Cellulose Nanomaterials as Binders: Laminate and Particulate Systems

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ABSTRACT: A novel application of cellulose nanomaterials, particularly cellulose nanofibrils (CNF) as a binder in conventional and novel laminate and particulate composite systems is discussed. Using cellulose nanomaterials as a reinforcing agent in conventional polymer composites faces several difficulties: 1) there are no easy ways to dry the CNF and maintain nanoscale dimensions, 2) there are compatibility issues related to cellulose-polymer bonding, and 3) there are issues related to obtaining a good distribution and redispersion of nanoscale materials inside a polymer matrix. An alternative strategy is applications in which cellulose nanomaterials can be used in the aqueous suspension form without first needing to dry them. In addition, applications should be targeted that take advantage of the impressive strength properties of these nanomaterials while capturing the nanoscale material property enhancements in the final product. It has been demonstrated that CNF is able to bond lamina of paper together to produce a new class of all-renewable paper nanolaminates with exceptional mechanical properties exceeding many reinforced plastic formulations. It has also been demonstrated that particleboard panels can be successfully manufactured without any added formaldehyde by complete replacement of urea-formaldehyde resin. Efforts to use cellulose nanomaterials in paper applications are also reviewed as well as adhesion mechanisms involved in such composite systems. The future outlook and potential market opportunities concerning this new application of cellulose nanomaterials, as well as known and potential limitations and challenges in the way of commercialization efforts, are presented.

KEYWORDS: Cellulose nanofibrils, binder, composites, laminates, particleboard, paper

1 INTRODUCTION

Cellulose nanomaterials, mainly cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC), have received a significant amount of attention in the last few years because of the promise of new, lightweight, and high strength products made from a sustainable resource. A number of review articles have been written that summarize the work [1–8]. Research groups have developed various ways to produce nanoscale cellulose by both mechanical and chemical methods and have incorporated these materials on a lab scale into polymers or other applications [1]. A recent review summarizes cellulose nanocomposites by processing methods [9]. In part, because of the physical form of the produced cellulose nanomaterials in the form of low consistency aqueous suspensions and partly because of current issues with developing appropriate drying and surface modification techniques for these highly interesting materials, most of the current applications of cellulose nanomaterials are limited to using them as additives for either water-based systems or hydrophilic polymeric resins. The relatively high price and large-scale unavailability of cellulose nanomaterials until very recently have also contributed to the general consideration of these materials as "additives" in conventional or novel systems.

A key roadblock to widespread use of CNF and CNC is a lack of large-scale applications. Using CNF or CNC as a reinforcing agent in a polymer melt has several challenges: 1) there are no easy methods to dry the material and maintain the nanoscale dimensions [10],

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2) there are compatibility issues related to cellulose hydrophobic polymer bonding, and 3) there are issues related to obtaining a good distribution and redispersion of nanoscale materials inside a polymer matrix. A better strategy is to find uses for cellulose nanomaterials where they can be utilized in the aqueous suspension form without first needing to dry them. In addition, applications should be targeted that take advantage of the impressive strength properties of these nanomaterials. With more data available on environmental health and safety issues, toxicology studies have also shown this material, even in dry form, to be relatively safe [9], which eliminates initial concerns regarding consumer safety considerations. Given the larger scale of production of CNF than CNC and the subsequent lower price of this type of cellulose nanomaterial, it is expected that CNF will eventually be used in large volume applications whereas CNC will find niche applications in specialty products.

It is also perceived that a key step towards commercialization of these materials is to find applications in which the materials are used in greater amounts and even to produce stand-alone end products. Herein, we are introducing a number of innovative approaches towards producing composite systems in which cellulose nanofibrils are used as the binder. These include production of a novel laminated nanocomposite manufactured from waste paper and an interior type particleboard product with no added formaldehyde-based adhesive as well as binder applications in paper and paper coatings. A review of adhesion mechanisms involved in the bonding process are presented in light of new findings of the strength of hydrogen bonds.

2 CNF AS THE BINDER: THE CONCEPT

Cellulose nanofibril makes excellent flexible and strong films by simply drying the material [1]. A field emission scanning electron microscope (FE-SEM) image of the CNF film made by casting a 0.5% solids content CNF suspension in a plastic petri dish followed by air drying is shown in Figure 1. The initial suspension was obtained by diluting the original 3% solids suspension produced on a pilot-scale by the Process Development Center of the University of Maine. The CNF material supplied by the University of Maine is produced through mechanical refining of bleached pulp by a low energy consumption method. The pulp is fed through a hopper into the refiner system where it is ground by the mechanical attrition of refiner plates in a continuous circulating flow until a fine fraction of over 95% is achieved. No chemical treatments are carried out and therefore the cellulose nanofibrils produced have no surface charge. The length scale of the nanofibrils is in the range of hundreds of nanometers whereas the widths can range anywhere from a few nanometers to 100 nanometers, giving the material a spaghetti-like look with very high aspect ratio. The image on the left is the upper side (air side) of the film whereas the image on the right depicts the lower side (dish side). Nanofibrils as narrow as 10 nm in thickness and as long as several micrometers in length are easily seen in both images. The clear difference between the two sides of the film is mostly related to the water evaporation process that occurs during casting and drying, leading to a more porous nanofibrillar structure on the top surface of the film and a much denser, tightly packed structure on the opposite side.

At film thicknesses on the micrometer scale, this structure can be considered to be a more or less plane isotropic system attributable to the considerable aspect ratio of CNFs and their tendency to lay flat in the x-y plane. Given that CNFs at low solid contents can be largely dispersed in water, a three-dimensional network of fibrils can be formed during the drying process that can encompass particles mixed with them and hold them together upon water removal. Considering
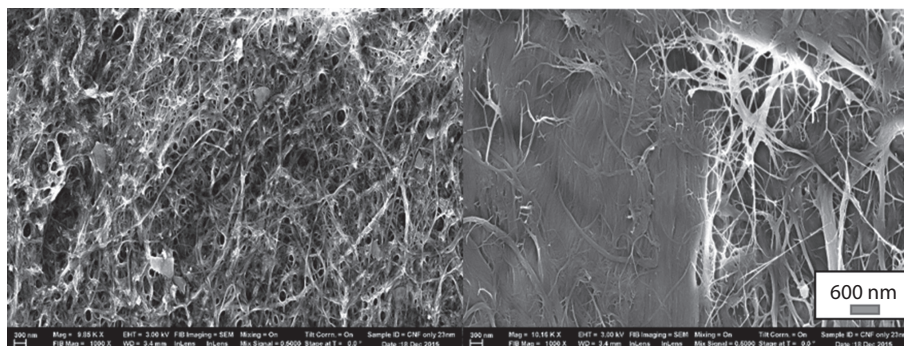

Figure 1 FE-SEM of the upper side (left) and lower side (right) of a film of CNF produced by casting a 0.5% solids content aqueous suspension.

the exceptionally high mechanical properties of cellulose nanoparticles [11] and excellent hydrogen bonding between cellulose nanoparticles and other types of cellulosic materials [12], cellulose nanofibrils can bind other cellulosic materials, including wood particles, pulp fibers and paper sheets, to form strongly bonded composite systems.

