~4-fold, and allowed to settle. The salt/sugar solution is then decanted from the solids, which are diluted a second time. At this point, the sodium sulfate concentration drops to about 1 wt% and the CNC particles begin to disperse in the solution. The CNC is then circulated through a tubular ultrafiltration membrane system where the salt/sugar solution passes through the membrane and the CNCs are retained. Reverse osmosis water (RO) is added as needed to maintain the CNC concentration to 1 wt%. Diafiltration is continued until the residual salt concentration is reduced to about 8 μM (requiring about 24 h and 20,000L RO dilution water). The colloidal CNC suspension is filtered using a 20 μm cartridge-style filter to remove dirt and concentrated to at least 5 wt% solids using the tubular ultrafiltration system. The cellulose yield is about 50% based on the

starting bleached pulp. Each bath of CNC requires about 8 h for CNC reaction and neutralization, 24–48 h for settling and initial purification, and 24 h membrane filtration for final salt removal. Current production is 25 kg per batch, with up to two batches per week [57]. One advantage of this process is that it is based on a well-known laboratory method whose CNCs are used as standards throughout the world. Disadvantages of the process include long processing/batch cycle times, high chemical costs due to the high sulfuric acid charge that is not recycled, and large water consumption. The Technical Association of the Pulp and Paper Industry (TAPPI) Nanocellulose Division estimates the commercial sales price of CNC produced from this method to be \$10–50/lb.

### ***9.4.2 Conventional Cellulose Nanofibrils Production***

While production of CNF gels was first demonstrated in the lab using a milk homogenizer by ITT Rayonier in 1977, today the University of Maine is the only known producer of commercial quantities of mechanically-derived CNF. Their Cellulose Nanofiber Pilot Plant is capable of producing up to one ton per day (dry basis) CNF. Several other small scale CNF pilot plants with capacities of several hundred lbs. per day are operated throughout the world by Nippon Paper (Japan), Borregaard (Norway), Innventia (Sweden), Namicell (France) and Oji Paper (Japan).

CNF is generally manufactured by mechanical treatment using a refiner, grinder, homogenizer, or fluidizer. The resulting material consists of fibrils of many different sizes with the width of the smaller fibrils or aggregates being around 20–40 nm, while their length can be several  $\mu\text{m}$ . The fibrils are highly branched and flexible. The high energy consumption of mechanical treatments may be reduced with different chemical or enzymatic pretreatments that facilitate the fibrillation of fibers during mechanical treatment. Several different pretreatments for obtaining cellulose nanofibrils have been published including mild enzyme pretreatment using endoglucanase, carboxy-methylation, and TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl radical) mediated oxidation [2]. Particularly in Japan there has been considerable exploration of applications with CNF that has been modified by TEMPO-oxidation. TEMPO is a tetramethyl-piperidine compound that is used as a catalyst in oxidizing cellulose microfibrils which introduces carboxyl groups on the surface of the fibrils. CNF produced by the TEMPO process can be quite uniform, with a diameter as small as 4 nm.

The University of Maine's CNF pilot plant was funded through a joint venture with the USDA's Forest Service. Typically, machine-dried Northern Bleached Softwood Kraft pulp is blended with water to 3 wt% solids before sending to a mechanical disc refiner. The pulp is refined using a series of progressively finer plates until a nanofibril gel is formed and the target particle size range is reached. This series of specific mechanical treatments significantly lowers the energy required to produce the nanofibrillated cellulose ( $\sim 2,000$  kWhr/MT) compared to

prior art mechanical methods like homogenizers and grinders. Refining is carried out with recirculation to provide nominally 30 passes through the refiner. The pilot plant is equipped with a spray dryer with the capacity to dry several pounds of nanocellulose per day. Advantages of this process include simplicity and low cost compared to chemical methods. Disadvantages of the process include high energy consumption and a large distribution in particle size compared to chemical treatment methods like TEMPO. The TAPPI Nanocellulose Division estimates the commercial sales price of CNC produced from this method to be \$4/lb.

The USDA's Forest Products Laboratory nanocellulose pilot plant also produces TEMPO-pretreated cellulose nanofibrils at the 2–3.5 kg scale. Using machine-dried market pulp, the yield of nanocellulose on original pulp is ~90% when using sodium hypochlorite at the primary oxidant. The method is based on laboratory work by Saito et al. [58] who demonstrated that the energy required to produce a nanoscale fibrillated product was reduced by TEMPO pretreatment. The pilot method alters the method by Saito by using a sodium carbonate buffer to control the pH to 10. Typically, commercial machine-dried eucalyptus bleached Kraft pulp is blended with water and then pretreated by mixing at 2 wt% solids, pH 2, and 2 wt% sodium chlorite ( $\text{NaClO}_2$ ) on pulp. The mixture is stirred overnight at room temperature, then filtered and washed to collect the pulp. Pretreated pulp is combined with sodium carbonate and stirred for an hour at room temperature. Sodium bicarbonate, sodium bromide, and TEMPO are added and the reaction is heated to 30 °C. Sodium hypochlorite ( $\text{NaClO}$ ) solution is added and the reaction stirred overnight at 30 °C. The treated pulp is filtered, washed, diluted to 2 wt% and refined using a disc refiner. Refining is carried out with recirculation and run long enough to provide nominally 25 passes through the refiner. A heat exchanger is included in the recirculation loop to control the temperature near 50 °C. After refining, the pulp is diluted to 0.1 wt% in water and treated with an ultrasonic probe for 6 s with an energy input of 300 W, passed through a centrifuge operating at 12,500 G and concentrated to at least 0.5 wt% solids using a tubular ultrafiltration system with a 200,000-MW cutoff membrane. Final clarification is performed by passing the material twice through a homogenizer (Microfluidics M-110EH-30) equipped with series 200 and 87  $\mu$  orifices [59]. A notable advantage of this process is the production of thin nanofibrils with a more uniform particle size distribution that produces transparent gels and films. The principle disadvantage of the process is the high cost of TEMPO which is not recycled. The TAPPI Nanocellulose Division estimates the commercial sales price of CNF produced from this method to be \$100/lb.

