Binder Applications of Cellulose Nanofibrils: New Developments

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ABSTRACT

A key path towards the commercialization of cellulose nanomaterials is to target large-volume applications in commodity products where a successful market introduction could potentially mobilize orchestrated efforts to revitalize the forest products industry. At the Laboratory of Renewable Nanomaterials we have introduced the concept of using cellulose nanofibrils (CNF) as binder in conventional wood based compressed panels. Binder applications take advantage of impressive hydrogen bonding capacity of CNF and have many other uses. In this presentation, we will present our findings in wet-formed particleboard bonded with cellulose nanofibrils (CNF). In an effort to lower the production cost, we have also shown that lingo-cellulose nanofibrils can be produced directly from wood and can be used as binder in the formulation of traditional fiberboard panels. Thermomechanical pulp (TMP) produced using atmospheric refining was ground to isolate lignocellulose nanofibrils (LCNF). The effect of using LCNF as adhesive replacement in fiberboard was assessed. Future outlooks, potential issue and methods to implement large volume applications of CNF are discussed.

Keywords: cellulose nanofibrils, binder, wood-based panels,

1 INTRODUCTION

This paper introduces the concept of using cellulose nanomaterials in particular cellulose nanofibrils (CNF) as binder in the formulation of conventional and novel woodbased composite panels. Cellulose nanomaterials, mainly cellulose nanofibrils (CNF) and cellulose nanocrystals (CNC) have recently been the focus of a significant number of research work because they promise the production of new, lightweight, and high strength sustainable products. A number of review articles have been written that summarize the work [1]. A recent review summarizes cellulose nanocomposites by processing methods [2].

In part, because of the physical form of the produced cellulose nanomaterials in the form of low-solid aqueous suspensions and partly because of current issues with developing appropriate drying and surface modification techniques, a large number of the current applications of cellulose nanomaterials are focused on 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 different systems.

A key roadblock to widespread use of CNF and CNC is a lack of large-scale applications. A better strategy than the "additive" approach 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. Considering 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.

The Laboratory of Renewable Nanomaterials (LRN) at the University of Maine is actively engaged in the large volume applications of cellulose nanofibrils where these materials are used as binder. It is believed that these applications are closer-to-market applications that will lead to rapid commercialization of these highly interesting products.

2 THE CONCEPT

Figure 1 shows the physical form and microscopic structure of CNF as produced at the Process Development Center, University of Maine. This material is produced by ultra-refining bleached softwood pulp in a specially designed

refiner until a pre-determined fine content (95%) is achieved. While the lengths of particles are in the range of micrometers, the diameters are in nano –scale giving the product a very high aspect ratio. No chemical pre-treatment is performed prior to refining.



Figure 1: Cellulose nanofibrils: (a) physical appearance of a 3 wt.% solids content slurry; and (b) TEM micrograph.



Figure 2: (a) Consolidation and dewatering phenomenon followed by drying led to bond formation at micro/nano scale; SEM image of (b) the surface of a southern pine particle and (c) a southern pine particle mixed with a 3% solids content CNF after air-drying overnight.

CNFs at low solids content can be largely dispersed and exfoliated in water, and can result in a three-dimensional network of fibrils upon drying. We have shown that if wood particles are present in the system, the CNF particles can encompass wood particles and hold them together upon water removal. Figure 2a depicts a wet mat formed by mixing CNF suspension and wood particles. Such a system is composed of wood particles, CNF, water, and air. Upon dewatering and subsequent drying, a three-dimensional network of CNF is formed that holds together the wood particles. At the micro/nano scale, smaller particles of CNF can penetrate into the porous structure of wood particles and provide strong bonds. Figure 2b shows the surface of a southern pine wood particle. The surface of a similar wood particle after being mixed with a CNF slurry and air-dried overnight is shown in Figure 2c. The CNF fibrils can be easily observed as distributed over the particle surface with some particles agglomerated into platelet shapes and some

preserving their fibrillar morphology with varying fibril widths. 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.

3 EARLY ATTEMPTS

The first panels were made by mixing a CNF slurry at 3 wt.% solids with wood particles at room temperature using a stand mixer. The mixture was then poured into a wooden forming box with the internal dimensions of 120 mm \times 120 $mm \times 60$ mm that was placed on top of a 40-mesh wire cloth. The mat was dewatered using a manual hydraulic press. Most of the free water was drained off during the cold pressing. The solids content of the mats before and after cold pressing were approximately 16% and 38%, respectively. This means that the cold pressing process was able to remove more than 50% of the water [3]. Then the lid and forming box were removed and the cold pressed mat was pressed and dried using a hydraulic hot press at 180 °C for 7 min between two wire mesh cloths. The particleboard panels were produced in four different groups of target density: 0.60 g cm⁻³ to 0.64 g cm⁻³, 0.65 g cm⁻³ to 0.69 g cm⁻³, 0.70 g cm⁻³ to 0.74 g cm⁻³), and 0.75 g cm⁻³ to 0.79 g cm⁻³. Each density group contained three samples of 15 wt.% and 20 wt.% dry CNF. The production procedure is presented in Fig. 2.



Figure 3: Particleboard panel production procedure: (1) raw materials: (a) 3 wt.% CNF slurry and (b) southern pine WP; (2) forming and cold pressing; (3) cold-pressed mat; (4) hot pressing; and (5) final panel.