3 CNF AS BINDER IN COMPOSITE MATERIALS

3.1 Cellubound

Cellubound is UMaine's patent-pending nanolaminate product that takes advantage of the excellent binding capabilities of cellulose nanofibrils to bind sheets of paper into a dense, highly stiff and strong composite laminate. Figure 2 exhibits examples of the produced laminates, a patent-pending cross-laminating layup method and a sample flexural stress-strain curve of the produced laminates. Briefly, the production procedure involves dipping strips of paper in a CNF suspension, cross folding the soaked strips into a wet mat and hot pressing in a hydraulic press to the final thickness and density of the laminate. This sample has a flexural strength of about 100 MPa and a flexural modulus of 8 GPa, exceeding those for short glass fiber polypropylene composites at 50 wt% fiber content [13].

The Cellubound bio-nanocomposite laminate systems are fully renewable and biodegradable as well as strong and stiff enough to meet and exceed the intended application requirements. The laminate systems are expected to find applications in the automotive industry for interior door panels and headliners and in the packaging industry for secondary packaging materials where highly stiff and strong materials are desired. These two industry sectors are among the most viable industry sectors dealing with the everyday life of billions of people worldwide. Light weighting is a key area of focus in both industries for fuel economy and transportation costs likewise. Other future applications of such composite materials can be for the production of molded biodegradable containers that can be formed in a variety of shapes during or post processing.

Mechanical properties of such laminates can be readily engineered to meet the desired levels in various directions. Assuming a randomly oriented CNF network and machine-made paper sheets with different machine direction (MD) and cross direction (CD) mechanical properties [14], various combinations of unidirectional, cross directional and angle directional composite laminates can be produced. In such laminate systems, the mechanical properties of individual laminae, adhesion between the layers, laminate density as well as laminae orientation will be important attributes impacting the resulting material properties of the composite. The mechanical properties of individual laminae will depend on paper sheet properties and nanocellulose type and consistency as well as other additives used in the formulation. The paper sheets can also be sourced from waste paper streams, which will provide additional motivation for the industry.

Figure 3 shows the surface of one individual sheet of paper before and after dipping in the CNF suspension. The image on the left shows the surface of a regular copy paper used in the production of Cellubound. A rough surface structure as well as individual and clustered mineral particles are easily visible. The image on the right shows the same piece of paper dipped in a 0.5% solids content CNF suspension for 1 minute and air dried overnight. This is identical to the Cellubound production method with the difference that the sheet of paper is air dried and not hot pressed. A full coverage of the surface with nanosized CNF particles is seen, indicating the efficiency of the dipping method to at least surface cover the paper sheets.

The image on the left of Figure 4 is the inside surface of a Cellubound laminate made without using
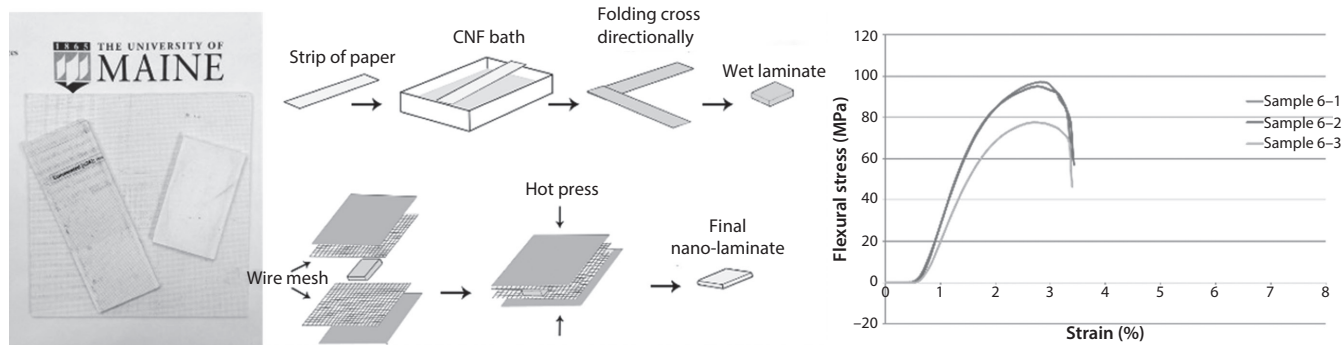

Figure 2 Sample laminates (left), cross-folding method (middle) and stress-strain curve of a sample (right).
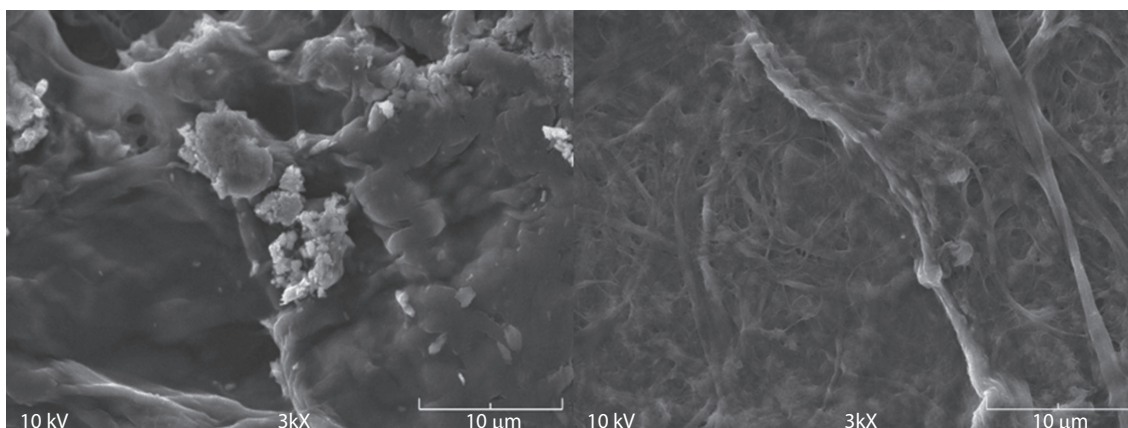
Figure 3 SEM micrograph of the surface of a regular copy paper (left) and the surface of the same paper after being dipped in a 0.5% solids content CNF suspension and air drying (right).
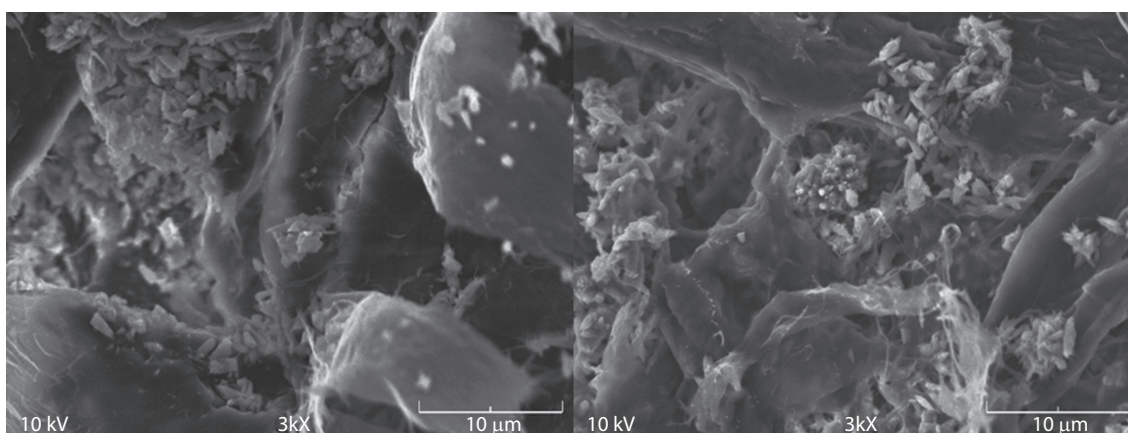

Figure 4 SEM micrograph of the peeled open inner surface of a paper laminate without CNF (left) and the same surface of the Cellubound (right).