### **9.4.3 AVAP Nanocellulose Production**

American Process Inc. has developed a single, cost-effective process for production of both cellulose nanocrystals (CNC) and cellulose nanofibrils (CNF) along with novel, hydrophobic, lignin coated versions of each. API's AVAP® technology

offers commercial-scale production of nanocellulose with flexibility in final product morphology and surface properties (hydrophilic or hydrophobic) that can service the wide variety of emerging end-use market segments. The novel hydrophobic lignin-coated variety of AVAP nanocellulose can be incorporated into plastics. This achievement overcomes a well-known barrier to commercial utilization of nanocellulose. Furthermore, AVAP nanocellulose is anticipated to be cost competitive with petroleum-based polymers as well as polymer additives. This break-through technology can help achieve the USDA's future global market size estimate for nanocellulose of 34 million tons per year [59]. In April 2015, API started up a nanocellulose production line at our existing AVAP Biorefinery in Thomaston Georgia for production of the full range of AVAP nanocellulose products for sale under the BioPlus™ trade name. The biorefinery currently demonstrates the AVAP pretreatment process for production of cellulose, cellulosic sugars and cellulosic ethanol from 3 bone dry tons per day of biomass. The biorefinery started in March 2013 and is the site of supply chain integrated alliances with downstream sugar and cellulose converters into chemicals, fuels, and other biobased materials. The facility is situated on 8 acres and includes 41,000 square feet of manufacturing space along with API's fully equipped corporate laboratory.

Figure 9.7 provides a simplified process flowsheet for API's nanocellulose process. The AVAP chemical pretreatment step uses sulfur dioxide (SO<sub>2</sub>) and ethanol to remove hemicelluloses, lignin, and the amorphous regions of cellulose from biomass. Sulfur dioxide acts a delignifying agent, effectively freeing cellulose and hemicelluloses from lignin. Ethanol acts as a solvent, aiding penetration of SO<sub>2</sub> into the wood, dissolving resins and extractives, and reducing degradation of crystalline cellulose. The strong liginosulfonic acids created during delignification hydrolyze the amorphous regions of cellulose. The final nanocellulose product morphology (CNF, CNC, or a novel mixture of CNF and CNC) is controlled by the time and temperature (i.e. severity) of the pretreatment step. The dissolved sugars extracted

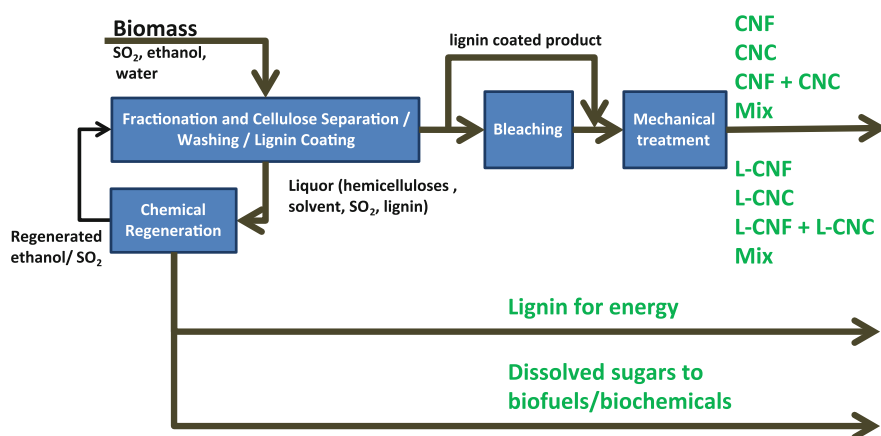
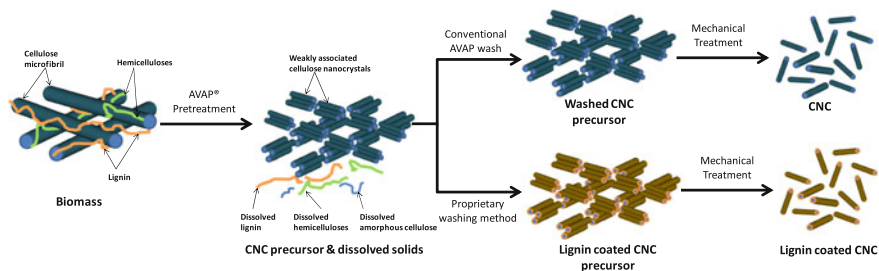


Fig. 9.7 A simplified process flow diagram of the AVAP nanocellulose process



**Fig. 9.8** AVAP process routes for traditional CNC and hydrophobic, lignin coated CNC

during pretreatment can be fermented into a cellulosic ethanol or other biochemical co-products for additional revenue. Lignin is removed from the process and burned, making the process self sufficient in energy use or a net energy (power) exporter, depending on the biomass feedstock. The pretreatment chemicals are recycled with high recovery rates in an energy efficient manner for reuse.

Following pretreatment, the chemically-fibrillated cellulose pulp is washed to remove the dissolved lignin and sugars. The pulp is then bleached to obtain pure cellulose. Alternatively, the cellulose is treated using a proprietary method that deposits lignin onto the surface of the fibrils or crystals. Following treatment of brown cellulose or optional bleaching, minimal mechanical energy is applied to the cellulose to liberate the individual nanocellulose particles (see Fig. 9.8) [6].

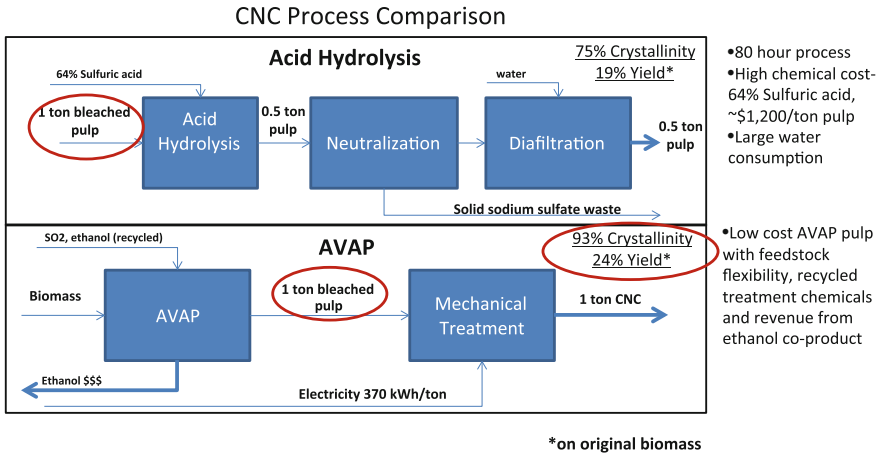
The AVAP nanocellulose process uses low cost raw biomass and pretreatment chemicals, a small number of process steps, and standard unit operations, which lead to low operating and capital cost requirements. In addition, the unique pretreatment chemicals (SO<sub>2</sub> delignifying agent and ethanol penetrating solvent) make the process suitable for all biomass feedstocks including spruce, red pine, Jack pine, loblolly pine, balsam fir, Douglas fir, larch, birch, beech, aspen, poplar, sugar maple, bark, corn cobs, corn stover, switchgrass, energy cane, eucalyptus, miscanthus, sugar cane straw, wheat straw, oil palm empty fruit bunches, forest residues, bamboo, and kenaf (a *Hibiscus cannabinus* plant that grows similar to bamboo) [60–66].

