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Mechanical performance of cellulose nanofibril film-wood flake laminate

Abstract: Homogeneous and transparent CNF films, fabricated from the (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO)-modified CNF suspension, were laminated onto wood flakes (WF) based on phenol-formaldehyde (PF) resin and the reinforcement potential of the material has been investigated. The focus was on the influence of CNF film lamination, relative humidity (RH), heat treatment, and anisotropic properties of WF on the CNF-WF laminate tensile properties (elastic modulus, ultimate tensile strength, strain to failure). Results demonstrated that CNF-WF laminates had improved mechanical performance as compared to the neat WF. In the WF transverse direction, there were gains of nearly 200% in Young's modulus and 300% in ultimate tensile strength. However, in the WF axial direction, the reinforcement effect was minor after PF modification of the wood and the presence of the CNF layers. The effective elastic moduli of the CNF-WF laminates were calculated based on the laminated plate theory, and the calculation in both axial and transverse directions were in agreement with the experimental results.

Keywords: cellulose nanofibrils, laminate, phenol-formaldehyde resin, relative humidity, wood flake

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Introduction

A large amount of low quality byproducts arise in the course of tree harvesting and production of wood products, such as slash, sawdust, splints, chips, flakes, etc. One route for utilization of wood wastes is their combination with cellulose nanomaterials (CNs), which are

cellulose-based, fibril shaped, nanoparticles isolated from plants and trees. The increasing interest in renewable, CO₂ neutral, and non-petroleum based materials also strengthened the research in CNs with their unique characteristics: they have high stiffness (110–220 GPa), high tensile properties (~7.5 GPa), high aspect ratio (10–100), low density (~1.6 g cm⁻³), low thermal expansion (4–6 ppm K⁻¹), low light scattering, and surfaces accessible to chemical functionalization. Additionally, CNs can be produced in industrial size (Samir et al. 2005; Moon et al. 2011; Lin et al. 2012). CNs have been tested as a reinforcement phase in polymer composites, protective coatings, barrier/filter membrane systems, antimicrobial films, network structures for tissue engineering, and substrates for flexible electronics. Neat and polymer composite films based on CNs (>70% CNs) have been produced with low density (1–1.5 g cm⁻³), high transparency (Iwamoto et al. 2005; Nogi et al. 2009), high tensile strength (~30–300 MPa), high elastic modulus (~10–25 GPa), and low coefficient of thermal expansion (CTE, ~8–20 ppm K⁻¹) (Iwamoto et al. 2005; Henriksson and Berglund 2007; Henriksson et al. 2008; Iwamoto et al. 2008; Nogi et al. 2009).

One class of CNs is cellulose nanofibril (CNF, ~4–20 nm wide by >1 µm in length), which is typically produced from wood pulp by either mechanical grinding (Iwamoto et al. 2007), high-shear homogenization (Zimmermann et al. 2004) or a mechano-chemical oxidation process (Saito et al. 2007, 2009). To date, most studies on CNF composites have focused on fabrication based on dispersing CNFs into a polymer matrix, or by impregnating polymer into precast CNF network films. There are a few studies available based on stacking/lamination processes to fabricate CN composites. Several authors stacked cellulose microfibrils (CMF), (Nakagaito and Yano 2004, 2008), bacterial cellulose (Nakagaito et al. 2005), and wood pulp mats (Nakagaito and Yano 2008), which were subsequently impregnated with phenol-formaldehyde resin (PF), to form high strength cellulose composites.

However, there are no studies on neat CNF films as reinforcement to strengthen the properties of materials via lamination. The objective of this study was to fabricate CNF films with good mechanical properties, and to laminate these onto logging-slash derived wood flakes (WF) for enhancing the mechanical properties of the WF.