CNF; that is by dipping the sheets of paper in pure water and then hot pressing them. The image is taken after the laminate is peeled open to separate the lamina edgewise. Mineral particles as well as clean pulp surfaces are observed. Small amounts of fibrillation are also observed that are attributed to the refining process of the pulp used to make the paper. The image on the right shows the peeled open inner surface of a Cellubound laminate made by dipping the paper sheets in a 0.5 wt% solids CNF suspension and hot pressing. More fibrillation on the surface can be seen, indicating the presence of CNF. In addition, minor agglomeration of CNF particles on the surfaces of pulp fibers can be seen as rugged topography when compared to the image on the left. The fact that individual fibers and mineral particles are observed here indicates two possibilities: first, the full coverage seen in Figure 3 when the paper is dipped in the CNF suspension might only be a surface phenomenon; that is,

the bulk of the paper sheets only received a smaller portion of the shorter CNF particle able to penetrate deep into the bulk. Second, the bonding strength at the interface between two adjacent paper layers is sufficient to result in delamination in the bulk of the paper layers and not at the interface between the two. This is in agreement with what was observed in flexural tests where no delamination was recorded in the failed specimens.

3.2 Particleboard Manufacture

Another binder application of CNF is as a complete replacement of the urea-formaldehyde resin used in the production of particleboard. Particleboard is a composite panel with wide applications to manufacture countertops, door cores, floor underlayment, and furniture. Particleboard is also regarded as a sustainable material because it utilizes wood residues from

other manufacturing processes that might otherwise be discarded. In 2012, North American particleboard manufacturers produced over 3.2 billion square feet (5.8 million cubic meters) of particleboard in 39 different facilities [15]. At an average density of 700 kg/m³, incorporation of 10% CNF in particleboards would translate into a potential market of 400,000 tons of CNF per year in North America.

One major drawback of particleboard is the use of formaldehyde, a well-known carcinogen, in its resin formulation and the subsequent formaldehyde emission both during manufacture and use [16–18]. Efforts have been made to lower formaldehyde emission from particleboard either through the use of an acrylic binder [19] or the newly developed soy protein resins [20] similar to the methods used for already commercialized plywood manufacture using soy resin [21]. At this time, however, urea-formaldehyde still continues to be the major resin used in the manufacture of particleboard and the issue of formaldehyde emission will continue to be persistent. By replacing the total amount of urea-formaldehyde resin with cellulose nanofibrils (CNF), the well-known hornification phenomenon [22], which takes place upon drying and dewatering of cellulose nanomaterials and is an issue for redispersion, can be well taken advantage of to produce strong bonding between wood particles in a no-added-formaldehyde manufacturing process. CNF provides an all-sustainable option for these systems as it does not rely on petroleum-sourced polymers or chemicals.

Although many research efforts have focused on the production of all-polysaccharide composites [23], the use of cellulose nanofibrils as a binder for wood composites is relatively unexplored in available peer reviewed publications. Kojima *et al.* produced composite boards with ball-milled cellulose fibers and wood flour [24]. Effects of ball milling conditions (i.e., defibrillation intensity) as well as the fiber binder content on flexural strength and modulus, water absorption and thickness swelling of the boards were evaluated. Mechanical properties were optimized at 20 wt% fiber binder level and physical properties were improved at longer ball milling times. No study on bonding mechanisms or adhesion performance was carried out. Moreover, the study was limited to boards of 3 mm thickness, not comparable to commercial particleboard panels. The same research group published a similar study in which a lignin containing CNF (LCNF) was used to bind wood flour particles [25]. With the same size limitation as the earlier publication, lower mechanical properties than those obtained when CNF was used were obtained.

Initial attempts made at the University of Maine to use CNF as the binder for particleboard production have been successful. This work was built upon a recent patent awarded to the University of Maine outlining the production of particleboard samples using CNF as a binder in mixture with mineral additives [26] expanding the idea into a process and final product. Figure 5 shows preliminary samples made by mixing southern pine wood particles with a 3 wt% CNF suspension and pressing. At 15 wt% CNF content, the mixture to be hot pressed contains over 600% moisture content (based on dry weight of the wood particles), making it impossible to hot press owing to the need to evaporate a large quantity of water and subsequent burst and delamination issues. Interestingly, most of the water in the mixture can be extracted using a simple cold press operation. This reduces the initial moisture content to around 100%, which is manageable by controlling the hot press cycle. Reduction of moisture content without using a heat source provides an additional energy savings as opposed to the initial drying method reported by Kojima *et al.*, who used a heated compounding machine to lower the initial moisture content to 30% [27].

As seen in Figure 6, the mechanical properties of the produced particleboard panels increase as the density of panels increases. The lines marked M and
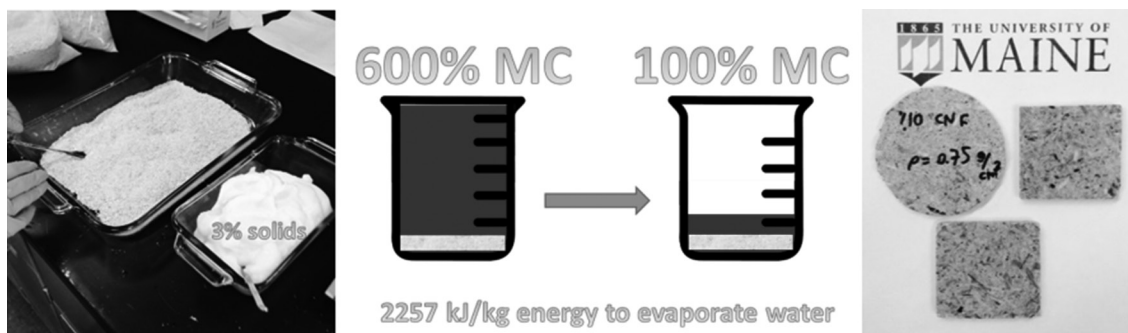