Figures 9.9 and 9.10 highlight the advantages of the AVAP process for making CNC and CNF over the conventional methods discussed above.

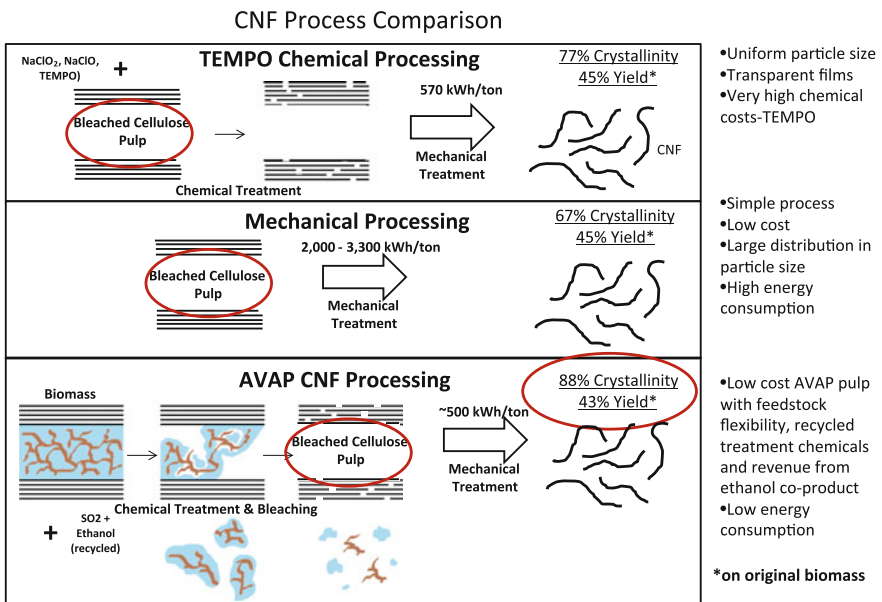
The key to the AVAP nanocellulose process is the “tunability” of the pretreatment step. For a given feedstock, the pretreatment conditions (time and temperature) can be selected that give the desired levels of fibrillation and removal of amorphous cellulose, as indicated by cellulose degree of polymerization (DP). As shown in Fig. 9.11, API has shown, using eucalyptus, softwood and cane straw, that two unique DP targets exist for production of CNF and CNC after mechanical treatment. Between the two targets, a mixture of CNF and CNC is produced.

The unique kinetics of the AVAP pretreatment step is an equally important attribute for nanocellulose production. In the acidic AVAP process the amorphous regions of cellulose are more fully hydrolyzed and dissolved while the crystalline cellulose is less accessible due to the non-swelling nature of the ethanolic cooking





**Fig. 9.9** Comparison between the AVAP nanocellulose processing method and the sulfuric acid method



**Fig. 9.10** Comparison between the AVAP cellulose nanofibrils processing method and conventional methods

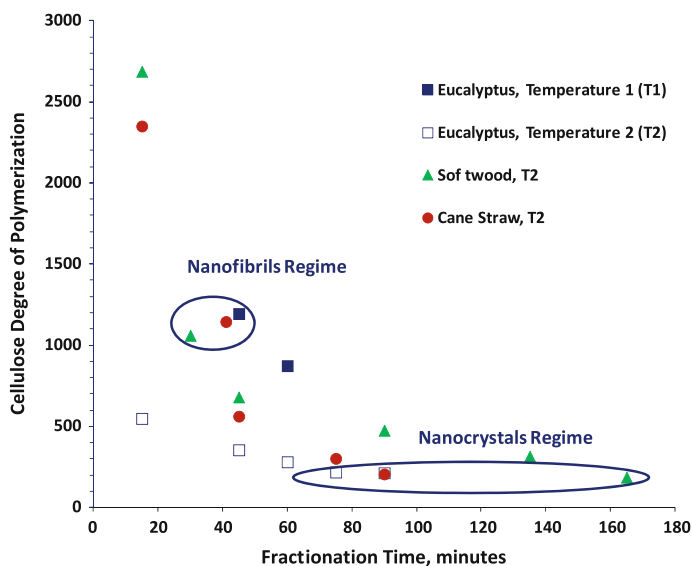


Fig. 9.11 Tunability of AVAP pretreatment step from different biomass feedstocks

liquor compared to that of other processes (e.g. the alkaline Kraft process). As a result, the crystallinity of both AVAP CNF and CNC are exceptionally higher than that produced by competing methods (see Table 9.2). Anticipated benefits of the high crystallinity include higher thermal stability and films and composites with higher strength and improved barrier properties.

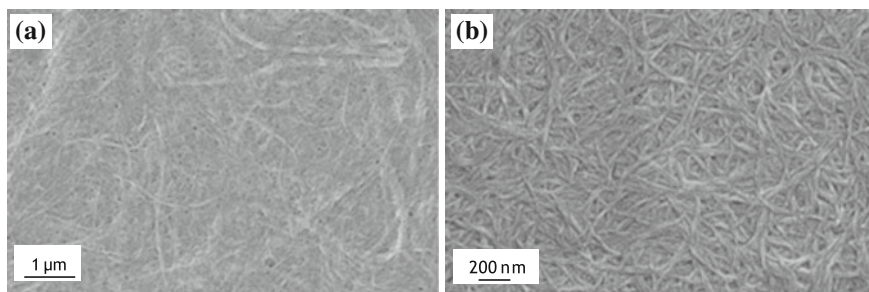
As shown in Fig. 9.12, AVAP CNFs from Eucalyptus have a high aspect ratio (5–200 nm wide, 500 nm to several microns in length). AVAP CNCs from Eucalyptus are rod-shaped (4–5 nm wide, 50–500 nm in length) [6].