Materials and methods

Sample description

CNFs, derived from Eucalyptus dry-lap cellulose fibers (Aracruz Cellulose, Sao Paulo, Brazil), were provided by the Forest Products Laboratory (FPL). The cellulose fibers were pulped in a hydropulper, and the pulp was suspended at 1% solids and adjusted to pH 2 by H_2SO_4 (Columbus Chemicals, Columbus, WI, USA) and NaClO_2 (Alfa Aesar, Ward Hill, MA, USA). The suspension was allowed to stir for 4 h at room temperature (r.t.) and followed by washing the pulp with reverse osmosis water. The purified pulp was then suspended in water containing (2,2,6,6-tetramethylpiperidin-1-yl) oxyl (TEMPO) (Alfa Aesar, Ward Hill, MA, USA), NaBr (Alfa Aesar, Ward Hill, MA, USA), NaHCO_3 (Alfa Aesar, Ward Hill, MA, USA), and Na_2CO_3 (Alfa Aesar, Ward Hill, MA, USA). The oxidation process consisted of slowly adding NaClO into the suspension at r.t. for 5 h. After reaction completion, the TEMPO-oxide pulp was then passed through refiners (0.1 mm and 0.05 mm gap) and microfluidizer (Microfluidics, Westwood, MA, USA), which is a high shear fluid processor generally applied for producing stable emulsions and dispersions, to get a 0.5% CNF aqueous suspension. The suspension was directly cast onto a 0.5 mm polyethylene terephthalate (PET) (McMaster-Carr, Elmhurst, IL, USA) substrate and allowed to dry at 23°C and 45–55% relative humidity (RH). Dried CNF films detached from the PET substrate had a mean density of 1.28 g cm^{-3} , with a 2D random CNF orientation within the films.

Green aspen slash wood with high moisture content (MC about 95%) was obtained from a local plantation forest in northern Wisconsin. The materials were mainly composed of branches removed from the forest as part of silvicultural managements. The branches with diameter of 50–76 mm were selected and cut into 136 mm long sections, which were stored in plastic bags to prevent moisture loss. The 136 mm long branch segments were then forced through a laboratory disc-flaker, being sliced longitudinally. The aspen flakes coming out of the flaker with thickness ranging from 0.45 to 0.65 mm, widths from 16 to 55 mm, and approx. The flakes were then dried in a laboratory tray dryer to a target MC of about 2.2%. To minimize sample to sample variation, a specific grain orientation on the WF was selected.

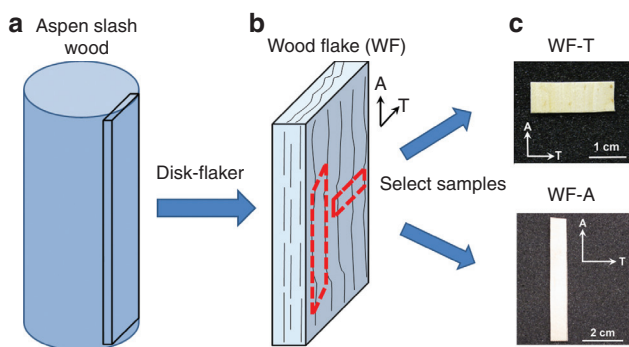


Figure 1 Schematic of wood flake (WF) specimen preparation. (a) Wood slash trimmed from a wood log, (b) selection a specific grain orientation on the WF, where the direction of WF specimen parallel to the longitudinal axis is defined as the axial direction (A), and the transverse direction (T) is perpendicular to the axial direction, and (c) the selection of WF samples that will be examined in axial (WF-A) and transverse (WF-T) directions.

The axial direction (A) of WF samples was parallel to the longitudinal axis and the transverse direction (T) included both radial and tangential axes (Figure 1). The specific selected WF samples, that will be examined the properties in axial (WF-T) and in transverse direction (WF-A), were also shown in the Figure 1b and c.

CNF-WF laminates (LAM) were fabricated by gluing CNF films on both sides of the WF with 50.5% water-soluble PF resin (Georgia-Pacific Chemicals LLC, Atlanta, GA, USA). A thin layer of PF resin was cast on the WF with a spread rate of 60 mm s^{-1} after which a CNF film was placed on top of the resin. The laminate was then pressed to squeeze out the excess resin. The laminating process was repeated on the other side of the WF. After adhering both sides of the WF with the CNF films, the laminate was clamped between metal plates (0.15–0.2 MPa) and heated at 80°C for 24 h and then equilibrated back to 23°C and 30–40% RH. During this process, the PF resin crosslinked and bonded the CNF films to the WF.