Figure 5 Raw materials (left) to produce CNF bound particleboard (right). A 500% reduction in the initial moisture content is achieved without using a source of heat, leading to significant energy savings (center).
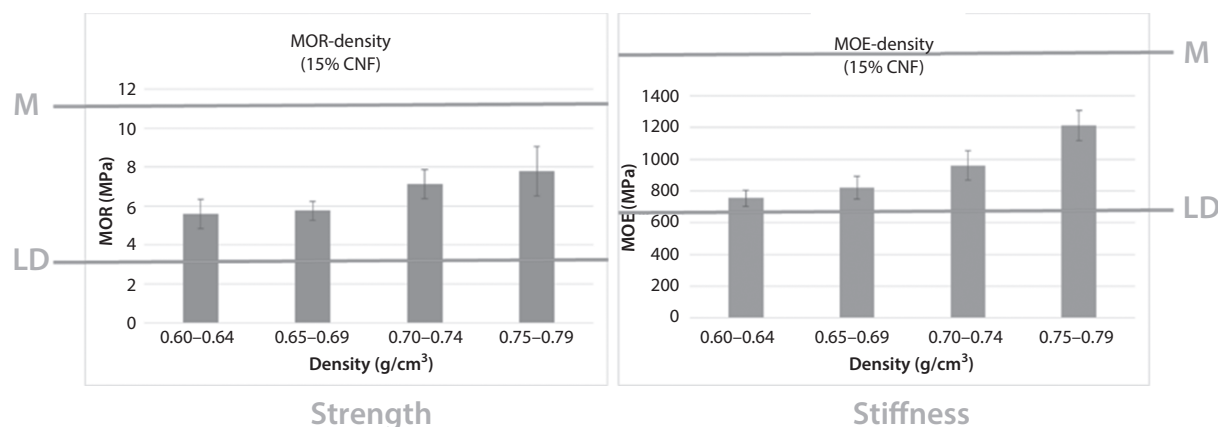
Figure 6 Comparison of the mechanical properties of preliminary particleboard panels made by using CNF as the sole binder. LD = low density; M = medium density as defined in ANSI A208.1-1999 [28].
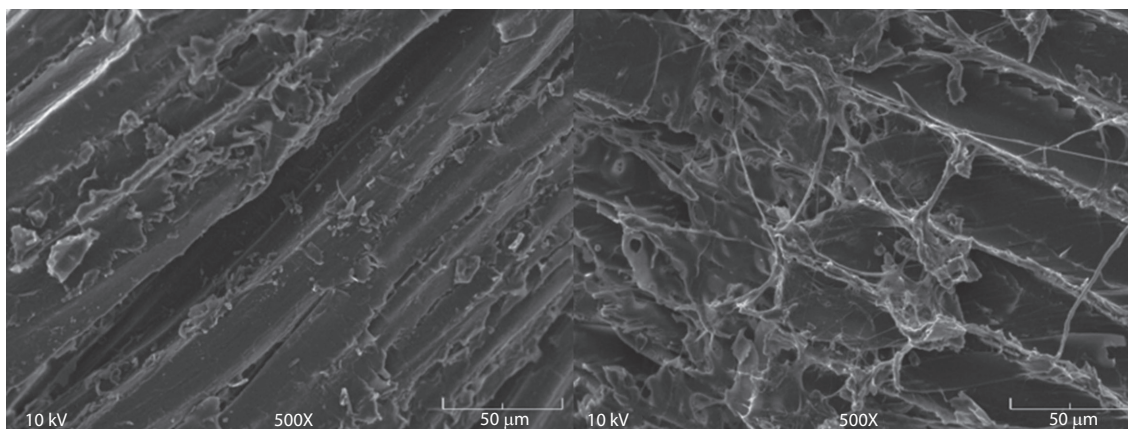

Figure 7 SEM image of the surface of a southern pine particle (left) and a particle mixed with a 3% solids content CNF after drying.

LD show the minimum modulus of rupture (MOR) and modulus of elasticity (MOE) of medium-density and low-density particleboard panels as described in ANSI 208.1-1999, the relevant industry standard [28]. The preliminary samples shown in Figure 6 easily meet the standard minimum levels of both properties for the low-density panels (densities below 0.65 g/cm³) but are approximately half the levels of medium-density fiberboards.

Figure 7 is helpful to demonstrate how wood particles can be bound together using CNF. The image on the left is the surface of a southern pine wood particle used in the production of the CNF-bound particleboard panels. The image on the right shows the surface of a similar wood particle after being mixed with a CNF slurry and air dried overnight. CNF nanofibrils are easily observed being distributed over the particle surface with some agglomerated into platelet shapes and some preserving their fibrillar nature. It is assumed that CNF particles in the suspension will penetrate into the pores and voids in the structure of wood particles. Once the wood particles with CNF surrounding them are in contact and hot pressed, a three-dimensional network of CNF fibrils forms and encompasses the particles in the panel structure, giving it strength and stiffness.

4 CNF AS BINDER IN PAPER AND PAPER COATINGS

4.1 Paper Reinforced with Cellulose Nanomaterials

It is well known in the area of papermaking, that beating and refining paper fibers often leads to an increase in strength of the produced paper. This is caused by the fibrillation of the fiber surface, generating a number of fine fibers attached to the large fiber [29]. These fine fibers increase the relative bonded area when two

paper fibers are dried near each other. It seems natural to explore the addition of nanometer scale fibers to increase paper strength properties.

A natural use for cellulose nanomaterials would be as an additive to a paper furnish, especially assuming that these materials would be produced on-site. Brodin *et al.* reviewed the use of CNF in paper furnishes and coatings [30]. A range of paper fibers were tested from mechanical pulps [31], thermo-mechanical pulps (TMP) [32–33], and chemical pulps [34–36]. A number of cellulose nanofiber types have also been studied, such as mechanically produced CNF [33, 37–38], sometimes called microfibrillated cellulose (MFC) or nanofibrillated cellulose (NFC) or some variation of these names. Chemically produced cellulose nanocrystals were studied by Ioelovich [39]. TEMPO-oxidized CNFs have also been tested as an additive in paper-making by a number of groups [40–43].

For all the above-mentioned studies, the addition of CNF or similar nanofibers increased the mechanical properties by a significant amount. The increase in the tensile index was in the range of a 20 to 300% increase. Su *et al.* reported a 600% increase in the tensile strength [44]. Potulski *et al.* reported a 300% increase in paper strength with CNF and no other additives [37]. In a number of these studies, the increase in strength is attributed to the increased bonding or adhesion between paper fibers caused by the nanofibers.

A key issue if fines are added to a paper furnish is the retention of those in the final sheet. This retention is often accomplished by the addition of a retention aid such as a cationic polymer or cationic starch. These retention systems may influence the strength properties as well, but the effects of these additives are challenging to quantify. An important drawback on using CNF in papermaking is the drainage and dewatering behavior. The addition of CNF decreases drainage rates as expected. However, Eriksen *et al.* report that if a balance between various properties of the retention aid and the CNF content can be obtained, good drainage and strength increase can be obtained [32].

As a filler is added to a sheet, or as fibers are recycled several times, the strength properties of the paper decrease. Here, opportunities to use CNF as a bonding aid have great potential. Mörseburg and Chinga-Carrasco have presented excellent images of how CNF can help bond cellulose fibers to minerals [33]. Figure 8 shows their results: cellulose fibers have little interactions with minerals but nanometer-scale cellulose fibers do seem to bond with the minerals. The goal is often to increase the mineral content of paper without decreasing the mechanical properties and this provides an interesting opportunity for cellulose
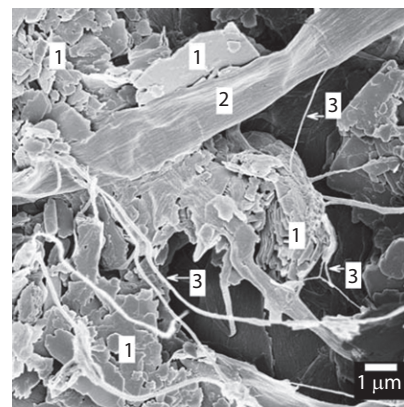

Figure 8 Surface field emission (SEM) image of an uncalendered paper sample. The image shows clay particles (1), fibrillar material from the TMP accept fibers (2) and fibrils (3). Note the nanosized fibrils extending on the surface and interacting with the clay and fibrous material. (Reprinted with permission from [33].)

nanofibers to be used to enhance fiber/pigment bonding. Delgado-Aguilar *et al.* demonstrated that the strength of recycled newsprint can be improved by 82% with the addition of CNF [31].