#### 9.4.4 AVAP Nanocellulose Process Chemistry

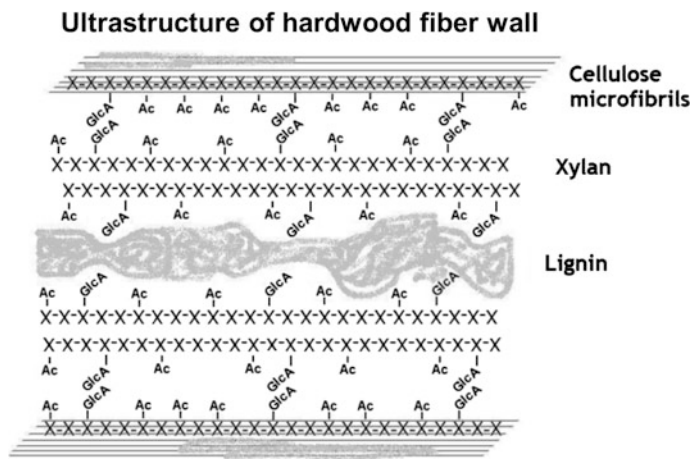
As discussed above the AVAP® process utilizes a mixture of ethanol and water with dissolved  $\text{SO}_2$  to rapidly fractionate all types of woody biomass into its principal components—pure cellulose (about 40%), hemicelluloses (about 35%) and lignin (about 25%) [67, 68]. Hemicelluloses are hydrophilic polymers, called xylan and glucomannan, consisting of about 100–200 linearly-linked sugar units of xylose and glucose plus mannose, respectively. Xylan and glucomannan also have other sugars as side groups such as arabinose, glucuronic acid and galactose, while some of the hydroxyl groups on the linear hemicelluloses chain are acetylated. Lignin is a hydrophobic amorphous polymer network of phenylpropane units. The components are arranged in woody biomass in a dense structure where the space between the hemicelluloses coated microfibrils is filled with lignin and hemicelluloses which are partly chemically bound to each other, as illustrated in Fig. 9.13.

**Table 9.2** Comparison between crystallinity of AVAP CNF and CNC and conventional nanocellulose

	Crystallinity from XRD (%)
CNF, AVAP from eucalyptus chips	88
CNC, AVAP from eucalyptus chips	93
CNF, Mechanical from northern bleached softwood kraft pulp, from UMAine pilot	67
CNF, TEMPO (NaClO <sub>2</sub> ) from eucalyptus bleached kraft pulp, from FPL pilot	77
CNC, Sulfuric acid hydrolysis from spruce pre-hydrolysis rayon grade dissolving pulp, from FPL	75



**Fig. 9.12** AVAP Cellulose **a** Nanofibrils and **b** nanocrystals from eucalyptus



Damstrom et. al. 2009, Bioresources4(1)3-14

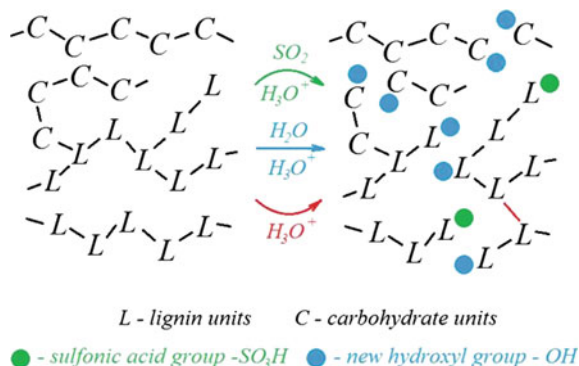
**Fig. 9.13** Ultrastructure of harwood fiber wall

This complex composite morphology is nature's answer to create a material with great strength and microbiological protection properties needed for sustained, tall vertical growth. It also explains the difficulty to find a fractionation process which is able to deconstruct lignocellulosic biomass cleanly into its separate components. The unique chemistry of the AVAP® process arises from the presence of both SO<sub>2</sub> and ethanol in the aqueous fractionation chemicals. SO<sub>2</sub>, a strong nucleophile, allows for efficient lignin removal, "delignification", of various feedstocks at relatively mild conditions (temperatures of 130–165 °C). SO<sub>2</sub> is responsible for lignin dissolution through sulfonation and depolymerisation. Hemicelluloses are dissolved through hydrolytic cleavage by SO<sub>2</sub> solvates ( $pK_{a1}$  for SO<sub>2</sub>·H<sub>2</sub>O in water of about 3.5 at 150 °C [69]) and especially lignosulfonic acids ( $pK_a$  in water close to 1 [70]). The major functions of ethanol are: (1) Fast transport of SO<sub>2</sub> to the reaction sites ( $\alpha$ -carbons in lignin), (2) moderating the acidity of the reaction system, and (3) dissolution of lignin at relatively low degree of sulfonation [71, 72]. The fast penetration of ethanol into the biomass allows rapid impregnation of SO<sub>2</sub>. This avoids impregnation times of one or several hours as customary for traditional biomass fractionation methods, or "pulping methods", such as the Kraft process or the acid sulfite process. The chemical impregnation efficiency of the AVAP process is evident by a low rejects content of the cellulose solids product ("pulp") even at relatively high lignin content and the fact that the process is not affected by variations in moisture content of the biomass feedstock [61]. After fractionation, the dissolved hemicelluloses are present in the liquid phase as monomers and oligomers in approximately equal amounts [71]. Lignin is produced in two fractions—a low-sulfonated fraction, obtained by precipitation after ethanol evaporation from the spent liquor, and more conventional lignosulfonates which can be isolated from the liquid stream after sugar utilization (e.g. after fermentation).

The AVAP process has proven optimal for production of various conventional and novel cellulose-based products, as well as biofuels, biomaterials and chemicals. For example, good quality papermaking [73] and dissolving pulp for rayon textiles [74, 75] as well as nanofibrillated cellulose and cellulose nanocrystals [76] have been demonstrated. Also, well-delignified cellulose from the AVAP process can easily be hydrolysed to glucose followed by conversion with or without coprocessing of the conditioned hemicelluloses monosugars to various biofuels and chemicals [77–79] like ethanol and butanol through fermentation of the sugars [64, 80–83].

There are several cost and operating advantages of AVAP® cooking over commercial Kraft and acid sulfite pulping and ethanol-based organosolv pulping (ALCELL). Because cellulosic fibers liberated by conventional pretreatment methods still contain most of the original lignin as well as a significant amount of hemicelluloses, they are not suited for high performance cellulose grades, like nanocellulose. Also extensive lignin condensation and hemicelluloses degradation are typical for conventional processes which makes the resulting products unusable except for low-value combustion for energy production. The capital cost of conventional processes is also significantly higher than AVAP because of their complex recovery cycles.