Mechanical properties of the panels were determined and compared with those recommended in ANSI 208.1. It was found that only low density panels met the MOR (modulus of rupture) and MOE (modulus of elasticity) requirements but all formulations met or exceeded the recommended internal bond (IB) values. However, once a crosslinking additive was added to the system, both MOR and MOE values were significantly improved to need standard values. Figure 4 shows the IB values of the produced panels were all panels met the standard requirement.



Figure 4: Internal bond strength of 15% and 20% CNF containing panels

4 SCALE-UP

Learning from the initial attempts, we produced larger size (30 cm by 30 cm by 1.2 cm) panels using a similar technique with the difference that a vacuum system was used in place of cold pressing to remove excess water. Two different press cycles (constant thickness and constant pressure) were used. Figure 5 shows the two press cycles.



Figure 5: Typical pressure and displacement curves for two pressing methods: a) constant thickness pressing method; b) constant pressure pressing method

Figure 6 shows the performance data of the MOE and MOR for increased CNF addition ratio and the comparison between the two pressing methods in relationship with ANSI A208.1 standard for particleboard. It shows that boards can be made that meet some low-, medium-, and high-density standards for several particleboard performance levels for MOE and MOR. When these plots were extrapolated, increased CNF addition ratio and density levels would provide improved performance to meet or exceed higher standards. It was also clear that the constant thickness pressing method provided improved bending performance, especially at higher CNF addition ratios, as compared with the constant pressure pressing method. Our results showed the scale-up improved properties most probably because of

the higher thickness of panels at similar particle size leading to stronger internal structure.



Figure 6: MOE a) and MOR b) plots for constant pressure (solid) and constant thickness (dashed) pressing methods with increasing CNF addition ratio in relationship with ANSI 208.1 standard

5 LIGNIN-CONTAINING CELLULOSE NANOFIBRILS

Binder applications of CNF imply that high purity of CNF might not be required should it be possible to produce lower-cost CNF from untreated wood chips having similar properties. At LRN, we developed methods to produce lignonanocellulose (LCNF) from wood chips. Figure 7 shows Figure 7 represents the SEM (a) and TEM (b) images showing the microstructure of lignocellulose nanofibrils (LCNF) isolated from unbleached thermomechanical pulp (TMP). LCNF appeared as random, elongated and branched particles with multiple ramifications forming a network assembly. The average diameter of the nanofibrils measured from TEM images was 12.9 ± 3.4 nm. These dimensions were in line with those previously reported for CNF. The high surface areas due to the higher degree of fibrillation and the entanglement of cellulose fibrils foster the formation of three-dimensional gel network in aqueous media with the vast amount of bound water at low concentrations. LCNF slurry, however, was is the form of a dense fluid and the presence of hydrophobic lignin on the fibrils interface tended to reduce the interaction between water and the fibrillated cellulose reducing particle swelling and the gel formation.



Figure 7: Microstructure of lignocellulose nanofibrils (LCNF) observed by SEM (a) and TEM (b).

These LCNF nanoparticles were used as binder to produce fiberboard panels made with TMP. Figure 8 shows the stress-strain curve of the boards (a) obtained using the ASTM D790-03 and the MOR and MOE as a function of the density of the panels (b). Compared to the reference board, the addition of LCNF led to increased strain before failure. The areas under the stress-strain curves showed values of about 33.6.10⁻³, 45.7.10⁻³, 60.4.10⁻³ and 72.3.10⁻³ MPa for the reference boards and boards containing 15, 20 and 25 % LCNF, respectively. This assumes that during the bending process, more energy was absorbed by the boards before rupture, due to the presence of LCNF. Both MOR and MOE increased slightly with the increase of density, independently from the LCNF content and press temperature (Figure 4b). As LCNF content increased, the energy absorption also increased, despite the fact that MOE did not show a clear variation. The improved strain behavior, strength and toughness with the increasing LCNF content, corroborated the variation in the boards mechanical properties.



Figure 8: Microstructure of lignocellulose nanofibrils (LCNF) observed by SEM (a) and TEM (b).

The potentiality of using lignin-containing cellulose nanofibrils (LCNF) to replace the current formaldehyde based resin adhesive in MDF manufacturing was evaluated in this present work. The isolation of LCNF via microgrinding of never-dried TMP was successful. The 3-D network formed by the nanofibrils acted as a binder between TMP fibers and filled the inter-fiber voids. By increasing the LCNF content in the formulation, results show that boards

with a MOE and IB values higher than the standards specified for commercial MDF can be obtained. The MOR for boards containing 20 % LCNF and pressed at 180 °C, however, reached values below the commercial standards. At a constant temperature, a linear dependence between MOR and IB was obtained. Increasing LCNF content densifies the core layer of the panels, thus reducing its density differential with the surface. The addition of 20 % LCNF and pressing the boards at 180 °C were considered to be the best processing conditions given the boards' physico-mechanical performances. Increasing the LCNF content in the formulation and the press temperature did not bring about further improvement in the board properties. Overall, LCNFbased MDF showed good physico-mechanical properties close to the commercial standards and resulted in products that do not use formaldehyde-based resins.

6 CONCLUSIONS

Binder applications of cellulose nanomaterials provide new opportunities for high-volume applications of CNF. 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 initial drying step by direct application in aqueous conditions, preserving the nanometer scale of the material in the end product. Other interesting applications have been reported by our reearch group [4].

Challenges remain in the binder applications of cellulose nanomaterials. 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 multi-daylight presses.

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