Experimental design

Neat CNF films were equilibrated at 23°C at either high RH (45–55%) or low RH (30–40%), and were named as CNF-HR and CNF-LR, respectively. Several CNF films also underwent a heat treatment (80°C for 24 h) and were equilibrated back to 23°C at either high RH or low RH and are named CNF-HRh and CNF-LRh, respectively. This heat treatment corresponds to the PF curing treatment for the production of CNF-WF laminates, and was necessary to account for any changes in the CNF film properties resulting from this thermal treatment.

WFs were equilibrated at 23°C at low RH (30–40%). Because of the anisotropy in the WF structure, the tensile properties in axial (WF-A) and transverse (WF-T) directions were measured. Several WF samples underwent a heat treatment (80°C for 24 h) and were equilibrated back to 23°C at low RH (30–40%) and are named WF-Ah and WF-Th for properties measured in the axial and transverse directions, respectively.

For the CNF-WF laminates, the properties were measured along axial direction (LAM-A) and transverse direction (LAM-T) with respect to the WF grain orientation. To elucidate the contribution of the PF resin or the CNF film on the laminate properties, reference WF samples were fabricated by casting thin PF resin layers on both sides of a WF without stacking of CNF films. Reference samples were also tested in axial (WF-PF-A) and transverse direction (WF-PF-T). All samples were equilibrated back to 23°C at low RH after the heat treatment.

Mechanical testing

Dynamic mechanical analysis (DMA) (Q800, TA Instrument, New Castle, DE, USA) was used in controlled force mode to investigate the elastic modulus (E), ultimate tensile strength (σ_f) and elongation to failure (ϵ_f) of CNF films, WFs, and CNF-WF laminates. However, the σ_f and ϵ_f for the WF-A, WF-Ah, LAM-A and WF-PF-A specimens could not be obtained from DMA testing because the load cell was too small for these strong specimens (see description in next paragraph). For mechanical testing of CNF films, the detailed mounting and testing processes were described elsewhere (Reising et al. 2013). Briefly: CNF-HR, CNF-LR, CNF-HRh and CNF-LRh specimens were prepared as rectangular strips with 10 mm length, 3–4 mm width and 10 μm thickness. The film strips glued onto a thin steel-foil frame, and the gage lengths for determining strain were measured as the distance between steel tabs. After mounting in the instrument, tabs were cut to

release the film. The testing conditions were the same as the CNF film equilibrating conditions at 23°C at high RH for CNF-HR and CNF-HRh specimens, and at low RH for CNF-LR and CNF-LRh specimens. For the property measurement of WF and CNF-WF laminate, the specimen dimensions for testing were as follows: for WF-A, WF-Ah, LAM-A and WF-PF-A specimens were 10–15 mm length, 4–6 mm width and 0.50–6 mm thickness, while for WF-T, WF-Th, LAM-T and WF-PF-T specimens were 57 mm in length, 4–6 mm width and 0.5–0.6 mm thickness. Specimens were directly gripped between the fixtures, and the gage lengths were measured as the distance between the upper and lower grips for determining the strain. The tensile tests were performed with a 1.0 N min⁻¹ load rate and initial pre-load of 0.01 N min⁻¹ at 23°C at low RH. At least five specimens were tested and averaged for each condition.

For the WF-A, WF-Ah, LAM-A, and WF-PF-A specimens, additional mechanical testing was completed with a universal tensile testing machine (MTS Insight, MTS System Corp., Eden Prairie, MN, USA) with 100 kN load cell (model 569330-01). All specimens were prepared with mean dimensions of 50–70 mm length, 7–10 mm width and 0.5–0.6 mm thickness. The specimens were directly clamped on the tensile fixtures, and the distances between two grips for determining strain were measured. The speed of testing was 0.127 mm min⁻¹ at 23°C at low RH. Five specimens were tested and averaged for each condition. Note that the properties for WF specimen in the transverse direction could not be tested because of received WF specimen size (10–12 mm) in this direction were too small to fit within the MTS loading grips.