**Fig. 9.14** Schematic of the four principal reactions during AVAP® fractionation



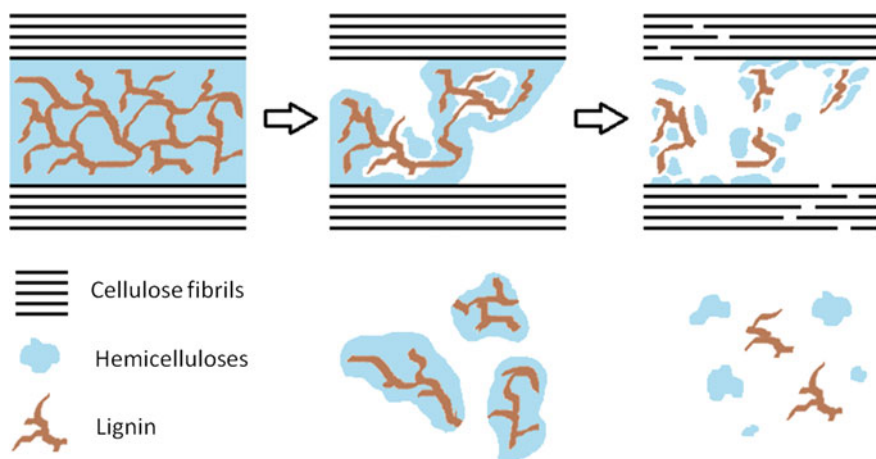
The principal chemical reactions in AVAP fractionation are lignin sulfonation, carbohydrate hydrolysis, lignin hydrolysis and lignin condensation reactions. The first three are positive for fractionation since they result in lower molecular weight and more hydrophilic lignin and carbohydrate polymers. The latter reaction increases the degree of polymerization of lignin and can be controlled to produce novel products like lignin-coated cellulose. The four reactions are schematically shown in Fig. 9.14.

As cooking proceeds,  $SO_2$  is consumed in reactions with lignin and in side reactions. However, the highest measured amount of bound sulfur corresponds to only 1.1% on spruce wood with the remainder recoverable as  $SO_2$ . Therefore the concentration of  $SO_2$  may be assumed essentially constant during cooking and equal to that of the fresh fractionation chemicals [72].

Pretreatment acidity is determined by the concentrations of  $SO_2$ , the formed strong lignosulfonic acid groups and ethanol. It has been shown that the acidity inside the fibers is the same as that in the external liquor [72]. Delignification is governed by chemical reaction rather than by diffusion, as can be inferred from the high values of the activation energies of the fractionation rates [61]. Biomass particle size has no significant effect on the delignification rate in the process [84].

In addition to the reactions leading to cleavage and dissolution of lignin, reactions between different lignin units, called condensation, are possible which form non-cleavable carbon-carbon bonds that prevent lignin removal from the biomass. Condensation is promoted by high acidity and temperature [85].

Like sulfite pulps, AVAP pulps are brighter and exhibit higher bleachability compared to Kraft pulps [73]. The reason for higher brightness of AVAP pulps in comparison with Kraft pulps is absence of strong chromophores such as quinones and stilbenes which are present in Kraft pulps. Better bleachability of AVAP and sulfite pulps in comparison with Kraft pulps is explained by lower amount of lignin-carbohydrate bonds which are mostly hydrolyzed in acidic conditions. Also hexenuronic acids, which are not present in AVAP or acid sulfite pulps, consume high amounts of bleaching chemicals when fully bleached Kraft pulps are produced.



**Fig. 9.15** Pictorial schematic of the two phases of AVAP® fractionation

The kinetics of AVAP delignification occurs in two phases. In the first phase, some lignin is removed while still being chemically bound to hemicelluloses as so-called lignin-carbohydrate complexes (LCC), which increases the void space between the cellulose microfibrils. In the second phase, most of the remaining LCCs and residual lignin and hemicelluloses are further sulfonated/hydrolyzed and removed as soluble separate fragments. Due to the removal of LCCs, cellulose chains become accessible to hydrolytic attack resulting in a decrease in the degree of polymerization. A pictorial representation of this delignification scheme is shown in Fig. 9.15.

Hemicelluloses hydrolyse and dissolve at acidic AVAP fractionation conditions. Hemicelluloses removal proceeds essentially in two phases—*initial* and *bulk*. More than half of hemicelluloses are removed in the *initial*, relatively short, phase. In this phase hemicelluloses are likely removed together with lignin as lignin-carbohydrate complexes (LCCs) [72]. During the second phase (called “*bulk*” phase) the removal is substantially slower and is first order in mannan and xylan. The lower removal rate of spruce glucomannan and xylan during the *bulk* phase may be related to the morphology of this residual fraction. Specifically this fraction of glucomannan is closely associated with cellulose in the original wood and is “crystallized” onto cellulose during the *initial* phase [72]. Also in the course of the *initial* phase most of the labile side units of the wood polysaccharides as well as pectins are removed [71].

Glycosidic bonds in cellulose are randomly hydrolyzed at the acid conditions of the AVAP process, leading to a decrease in average Degree of Polymerization (DP) of cellulose. However, for conventional pulps the DP is still higher than 1,000 and cellulose is retained in high (or full) yield in the fibrous residue. For cellulose nanocrystals production, hydrolysis is extended to the third stage (see below). The higher cellulose yield of the AVAP process for conventional pulps compared to alkaline processes is related mostly to the absence of peeling reactions in the former.

When subjected to heterogeneous acid hydrolysis, cellulose exhibits a very fast initial hydrolysis rate which is attributed to the presence of so-called “weak links”, attributed to inductive effects of electrophilic substituents (e.g. carboxylic groups) or to physical strains at the folds of cellulosic microfibrils. In the slower second stage, hydrolysis of the “regular” glycosidic bonds takes place in the amorphous regions. After the amorphous cellulose is hydrolysed, the cellulose hydrolysis enters a third, slower stage during which the DP approaches the so-called levelling-off DP value that correspond to the length of the cellulose crystallites.

Similarly to acid sulfite pulps, AVAP pulps have a considerably higher cell-wall pore volume (i.e. fiber swelling) and lower cell-wall cohesion compared to Kraft pulps which explains the fact that AVAP® pulps refine to fibrils much faster [73]. Another explanation for the lower refinability of Kraft pulp accord is that paracrystalline regions of cellulose become amorphous during cooking in a cellulose-swelling medium, e.g. alkaline solutions [86]. On the contrary, acid sulfite and AVAP® liquors are non-swelling agents for cellulose. The higher fraction of amorphous cellulose in Kraft pulp leads to higher energy absorption during beating and thus to less fracture.