4.2 CNF as a Binder in Conventional Paper Coatings

Lavoine *et al.* reviewed the potential of using CNF as a coating on paper [45], but the use of CNF as a binder in a conventional paper coatings is also of potential interest. If latex use in the binder system can be reduced and improved properties of the coated paper obtained, then CNF could be a benefit to coated papers and coated paperboards. Two groups reported on the potential of adding CNF up to 5 parts per hundred parts pigment to a paper coating, aiming for better mechanical properties or for the potential to replace latex with CNF [46, 47]. These studies show the prospective of obtaining good mechanical properties of a coating layer even if latex content is reduced. We found an increase in bending stiffness and printing pick resistance with coatings that contain CNF [46]. Figure 9 shows the stiffness results for various levels of CNF addition; note that the values for CNF containing coatings are often 30% larger than similar coatings made with starch and latex.

Figure 10 shows the pick velocities that various coating formulations can obtain. A high pick velocity indicates a strong coating layer that is able to withstand forces in the out-of-plane direction. Again, coatings that contain CNF are stronger than coating layers that contain the normal co-binders of starch and latex or only latex.
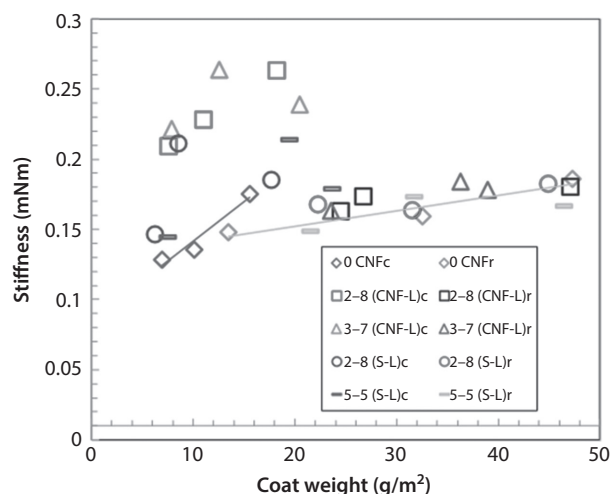
Figure 9 Taber stiffness results for papers coated with pigmented coatings that contain CNF and latex compared to those that contain starch and latex. 0 CNFc and 0 CNFr are blade coated and rod coated samples, respectively, with no CNF added, only latex as a binder. The lines fit these results. Numbers, such as 2–8, 3–7 or 5–5, show the ratio of CNF to latex or starch and latex used as binders. S = starch; L = latex. (Reprinted with permission from [46].)
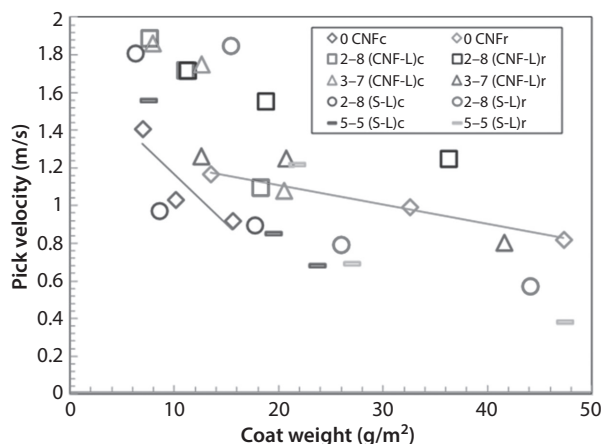

Figure 10 Pick velocity results for papers coated with pigmented coatings that contain CNF and latex compared to those that contain starch and latex. Abbreviations are the same as in Figure 9. (Reprinted with permission from [46].)

A number of other groups have reported on the potential to use CNF in paper coatings to modify the rheology of these coatings and the final properties. It has been shown how CNF added to a paper coating changes the flow properties and the final properties of the coated product [48–50]. Ridgway and Gane showed how the addition of CNF can increase the stiffness of coated board grades [51]. Bonding of pigmented layers using CNF has also been reported [52–53].

Table 1 Comparison of cellulose adhesion interactions relative to length scale [57].

Category of adhesion mechanism	Type of interaction	Length scale
Acid-Base interaction	Charge	0.1 – 0.4 nm
Hydrogen bonding	Charge	0.235 – 0.27 nm
Lifshitz-van der Waals	Charge	0.5 – 1 nm
Mechanical	Interlocking or entanglement	0.01 – 1000 µm
Diffusion	Interlocking or entanglement	10 nm – 2 mm

5 HOW DOES CNF BOND CELLULOSIC MATERIALS?

5.1 Review of Adhesion Mechanisms

The currently accepted mechanisms of adhesion are listed below [54–55]:

1. Mechanical interlocking
2. Electronic or electrostatic
3. Adsorption (thermodynamic) or wetting
4. Diffusion
5. Chemical (covalent) bonding
6. Acid-base interactions
7. Theory of weak boundary layers

Adhesion theories that have been examined in an effort to explain the bonding of cellulose to cellulose include: mechanical interlocking, adsorption or wetting theory, diffusion theory, acid-base theory and the theory of weak boundary layers [56]. Practical adhesion in cellulose-based materials occurs over a length scale ranging from the nanoscale (molecular) to millimeters (Table 1).

The bond strengths of various types of chemical bonds and intermolecular forces that can contribute to adhesion are listed in Table 2. Ionic or electrostatic interactions and covalent bonding exhibit the greatest bond strengths. In cellulose-cellulose adhesion, hydrogen bonds and Lifshitz-van der Waals forces account for the majority of intermolecular forces contributing to adhesion bond strength. Covalent bonds are not thought to occur in the bonding of cellulose-cellulose interactions. In fact, hydrogen bonding has long been believed of central importance in the intermolecular forces contributing to adhesion in cellulose [58]. There is controversy in the cellulose research field regarding whether Lifshitz-van der Waals forces or hydrogen bonding contribute more to bond strength in cellulose-cellulose bonding. An improved understanding of hydrogen bond strength

Table 2 Bond strength of various types of chemical bonds and intermolecular forces.*

Chemical bond or intermolecular force	Bond strength (kJ/mol)	Bond length
Electrostatic (Ionic)	418	0.1 – 1 μm
Lifshitz-van der Waals	8.4 – 21	0.5 – 1.0 nm
Covalent bonding	147 – 628	0.1 – 0.2 nm
Hydrogen bonding**	4.2 – 188	0.15 – 0.45 nm

*adapted from [57].
**adapted from [59].

Table 3 Cellulose surface energy components determined via inverse gas chromatography (IGC).