Results are expressed as mean ±SD (one standard deviation). Comparisons of means were performed with Student's t-test on Microsoft Excel, where two tails (two-tailed distribution) and two-sample equal variance were chosen as Function Arguments. $P < 0.05$ was taken as significant.

Laminated plate theory (LPT)

The elastic modulus of the CNF-WF laminate was predicted by LPT (Staab 1999; Daniel and Ishai 2006). Briefly: the E of the CNF-WF laminate in axial (E_x) and transverse (E_y) directions can be determined as

$$E_x = \frac{1}{hA'_{11}}, \quad E_y = \frac{1}{hA'_{22}} \quad (1)$$

where h is the CNF-WF laminate thickness, and the two variables (A'_{11} and A'_{22}) can be investigated from the extensional stiffnesses ($[A]$) of the laminate

$$A'_{11} = \frac{A_{22}}{A_{11}A_{22} - A_{12}^2}, \quad A'_{22} = \frac{A_{11}}{A_{11}A_{22} - A_{12}^2} \quad (2)$$

Additionally, A_{11} , A_{22} , and A_{12} can be calculated in the following equation:

$$A_{ij} = Q_{ij}^{CNF} t_{CNF} + Q_{ij}^{WF} t_{WF} + Q_{ij}^{CNF} t_{CNF} \quad i, j = 1, 2 \quad (3)$$

where t_{CNF} and t_{WF} are the thickness of CNF film and WF, respectively. In this study, the loading direction is parallel to the axial direction (x axis) of the CNF-WF laminate and CNF films are 2-D random which can be considered to be isotropic. The reduced stiffness Q_{ij}^{CNF} and Q_{ij}^{WF} then can be presented in a general form

$$Q_{ij}^w = \begin{bmatrix} \frac{E_x^w}{1-\nu_{xy}^w \nu_{yx}^w} & \frac{\nu_{xy}^w E_y^w}{1-\nu_{xy}^w \nu_{yx}^w} & 0 \\ \frac{\nu_{xy}^w E_y^w}{1-\nu_{xy}^w \nu_{yx}^w} & \frac{E_y^w}{1-\nu_{xy}^w \nu_{yx}^w} & 0 \\ 0 & 0 & G_{xy}^w \end{bmatrix} \quad (4)$$

E_x^w and E_y^w are the elastic modulus in the axial and the transverse direction, respectively. ν_{xy}^w and ν_{yx}^w are the Poisson's ratio and G_{xy}^w presents the shear modulus. w can be replaced as CNF or WF that dictates the properties of CNF films and WF, respectively.

Results and discussion

Properties of cellulose nanofibril films (CNFs)

Homogeneous CNF films fabricated in this study were flexible and optically transparent with high clarity (Figure 2a). The transparency of the films was almost 90% in the visible spectrum range. The tensile properties (E , σ_f and ϵ_f) of the CNF films, summarized in Figure 3, showed

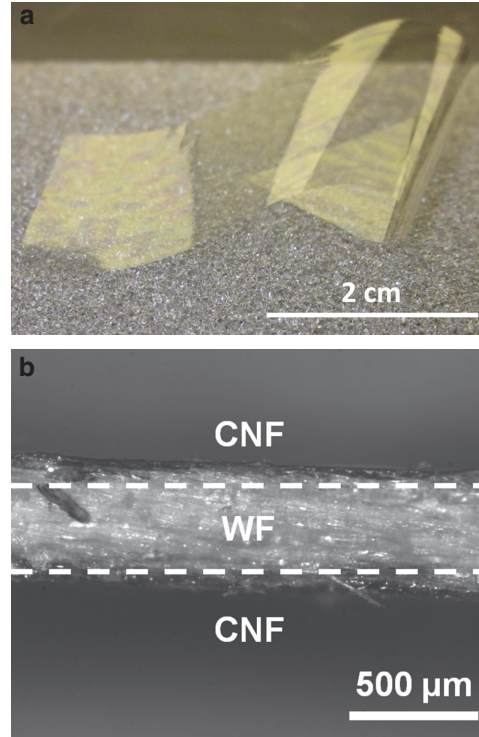


Figure 2 (a) A photograph of the CNF film. It was fabricated via casting and folded on the table. It shows high transparency, clarity and good flexibility. (b) The fracture section of CNF-WF laminate, where CNF films were tightly bound on the WF surface.