The high energy needed to break fibers into fibrils is of great concern for the production of cellulose nanofibrils. However, because of their low refining energy consumption, AVAP pulps are highly suitable for nanocellulose production. In addition, increased fiber swelling (internal fibrillation) also leads to easier rupture of the loosened internal fiber wall structure into fibrils [73]. Evidence for the lower energy required to produce nano/microfibrillar cellulose from AVAP pulps is provided in a recent fundamental study by Morales et al. 2014 [87]. In this study AVAP® fibers were subjected to shear forces that broke up the cell wall structure and produced lignocellulose nanofibrils (LCNF) as a gel-like dispersion. Ten passes through the microfluidizer were sufficient to yield nanofibrils with diameters of less than 20 nm. This represents a significant reduction in energy consumption compared to nanofibrillation of other lignocellulosic materials that required more than 20 passes to attain similar results [88]. Research related to differences in energy consumption upon nanofibrillation of softwood fibers with various lignin contents have been reported [89, 90]. However a most important finding by Morales et al. 2014 is that AVAP fibers obtained at widely different fractionation conditions allowed the production of LCNFs at similar energy costs despite the significant differences in cell wall composition [87].

## **9.5 Manufacturing Challenge: Hydrophobic surface modification for Incorporation into Plastics**

Since cellulose is hydrophilic, nanocellulose does not disperse well in hydrophobic materials such as oils, solvents, or polymers such as polyethylene (PE), polypropylene (PP) or polylactic acid (PLA). As such, an active area of research has

been the chemical modification of the reactive surface  $\text{CH}_2\text{OH}$  components of nanocellulose to make the surface hydrophobic and compatible with hydrophobic media. The hydrophobic surface modification is used to improve not only the distribution of nanocellulose in polymers, plastics, or resins during composite processing, but also interfacial compatibility between the particles and matrices. By limiting hydrogen bonding that contributes to polar character of the nanocellulose, lower degree of hydrophilicity of nanocellulose can be anticipated [24, 91–94].

As discussed below, hydrophobic surface modification of nanocellulose has been successfully performed using various chemical treatments. However the laboratory methods demonstrated are not expected to be economically feasible at large scale due to the use of exotic and expensive solvents and grafting chemicals. API's low cost solution to this challenge is also presented below after a review of current methods.

Two primary approaches are most often demonstrated for the chemical surface modification of nanocellulose: physical adsorption and covalent bonding. For the physical adsorption approach, surfactant and polyelectrolyte solutions are used to tune the surface properties of nanocellulose [13, 91, 93, 95, 96]. Modifying the surface with surfactants improved particle/matrix interactions and dispersion quality [97, 98]. However, migration of the adsorbed moieties from modified nanocellulose surface into the matrix is the main drawback for this approach [91, 93]. The added surfactant or polyelectrolyte could induce weakness in strength leading to lower overall mechanical performance of polymer composite even though nanocellulose compatibility is improved [97]. Surface chemical reaction is introduced to form stable covalent bonding on the hydroxyl groups of nanocellulose.

Covalently bonded hydrophobic surface modification methods of nanocellulose are mainly molecule grafting or polymer grafting [13, 91–93, 96, 99]. Molecule grafting involves esterification where reagents containing carboxylic acid, acid anhydride, or acyl chlorides are used to perform esterification. The resulting nanocellulose ester derivatives, such as acetylated nanocellulose [41, 100–103], facilitate an increase in the degree of hydrophobicity indicated by higher water contact angle. The change in contact angle value varies depending on the degree of substituted hydroxyl groups of nanocellulose. Contact angle values up to  $115^\circ$  have been reported for acetylated nanocellulose using acetic anhydride in pyridine medium [100, 101]. Similarly, hydrophobization of nanocellulose with contact angle value of approximately  $105^\circ$  can also be achieved using alkylketene dimers (AKD) in the cellulose solvent 1,3-dimethyl-2-imidazolidinone/lithium chloride (DMI/LiCl) [104]. Recently, alternative esterifications using environmentally friendly approaches that minimize toxic solvent (or reagents) or solvent exchange process are proposed. Esterifications of various anhydrides, including acetic, butyric, hexanoic and alkenyl succinic anhydrides, and fatty acids chlorides, such as hexanoyl and stearyl chloride, under ionic liquid have been successfully reported to give contact angle values in the range of  $80$ – $104^\circ$  [103, 105]. Gas-phase esterification through a vapor mixture of trifluoroacetic acid anhydride and acetic acid can also reduce the hydrophilicity of nanocellulose [106]. AKD nano-emulsion exhibits water-based esterification with a contact angle value of  $105.8^\circ$  [107].



Another common molecule grafting method for nanocellulose surface hydrophobization is silylation. Surface silylation with chlorodimethyl isopropylsilane in toluene exhibits improved contact angle values in the range of 117–146° [108]. Similarly, silane treatments in acetone medium using 3-aminopropyltriethoxysilane and 3-glycidoxypropyltrimethoxysilane increase contact angle values to 90 and 64°, respectively [109]. Other coupling agents, such as titanate modifier (Lica 38), also demonstrate hydrophobic surfaces with contact angles of 110° [109].

Hydrophobization surface modifications can also be achieved by polymer grafting. The grafted polymers decrease the polar character of the nanocellulose and considerably increase their apolar character. Polymer grafting generally proceeds either through “grafting from” or “grafting onto”. The “grafting from” approach involves growing polymer chains from the active sites of cellulose, while “grafting to” involves attaching pre-formed polymer chains onto the cellulose backbone [93, 95, 96, 110–113].

The “grafting to” approach is typically mediated by a coupling agent to attach the high molecular weight hydrophobic polymer to the surface of nanocellulose [93, 96, 112]. Coupling agents like isocyanate, peptide, or anhydride moieties have been reported to effectively perform chemical surface modification on nanocellulose [95, 96, 112, 113]. The time scale for activation and grafting steps in this method is very rapid compared to that of “grafting from” [114]. The grafting density, however, is expected to be low due to steric hindrance of long polymer chains [93, 95, 110, 112, 115].