Cellulose type	γ (mJ/m²)	K_A	K_B
Bleached Kraft Pulp 22 °C [63]	43.8	0.09	0.35
Recycled Kraft Pulp 22 °C [63]	45.0	0.09	0.28
Cotton 20 °C [64]	40.0	0.06	0.50
Sisal 20 °C [64]	35.5	0.38	0.74
Microcrystalline cellulose 90 micron 30 °C [65]	55.7	0.43	0.60
Microcrystalline cellulose 50 micron 30 °C [65]	59.7	0.47	0.67
Spray-dried nanofibrillated cellulose 30 °C [66]	52.6	0.42	0.63
Spray-dried cellulose nanocrystals 30 °C [66]	60.5	0.66	1.39
Supercritical dried NFC 30 °C [66]	98.3	0.68	1.28

has elevated its importance in the adhesion of cellulose-based materials [59–60]. Molecular modeling work using *ab initio* calculations has documented theoretical hydrogen bond strength between paired cellulose chains to be 202 kJ/mol [61]. However, other research suggests that Lifshitz-van der Waals forces are most important in cellulose-cellulose bonding [62]. Additional research should address this controversy.
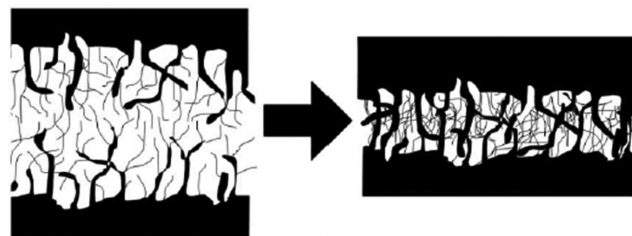
The dispersive surface energy (γ) and acid-base character (K_A and K_B) of various types of cellulose determined by inverse gas chromatography are listed in Table 3. The dispersive surface energy is greater for cellulose on the micron- and nanoparticle length scale compared to pulp and plant fibers that are on the millimeter length scale. The acid-base character of the micron- and nanoscale particle sizes is also greater for the fine scale cellulose than the pulp samples. These surface energy component data support the improved adhesion characteristics of the smaller length scale cellulose particles. A possible explanation for the higher surface energy and acid-base character on the smaller size scale may be attributed to the greater surface area and hydroxyl functional group availability.

5.2 Cellulose-Cellulose Bonding Phenomenon

Cellulose-cellulose bonding also relies on entanglement via diffusion interactions and mechanical interlocking. A conceptual illustration showing the mechanical interactions and diffusion mixing of macromolecular cellulose segments extending from two surfaces condensing into a bonded adhesion joint is shown in Figure 11 [58]. In the bonding of pulp fibers to make paper or fiberboard, the refining process provides for fibrillation of the fibers on the micron scale to promote mechanical interlocking of the fibers. There are also smaller molecular segments that arise both from the refining process and the pulping process that can contribute to interdiffusion. Eriksson performed

Figure 11 Conceptual illustration showing diffusional mixing of macromolecular cellulose segments extending from two wetted surfaces condensing into a bonded adhesion joint. (Reprinted with permission from [57].)

a comprehensive study on the influence of molecular adhesion on paper strength [67]. Amorphous cellulose offers greater possibility for surface groups to arrange themselves to participate in molecular interactions in a cellulose-cellulose adhesive bond.

On a smaller length scale, cellulose nanofibrils are able to be more easily arranged and interact to contribute to stronger cellulose adhesion (see Figure 1). The oven-dried CNF exhibits a bulky, coalesced structure on the micron scale where it is difficult to differentiate individual CNF fibrils. The freeze-dried CNF is a more porous structure with both nanoscale and millimeter scale morphology. The adhesion of oven-dried CNF and freeze-dried CNF creates interesting materials on the macroscale. Oven-dried CNF behaves like a bulk plastic material while freeze-dried CNF produces a low-density foam material [68].

The adhesion theory of weak boundary layers has garnered considerable attention in the pulp and paper field over the years because of the issue of fiber "hornification" or reduction in bonding capacity in

the recycling of pulp fibers to make paper [65, 69]. "Hornification" refers to both the changes in bulk behavior of cellulose fibers from reduced swelling ability and reduction in fiber bonding. The reduction in fiber bonding is attributable to the surface properties of the fibers: drying of fibers decreases wettability and reduces the number of surface hydroxyl groups. Although the total surface energy of once dried pulp fibers is similar to virgin fibers, the acid-base or polar surface energy of dried fibers is reduced as compared to the nonpolar surface energy component [63]. The reduction in cellulose acid-base surface energy during drying is also manifest on the nanometer length scale [66]. Depending on the drying conditions, the surface energy of cellulose nanofibrils are reduced except in the case of careful drying using supercritical carbon dioxide shown in Table 3. Once dried, unless surface modification or other surface treatments of the cellulose nanofibrils are conducted, it is difficult to rewet or properly redisperse them in water. This suggests that the "hornification" or reduction in surface bonding of cellulose is multiscalar from the millimeter down to the nanometer length scale. Hydrogen bonding in the bulk cellulose material is so strong that water has a difficult time penetrating and redispersing the cellulose nanofibrils.

The presence of water in any bonding phenomenon involving cellulose nanomaterials is essential. Dried or surface modified CNF in organic solvent completely loses its adhesion potential, in a similar manner to the papermaking process when water is not used in the process. This further highlights the key role of hydrogen bonding in the adhesion mechanism of cellulose nanomaterials.

6 CONCLUDING REMARKS

Binder applications of cellulose nanomaterials provide new opportunities for high volume applications and production of these highly interesting renewable nanomaterials. In contrast to traditional "additive" or "reinforcement" applications of nanocellulose that are limited in scope and volume and suffer from the lack of appropriate drying methods, binder application removes the need for an initial drying step by direct application in aqueous conditions, preserving the nanometer scale of the material in the end product. The Cellubound and adhesive-free particleboard products introduced here are perfect examples of the potential to use cellulose nanomaterials in a new way. The paper industry is by far the most natural industry target for cellulose nanomaterials. The review presented here emphasizes that CNF can be

successfully added to conventional paper coatings to enhance strength properties.

From the wide ranging research activity on cellulose adhesion and surface properties reported in the literature, it has been revealed that most of the fundamental adhesion mechanisms can be applied to cellulose-cellulose bonding. The entanglement mechanisms of mechanical interlocking on the macro length scale and diffusion entanglement on the molecular length scale have been shown to occur in cellulose-cellulose bonding. The charge interactions of acid-base, Lifshitz-van der Waals forces and especially hydrogen bonding have also been shown to be important in cellulose-cellulose bonding. The nature of cellulose-cellulose bonding mechanisms continues to be of considerable interest in the field.

Challenges remain in the binder applications of cellulose nanomaterials as well. The current technologies to produce conventional particleboard panels, for instance, rely on dry manufacturing processes where water tolerance is low. To avoid imposing significant capital costs to existing particleboard and fiberboard mills, efforts need to be directed towards low moisture mats that can be pressed in conventional multidaylight presses. Addition of CNF to paper and paper coatings increases the viscous and elastic properties of the coating, which may lead to application issues. However, the final mechanical properties are often increased to a significant extent. A balance is needed between CNF incorporation that still allows application but results in improved properties of the final coating layer.

REFERENCES

1. A. Dufresne, *Nanocellulose: From nature to high performance tailored materials*, Walter de Gruyter, Berlin (2012).
2. D. Klemm, F. Kramer, S. Moritz, T. Lindström, M. Ankerfors, D. Gray, and A. Dorris, Nanocelluloses: A new family of nature based materials. *Angew. Chem. Int. Ed.* **50**(24), 5438–5466 (2011).
3. D.J. Gardner, M. Blumentritt, A. Kiziltas, E.E. Kiziltas, Y. Peng, and N. Yildirim, Polymer nanocomposites from the surface energy perspective. *Rev. Adhes. Adhes.* **1**(2), 175–215 (2013).
4. M.A. Hubbe, O.J. Rojas, L.A. Lucia, and M. Sain, Cellulosic nanocomposites: A review. *BioResources* **3**(3), 929–980 (2008).
5. H. Charreau, M.L. Foresti, and A. Vázquez, Nanocellulose patents trends: A comprehensive review on patents on cellulose nanocrystals, microfibrillated and bacterial cellulose. *Recent Pat. Nanotechnol.* **7**(1), 56–80 (2013).
6. C.J. Chirayil, L. Mathew, and S. Thomas, Review of recent research in nano cellulose preparation from

different lignocellulosic fibers. *Rev. Adv. Mater. Sci.* **37**, 20–28 (2014).