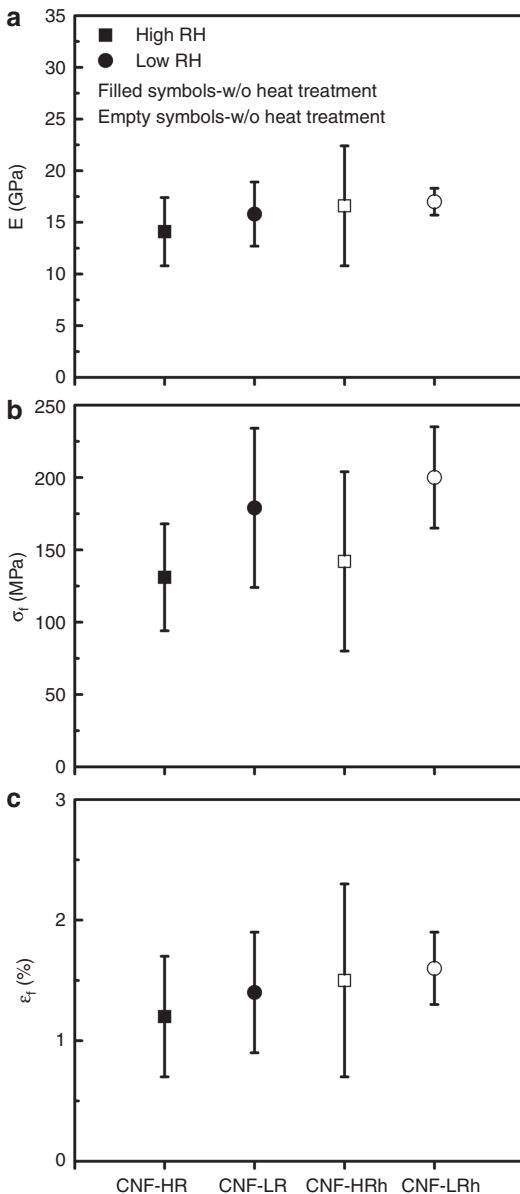


Figure 3 Tensile properties of CNF films as a function of RH and heat treatment. (a) Elastic modulus (E), (b) ultimate tensile strength (σ_f), and (c) elongation to failure (ε_f). Films equilibrated at high RH (squares), low RH (circles), with heat treatment (empty symbols), and without heat treatment (filled symbols).

that small changes in RH ($\sim 15\%$) did not influence the E and ε_f of CNF films, but appeared to affect the σ_f . When comparing CNF-HR ($E=14.1\pm 3.3$ GPa, $\sigma_f=131\pm 37$ MPa, $\varepsilon_f=1.2\pm 0.5\%$) and CNF-LR ($E=15.8\pm 3.1$ GPa, $\sigma_f=179\pm 55$ MPa, $\varepsilon_f=1.4\pm 0.5\%$), there was no significant change of E and ε_f , while the increase in σ_f of the CNF-LR was significant ($P=0.03$). Similarly, for the heat treated CNF films, small changes in RH had no significant influence on E , and ε_f , but an apparent significant influence on σ_f (i.e., CNF-HRh $\sigma_f=142\pm 62$ MPa, and CNF-LRh $\sigma_f=200\pm 35$ MPa, with a $P=0.05$, at the boundary).