The “grafting from” approach is introduced in order to achieve high grafting density. Common methods include conventional free-radical graft polymerization, direct oxidation, ionic graft polymerization, and ring opening polymerization [95, 111, 113, 114]. Various free-radical initiators such as dibenzoyl peroxide (BPO), azobis(isobutyronitrile) (AIBN), potassium persulfate, potassium permanganate, and Fenton’s reagent, can be applied for conventional free-radical graft polymerization [114, 116], while direct oxidation typically utilizes transition metal ions like ceric ammonium nitrate to initiate free-radical exclusively on the cellulose backbone [111, 114, 116]. Monomer solubility in the solvent, monomer concentration, swelling properties of cellulose in solvent, generation of free radicals in the presence of the solvent, and the role of additives play important role in graft copolymerization [114, 117]. Several studies on nanocellulose polymer grafting based on ring opening polymerization have been reported for the grafting of  $\epsilon$ -caprolactone and L-lactic acid [113]. The most commonly accepted mechanism for this method requires stannous octoate,  $\text{Sn}(\text{Oct})_2$ , as the catalyst [113, 118]. Molecular weight of grafted polymer can be controlled based on the ratio of alcohol groups to monomers [118].

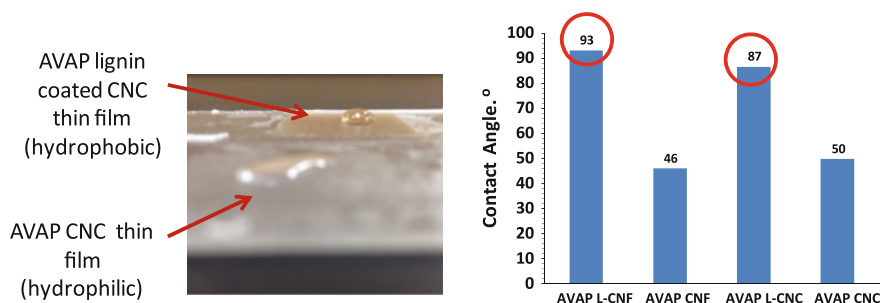
Major drawbacks of the “grafting from” method include inability to control the polydispersity and molecular weight distribution of the polymers [110, 111, 114, 119, 120]. Controlled polymerization methods can be achieved using living polymerization methods. These methods utilize no chain breaking mechanism, such as chain transfer or irreversible termination, as the polymer grows. Living polymerization methods, including atom transfer radical polymerization (ATRP), nitroxide

mediated polymerization (NMP), and reversible addition fragmentation chain-transfer (RAFT), have been successfully introduced to modify nanocellulose [110, 111, 114, 119, 120]. However, these treatments are currently very costly [110].

API's low cost method of precipitating the lignin that was dissolved from biomass during the AVAP pretreatment step onto the surface of the cellulose nanoparticles makes a fully hydrophobic surface that has been shown to be compatible with hydrophobic polymers. As shown in Fig. 9.16, thin films of lignin coated nanocellulose have significantly higher water contact angles compared to the pure cellulose varieties.

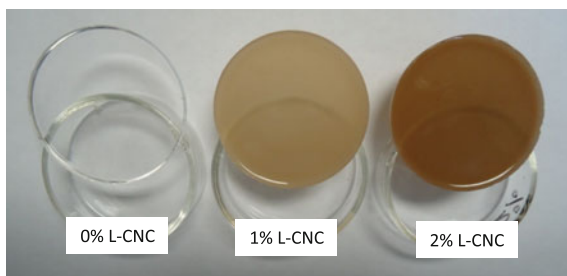
As shown in Fig. 9.17, API's freeze-dried lignin coated cellulose nanocrystals (L-CNC) were easily dispersed in highly hydrophobic silicone. The optical translucency of the composites confirms that the nanoparticles were dispersed as individual particles without agglomerations. Freeze-dried and spray dried L-CNC has also been dispersed effectively in other polymers including poly lactic acid, polyhydroxybutyrate, polypropylene, polystyrene, and polyethylene.

Figure 9.18 illustrates that a good distribution and dispersion of nanoparticles within a composite matrix is critical for composite quality and strength advancement. Other factors impacting polymer composite quality that are offered by API's lignin-coated nanocellulose include high aspect ratio and interfacial compatibility between fiber surface and polymer matrix (i.e. wetting).

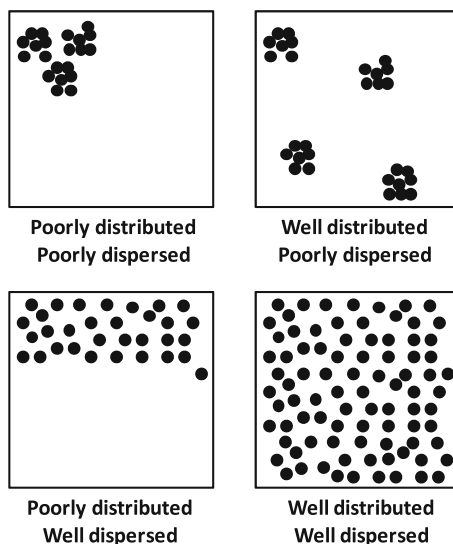


**Fig. 9.16** Water contact angle of lignin coated and pure cellulose AVAP nanocellulose

**Fig. 9.17** Lignin coated cellulose nanocrystals dispersed in silicone



**Fig. 9.18** Quality of distributed and dispersive mixing of nanoparticles in a composite matrix



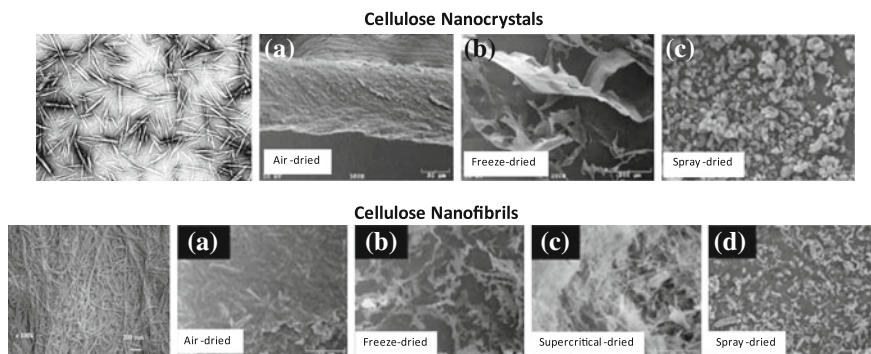
## 9.6 Other Nanocellulose Manufacturing Grand Challenges

There are a few grand challenges that remain to be solved in the field of nanocellulose manufacturing to ensure rapid utilization and commercialization including:

- Economical drying of nanocellulose suspensions and preservation of discrete nanocellulose particle morphology during drying for effective re-dispersion during end-use
- Development of international standards along the supply chain
- Development of rapid, low cost characterization methods for process and product quality control

### 9.6.1 Drying

Shipping high water content nanocellulose gels (90–97 wt% water) to their end-use destination is costly and impractical at large volumes and long distances. A nanocellulose drying method must be developed that is scalable, low cost, and that maintains product quality and particle morphology. The most common drying technologies for nanocellulose reported in the literature are freeze drying and spray drying. However, researchers have shown that drying methods can have a negative impact on nanocellulose properties including crystallinity, thermal stability, and irreversible inter-particle aggregation/bonding, known as hornification [121–123].