7. R.J. Moon, A. Martini, J. Nairn, J. Simonsen, and J. Youngblood, Cellulose nanomaterials review: Structure, properties and nanocomposites. *Chem. Soc. Rev.* **40**(7), 3941–3994 (2011).

8. I. Siró and D. Plackett, Microfibrillated cellulose and new nanocomposite materials: A review. *Cellulose* **17**(3), 459–494 (2010).

9. K. Oksman, Y. Aitomäki, A.P. Mathew, G. Siqueira, Q. Zhou, S. Butylina, S. Tanpichai, X. Zhou, and S. Hooshmand, Review of the recent developments in cellulose nanocomposite processing. *Composites Part A.* In press (2015).

10. Y. Peng, D.J. Gardner, and Y. Han, Drying cellulose nanofibrils: In search of a suitable method. *Cellulose* **19**(1), 91–102 (2012).

11. A.B. Reising, R.J. Moon, and J.P. Youngblood, Effect of particle alignment on mechanical properties of neat cellulose nanocrystal films. *J. Sci. Technol. For. Prod. Process.* **2**, 32–41 (2013).

12. J.P. Joseleau, V. Chevalier-Billosta, and K. Ruel, Interaction between microfibrillar cellulose fines and fibers: Influence on pulp qualities and paper sheet properties. *Cellulose* **19**(3), 769–777 (2012).

13. M. Etcheverry and S.E. Barbosa, Glass fiber reinforced polypropylene mechanical properties enhancement by adhesion improvement. *Materials* **5**(6), 1084–1113 (2012).

14. K. Niskanen (Ed.), *Mechanics of Paper Products*, Walter de Gruyter, Berlin (2011).

15. Environmental Product Declaration: Particleboard. American Wood Council & Canadian Wood Council. p. 17 (2013).

16. R. Christensen, P. Robitschek, and J. Stone, Formaldehyde emission from particleboard. *Holz als Roh-und Werkstoff* **39**(6), 231–234 (1981).

17. W.H. McCredie, Formaldehyde emissions from UF particleboard voluntary standards vs EPA regulation, in *Proceedings of the Twenty-Sixth Washington State University International Particleboard Composite Materials Symposium* (1992).

18. M.Z. Salem, M. Böhm, Š. Barcík, and J. Srba, Interlaboratory comparison of formaldehyde emission from particleboard using ASTM D 6007-02 method. *Eur. J. Wood Wood Prod.* **70**(5), 621–628 (2012).

19. P. Amazio, M. Avella, M. Emanuela Errico, G. Gentile, F. Balducci, A. Gnaccarini, J. Moratalla, and M. Belanche, Low formaldehyde emission particleboard panels realized through a new acrylic binder. *J. Appl. Polym. Sci.* **122**(4), 2779–2788 (2011).

20. L. Prasittisopin and K. Li, A new method of making particleboard with a formaldehyde-free soy-based adhesive. *Composites Part A* **41**(10), 1447–1453 (2010).

21. K. Li, S. Peshkova, and X. Geng, Investigation of soy protein-Kymene® adhesive systems for wood composites. *J. Am. Oil Chem. Soc.* **81**(5), 487–491 (2004).

22. J.F. Diniz, M.H. Gil, and J.A.A.M. Castro, Hornification–its origin and interpretation in wood pulps. *Wood Sci. Technol.* **37**(6), 489–494 (2004).

23. I. Šimkovic, Unexplored possibilities of all-polysaccharide composites. *Carbohydr. Polym.* **95**(2), 697–715 (2013).

24. Y. Kojima, J. Minamino, A. Isa, S. Suzuki, H. Ito, R. Makise, and M. Okamoto, Binding effect of cellulose nanofibers in wood flour board. *J. Wood Sci.* **59**(5), 396–401 (2013).

25. Y. Kojima, A. Isa, H. Kobori, S. Suzuki, H. Ito, R. Makise, and M. Okamoto, Evaluation of binding effects in wood flour board containing ligno-cellulose nanofibers. *Materials* **7**(9), 6853–6864 (2014).

26. M.A. Bilodeau and D.W. Bousfield, US Patent Application No. 14/446,712 (2014).

27. Y. Kojima, A. Ishino, H. Kobori, S. Suzuki, H. Ito, R. Makise, I. Higuchi, and M. Okamoto, Reinforcement of wood flour board containing ligno-cellulose nanofiber made from recycled wood. *J. Wood Sci.* **61**(5), 492–499 (2015).

28. Composite Panel Association. American National Standard: Particleboard ANSI A208.1-1999. CPA, Gaithersburg, MD, 11 (1999).

29. G.A. Smook and M.J. Kocurek, *Handbook for Pulp & Paper Technologists*, TAPPI; Canadian Pulp and Paper Association, Montreal, Canada (1982).

30. F.W. Brodin, Ø.W. Gregersen, and K. Syverud, Cellulose nanofibrils: Challenges and possibilities as a paper additive or coating material – A review. *Nord. Pulp Pap. Res. J.* **29**, 156–166 (2014).

31. M. Delgado-Aguilar, E. Recas, J. Puig, G. Arbat, M. Pereira, F. Vilaseca, and P. Mutjé, Addition of nanofibrillated cellulose to the stone groundwood suspensions and on surface: A good alternative to classic beating process. *Maderas: Cienc. Tecnol.* **17**(2), 293–304 (2015).

32. O. Eriksen, K. Syverud, and O. Gregersen, The use of microfibrillated cellulose produced from kraft pulp as strength enhancer in TMP paper. *Nord. Pulp Pap. Res. J.* **23**(3), 299–304 (2008).

33. K. Mörseburg and G. Chinga-Carrasco, Assessing the combined benefits of clay and nanofibrillated cellulose in layered TMP-based sheets. *Cellulose* **16**(5), 795–806 (2009).

34. H. Sehaqui, M. Allais, Q. Zhou, and L.A. Berglund, Wood cellulose biocomposites with fibrous structures at micro-and nanoscale. *Compos. Sci. Technol.* **71**(3), 382–387 (2011).

35. T. Taipale, M. Österberg, A. Nykänen, J. Ruokolainen, and J. Laine, Effect of microfibrillated cellulose and fines on the drainage of kraft pulp suspension and paper strength. *Cellulose* **17**(5), 1005–1020 (2010).

36. S. Ahola, M. Österberg, and J. Laine, Cellulose nanofibrils-adsorption with poly (amideamine) epichlorohydrin studied by QCM-D and application as a paper strength additive. *Cellulose* **15**(2), 303–314 (2008).

37. D.C. Potulski, G.I.B. de Muniz, U. Klock, and A.S. de Andrade, The influence of incorporation of microfibrillated cellulose on mechanical strength properties of paper. *Scientia Forestalis* **42**(103)**,** 345–351 (2014).

38. S.H. Osong, S. Norgren, and P. Engstrand, Paper strength improvement by inclusion of nano-ligno-cellulose to chemi-thermomechanical pulp. *Nord. Pulp Pap. Res. J.* **29**(2), 309–316 (2014).