This increase in σ_f at the lower RH might result from the lower MC within the films. In general, at higher RH, the films would be expected to absorb more water because of the hydrophilic nature of CNFs (Henriksson and Berglund 2007). A higher MC within the film might alter CNF-CNF interfaces, and allow the CNFs to move more easily when the films were under an external force, and thus alter the tensile properties (Capadona et al. 2008).

The heat treatment (80°C for 24 h), influences only minimal the CNF film tensile properties, as determined by comparing CNF films equilibrated at the same RH (e.g., CNF-HR vs. CNF-HRh and CNF-LR vs. CNF-LRh). The changes of CNF film properties upon thermal treatment can be described as a result of hornification, in this case due to water loss at CNF-CNF interfaces, resulting in increased inter-CNF hydrogen bonding, and thus in altered CNF-CNF interface properties. The unchanged mechanical properties of CNF films upon heat treatment demonstrate that the PF curing heat treatment in the course of CNF-WF laminate does not play an essential role.

Properties of wood flakes (WF)

Wood mechanical properties are anisotropic, being dependent on the orientation of the wood structure, and are higher in axial than in transverse directions. The tensile properties (E , σ_f , ε_f) of WF in the axial and transverse directions, and the result of the thermal treatment, (e.g., WF-A, WF-T, WF-Ah and WF-Th) are summarized in Figure 4. The DMA results confirm the expectation concerning WF-T ($E=0.3\pm 0.1$ GPa, $\sigma_f=2\pm 0.8$ MPa, $\varepsilon_f=1.3\pm 0.3\%$), WF-Th ($E=0.6\pm 0.3$ GPa, $\sigma_f=1.3\pm 0.2$ MPa, $\varepsilon_f=0.7\pm 0.2\%$), WF-A ($E=7.5\pm 3.0$ GPa, $\sigma_f=N/A$, $\varepsilon_f=N/A$), and WF-Ah ($E=10.5\pm 3.1$ GPa, $\sigma_f=N/A$, $\varepsilon_f=N/A$) that the E is higher in the axial direction than in transverse direction (e.g., WF-T vs. WF-A and WF-Th vs. WF-Ah). Comparing the WF properties with and without heat treatment, the results of E (WF-T vs. WF-Th and WF-A vs. WF-Ah) or σ_f (WF-T vs. WF-Th) showed no significant difference. In contrast, the ε_f (WF-T vs. WF-Th) is significantly different ($P<0.01$). However, the size of DMA samples was so small (5–7 mm in length) that the strain difference (50 μm) between WF-T and WF-Th might originate from the measurement error. Similarly, the MTS results for WF-A ($E=6.4\pm 0.8$ GPa, $\sigma_f=49\pm 13$ MPa, $\varepsilon_f=1.3\pm 0.9\%$), and WF-Ah ($E=6.5\pm 1.8$ GPa, $\sigma_f=45\pm 7.0$ MPa, $\varepsilon_f=1.0\pm 0.2\%$) showed that there was no significant difference as a result of the heat treatment on E , σ_f or ε_f . When comparing the results between DMA and MTS, the variance from these two testing methods might result from the specimen size. Specimens for DMA were about