**Fig. 9.19** Cellulose nanomaterials obtained from different drying technologies

As shown in Fig. 9.19, cellulose hornification into large agglomerated structures that lose the individual nanoparticle morphology is a significant challenge across all conventional drying methods for both CNF and CNC [124].

Recently, Missoum et al. showed freeze drying to be a good method to prepare dried CNF that maintains discrete particle morphology by adding inorganic salt to a CNF suspension before drying. They indicated that the salt separates the CNF during the drying process so that aggregation and bonding of the particles during drying could be avoided [125]. The salt acts as an inter-particle “hydrogen bonding blocker”. As a result, the dried CNF could be redispersed in water as individual nanoparticles. Disadvantages of the method include that the large amount of salt used had to be removed by dialysis in water before end-use and that the method is not applicable for dispersion of nanocellulose in hydrophobic polymers or solvents.

API is actively involved in technology development for scalable, low cost drying of both lignin-coated nanocellulose and pure, hydrophilic nanocellulose. As discussed in the previous section, freeze-drying of API’s lignin-coated nanocellulose maintains individual nanoparticle morphology, as demonstrated by uniform redispersion in silicone. The lignin coating appears to function as a separator to prevent the hydrogen bond formation between cellulose during drying. Transmission electron microscopy (TEM) images support this conclusion (not shown). Development of a low cost, hydrogen bonding blocker for freeze-drying of conventional pure nanocellulose that maintains original surface properties and color/transparency is ongoing.

## 9.6.2 International Standards

The development of standards is critical for commercialization of new technologies. Standards represent agreed upon performance characteristics, technical criteria, measurement and reporting requirements, and importantly, terminology. For example, fibrillated cellulosic material is often referred to under a variety of names

including cellulose nanofibrils, cellulose microfibrils, cellulose microfibers, microfibrillar cellulose, nano-fibrillated cellulose, and refined pulp. This diversity and lack of precision in terminology creates confusion in the market about the relationship of characteristics and performance properties to name. As with most nanostructured materials, CNF and CNC are a mixture of fibrous materials with a distribution of sizes in terms of length, diameter, and level of aggregation. Sound, agreed upon definitions and requirements are critical for successful business interactions.

Recognizing this need, several organizations are working toward the development of international voluntary standards for nanomaterials and nanotechnology. The Nanotechnology Division of the Technical Association of the Pulp and Paper Industry (TAPPI) has held annual workshops since 2011 on the development of standards for nanocellulose and published a roadmap describing the planned activities under the International Nanocellulose Standards Coordination Committee (INSCC) [126]. Their efforts are coordinated with the American National Standards Institute (ANSI) Nanotechnology Standards Panel, and the International Standards Organization (ISO) Technical Committee 229. TAPPI is working toward terminology, measurement and standards for environmental health and safety (EHS) for forms of nanocellulose. At the time of writing, the Canadian Standards Authority has proposed an ISO Standard for characterization of cellulose nanocrystals based on a standard reference material developed by the National Research Council of Canada to measure particle morphology, purity and surface properties. The ISO TC 229 has developed about 40 standards relating to the measurement and evaluation of EHS of nanomaterials. However, few of these are specific to certain nanomaterials. Nanomaterials are challenging to assess because of measurement issues related to their small size, and different surface to volume characteristics. Nanocellulose adds to the challenge because it is an organic molecule with a high aspect ratio.

### ***9.6.3 Rapid, Low Cost Characterization Methods***

Another challenge to the large-scale economical manufacture of nanocellulose is converting the expensive, high-tech characterization methods employed within the field of nanotechnology to rapid methods for the operating floor. With this goal in mind, the U.S. National Institute of Standards and Technology (NIST) in conjunction with TAPPI held a workshop in June 2014 entitled “Measurement Needs for Cellulose Nanomaterials”. Invited representative manufacturers, researchers and product development stakeholders shared their metrology needs and efforts along the end-product value chain. Dr. Kim Nelson presented API’s measurement needs from a manufacturer’s perspective which includes [127]:

- Particle size distribution (current method: scanning electron microscopy (SEM), transmission electron microscopy (TEM))
- Lignin content (tedious wet chemistry)

- Crystallinity (X-ray diffraction (XRD))
- Thermal stability (thermal gravimetric analysis (TGA))
- Purity (inductively coupled plasma atomic emission spectroscopy (ICP-OES))

The principle disadvantages of the existing methods above are capital cost (~\$1.4 million total), length of time required for sample preparation and measurement (up to several hours), high level of technical expertise required, and high facility construction costs due to special environmental requirements for many of the instruments in terms of acoustic and mechanical vibrations, electromagnetic fields etc. API and other manufacturers desire methods that can be performed on the operating floor or in a standard process control laboratory, and that have low associated costs, short characterization and test times (minutes) and require minimal training and expertise. Development of these methods will require collaboration between academia, government, industry, and equipment suppliers.

### 9.6.4 Hiring and Education Needs

The technology, process development, and scale-up of versatile, economical nanocellulose materials require strong skills in chemical engineering with a preferred background in biomass chemistry and processing. The development of commercial end-use applications across a wide variety of industries requires candidates with multidisciplinary focus and skills across materials science, nanotechnology, and polymer processing and chemistry. Luckily, nanocellulose and nanotechnology are popular research topics at universities throughout the world. Recruiting in this field has not been a challenge. Our efforts to commercialize this new material requires members of our team to interact productively with colleagues from diverse fields including R&D and technology development, engineering, operations, marketing and business development, and finance. We seek individuals who are intellectually rigorous, creative, enthusiastic, energetic, and curious and who are committed to our company's mission of fostering adaptation of renewable bio-based materials. We find these traits ensure effective collaborative and team work throughout our business.

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