39. M. Ioelovich, Nano-structural concept of papermaking. *Sci. Israel Technol. Advant* **11**, 52–60 (2009).

40. I. González, S. Boufi, M.A. Pèlach, M. Alcalà, F. Vilaseca, and P. Mutjé, Nanofibrillated cellulose as paper additive in eucalyptus pulps. *BioResources* **7**(4), 5167–5180 (2012).

41. M.L. Hassan, J. Bras, E. Mauret, S.M. Fadel, E.A., Hassan, and N.A. El-Wakil, Palm rachis microfibrillated cellulose and oxidized-microfibrillated cellulose for improving paper sheets properties of unbeaten softwood and bagasse pulps. *Ind. Crops Prod.* **64**, 9–15 (2015).

42. M. Alcalá, I. González, S. Boufi, F. Vilaseca, and P. Mutjé, All-cellulose composites from unbleached hardwood kraft pulp reinforced with nanofibrillated cellulose. *Cellulose* **20**(6), 2909–2921 (2013).

43. I. González, M. Alcalà, G. Chinga-Carrasco, F. Vilaseca, S. Boufi, and P. Mutjé, From paper to nanopaper: Evolution of mechanical and physical properties. *Cellulose* **21**(4), 2599–2609 (2014).

44. J. Su, W.K. Mosse, S. Sharman, W.J. Batchelor, and G. Garnier, Effect of tethered and free microfibrillated cellulose (MFC) on the properties of paper composites. *Cellulose* **20**(4), 1925–1935 (2013).

45. N. Lavoine, I. Desloges, B. Khelifi, and J. Bras, Impact of different coating processes of microfibrillated cellulose on the mechanical and barrier properties of paper. *J. Mater. Sci.* **49**(7), 2879–2893 (2014).

46. F. Richmond, C. Haugwout, and D.W. Bousfield, The use of cellulose nanofibers in paper coating formulation, in *Proc. TAPPI PaperCon 2014*, Nashville, TN, USA (2014).

47. H. Pajari, H. Rautkoski, P. Moilanen, and A. Wigsten, Replacement of synthetic binders with nanofibrillated cellulose in board coating: Pilot scale studies. Paper presented at TAPPI International Conference on Nanotechnology for Renewable Materials (2012).

48. T. Salo, K. Dimic-Misic, P. Gane, and J. Paltakari, Application of pigmented coating colours containing MFC/NFC: Coating properties and link to rheology. *Nord. Pulp Pap. Res. J.* **30**(1), 165–178 (2015).

49. K. Dimic-Misic, C. Ridgway, T. Maloney, J. Paltakari, and P. Gane, Influence on pore structure of micro/nanofibrillar cellulose in pigmented coating formulations. *Transp. Porous Media* **103**(2), 155–179 (2014).

50. K. Dimic-Misic, T. Salo, J. Paltakari, and P. Gane, Comparing the rheological properties of novel nanofibrillar cellulose-formulated pigment coating colours with those using traditional thickener. *Nord. Pulp Pap. Res. J.* **29**(2), 253–270 (2014).

51. C.J. Ridgway and P.A. Gane, Constructing NFC-pigment composite surface treatment for enhanced paper stiffness and surface properties. *Cellulose* **19**(2), 547–560 (2012).

52. M. Schenker, J. Schoelkopf, D. Gantenbein, and P.A.C. Gane, Development of pigmented composites on the basis of nano and microfibrillated cellulose. Paper presented at TAPPI International Conference on Nanotechnology for Renewable Materials, Stockholm, Sweden (2013).

53. M. Schenker, J. Schoelkopf, P.J. Mangin, and P.A.C. Gane, Pigment Micro-nanofibrillated cellulose (MNFC) as

54. A. Baldan, Adhesion phenomena in bonded joints. *Int. J. Adhes. Adhes.* **38**, 95–116 (2012).

55. J. Schultz and M. Nardin, Theories and mechanisms of adhesion, in *Handbook of Adhesive Technology*, A. Pizzi and K.L. Mittal (Eds.), 53–67 (2003).

56. D.J. Gardner, G.S. Oporto, R. Mills, and M.A.S.A. Samir, Adhesion and surface issues in cellulose and nanocellulose. *J. Adhes. Sci. Technol.* **22**(5–6), 545–567 (2008).

57. D.J. Gardner, M. Blumentritt, L. Wang, and N. Yildirim, Adhesion theories in wood adhesive bonding. *Rev. Adhes. Adhes.* **2**(2), 127–172 (2014).

58. M.A. Hubbe, Bonding between cellulosic fibers in the absence and presence of dry-strength agents–a review. *BioResources* **1**(2), 281–318 (2006).

59. G. Gilli and P. Gilli, *The Nature of the Hydrogen Bond: Outline of a Comprehensive Hydrogen Bond Theory*, Oxford University Press, Oxford, UK (2009).

60. D.J. Gardner and M. Tajvidi, Hydrogen bonding in wood-based materials: An update. Submitted to *Wood Fiber Sci.* (2015).

61. X. Qian, The effect of cooperativity on hydrogen bonding interactions in native cellulose Iβ from *ab initio* molecular dynamics simulations. *Mol. Simul.* **34**(2), 183–191 (2008).

62. U. Hirn and R. Schennach, Comprehensive analysis of individual pulp fiber bonds quantifies the mechanisms of fiber bonding in paper. *Sci. Rep.* **5** (2015).

63. W.T. Tze and D.J. Gardner, Contact angle and IGC measurements for probing surface-chemical changes in the recycling of wood pulp fibers. *J. Adhes. Sci. Technol.* **15**(2), 223–241 (2001).

64. R.H. Mills, W.T. Tze, D.J. Gardner, and A. van Heiningen, Inverse gas chromatography for the determination of the dispersive surface free energy and acid–base interactions of a sheet molding compound. I. Matrix material and glass. *J. Appl. Polym. Sci.* **109**(6), 3519–3524 (2008).

65. Y. Peng and D.J. Gardner, Surface energy of cellulosic materials: The effect of particle morphology, particle size, and hydroxyl number. *TAPPI J.* **14**(9), 565–576 (2015).

66. Y. Peng, D.J., Gardner, Y. Han, Z. Cai, and M.A. Tshabalala, Influence of drying method on the surface energy of cellulose nanofibrils determined by inverse gas chromatography. *J. Colloid Interface Sci.* **405**, 85–95 (2013).

67. M. Eriksson, The influence of molecular adhesion on paper strength. PhD Thesis, KTH Royal Institute of Technology, Stockholm, Sweden, p. 83 (2006).

68. N. Yildirim, S.M. Shaler, D.J. Gardner, D.W. Bousfield, and R. Rice, Cellulose nanofibril (CNF) insulating foams, in *Production and Applications of Cellulose Nanomaterials*, M.T. Postek, R.J. Moon, A.W. Rudie, and M.A. Bilodeau (Eds.), pp. 317–319, TAPPI Press, Peachtree Corner, GA (2013).

69. W.T. Tze and D.J. Gardner, Swelling of recycled wood pulp fibers: Effect on hydroxyl availability and surface chemistry. *Wood Fiber Sci.* **33**(3), 364–376 (2001).

packaging composite material: A first assessment. Paper presented at TAPPI PaperCon 2015, Atlanta, GA (2015).