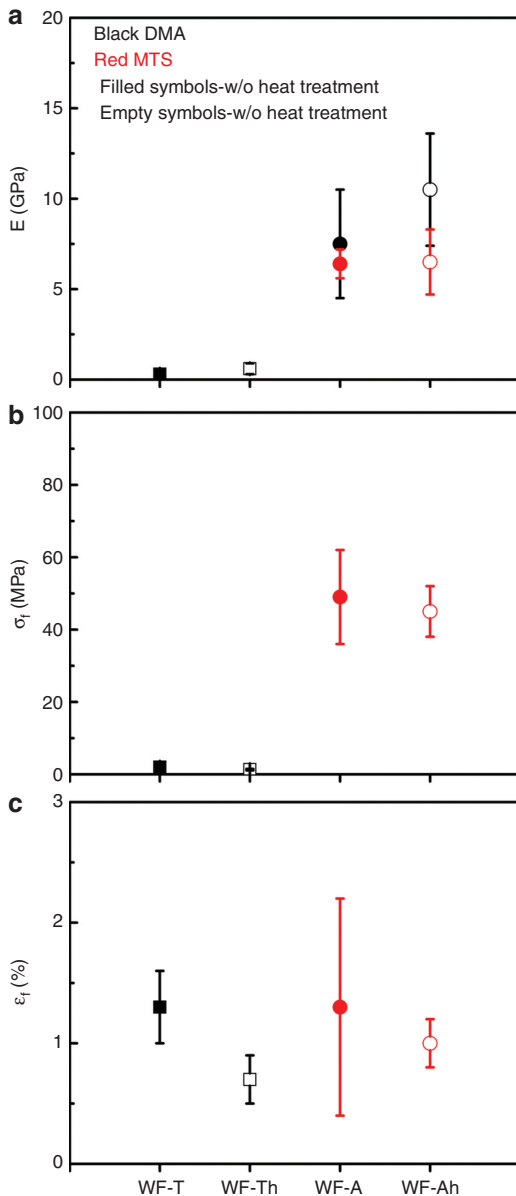


Figure 4 Tensile properties of WF as a function of orientation and heat treatment. (a) Elastic modulus (E), (b) ultimate tensile strength (σ_f) and (c) elongation to failure (ϵ_f). WF with heat treatment (empty symbols) and without heat treatment (filled symbols) examined via DMA (black) and MTS (red) in axial (circle) and in transverse (square) direction.

1/3 the size of MTS specimens. Large MTS testing specimens likely contained more structural defects, and these defects resulted in lower E . The properties σ_f are larger in the axial (e.g., WF-A and WF-Ah) than in the transverse (WF-T and WF-Th) direction, while ϵ_f measured from both methods stayed within the similar range (0.7–1.3%).

Mechanical properties are negatively influenced by the amount of bound water (as opposed to free water in

the lumens) within the wood [Forest Products Laboratory (U.S.) 1999]. Additionally, water adsorption and desorption in wood is not a linear relation and shows a hysteresis. Heat treatment applied in this study for the PF resin curing in CNF-WF laminate, might alter the water content within WF even after it is equilibrated back to the testing conditions (23°C for 30–40% RH) and thus its mechanical properties. However, the tensile properties with and without heat treatment (e.g., WF-A vs. WF-Ah, and WF-T vs. WF-Th) are essentially unchanged. Thus heat treatment does not influence CNF-WF laminate properties.

Properties of laminates

Well-bonded CNF-WF laminate was produced with PF resin as adhesive (Figure 2b). The fracture surface did not reveal delamination of the CNF-WF laminate after PF resin crosslinking. Mechanical properties of WF (WF-Th and WF-Ah), PF resin coated WF, and CNF-WF laminates (for both transverse and axial directions) are summarized in Figure 5. The WF properties underwent the same heat treatment as PF resin coated WF and CNF-WF laminates. For testing in the transverse direction, the DMA results showed (Figure 5a–c) of WF-Th ($E=0.6\pm0.3$ GPa, $\sigma_f=1.3\pm0.2$ MPa, $\epsilon_f=0.7\pm0.2\%$), WF-PF-T ($E=0.9\pm0.1$ GPa, $\sigma_f=3.5\pm0.5$ MPa, $\epsilon_f=0.7\pm0.1\%$), and LAM-T ($E=1.9\pm0.3$ GPa, $\sigma_f=5.6\pm1.0$ MPa, $\epsilon_f=0.6\pm0.1\%$) that the PF resin coated WF and laminate both had higher E and σ_f in comparison with WF, while there was no significant change in ϵ_f . WF-PF-T gave a 50% improvement in E and 170% gains in σ_f , and LAM-T showed almost 200% gains in E and 300% improvement in σ_f . In contrast, for the axial direction, the results of WF-Ah ($E=10.5\pm3.1$ GPa, $\sigma_f=N/A$, $\epsilon_f=N/A$), WF-PF-A ($E=15.1\pm2.8$ GPa, $\sigma_f=N/A$, $\epsilon_f=N/A$) and LAM-A ($E=13.0\pm3.4$ GPa, $\sigma_f=N/A$, $\epsilon_f=N/A$) did not reveal significant improvement of E . Only WF-PF-A had a statistically higher E than WF-Ah ($P=0.02$), suggesting that the PF resin has a more dominant role in stiffening the laminate than the CNF films. To obtain σ_f and ϵ_f in the axial direction, specimens were also measured by MTS. The MTS results of WF-Ah ($E=6.5\pm1.8$ GPa, $\sigma_f=45\pm7$ MPa, $\epsilon_f=1.0\pm0.2\%$), WF-PF-A ($E=6.4\pm1$ GPa, $\sigma_f=58\pm13$ MPa, $\epsilon_f=1.1\pm0.3\%$) and LAM-A ($E=5.8\pm0.6$ GPa, $\sigma_f=67\pm9$ MPa, $\epsilon_f=1.3\pm0.4\%$) demonstrated that there was no significant difference on E , σ_f or ϵ_f , except for LAM-A having a ~50% increase in σ_f as compared with WF-Ah ($P<0.01$). We interpret the differences in DMA and MTS results (Figure 5d) as a consequence of larger specimen sizes for the MTS testing.

The results demonstrate that lamination enhances the tensile properties of WF more in the transverse direction

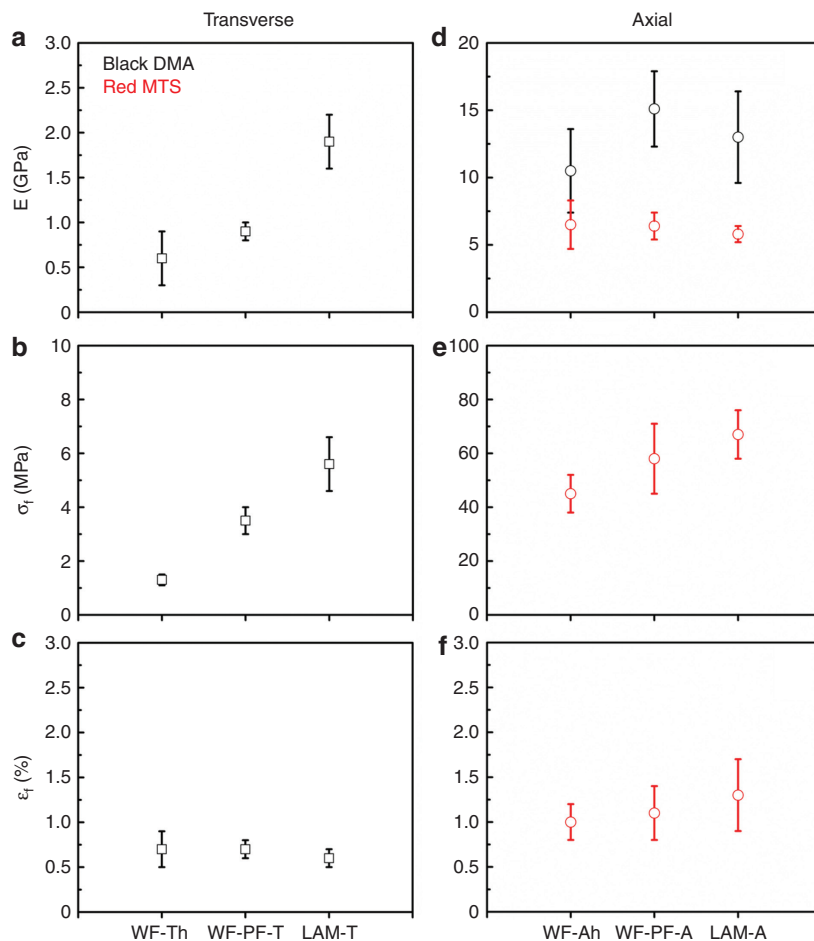


Figure 5 The elastic modulus (E), ultimate tensile strength (σ_t) and elongation to failure (ε_t) of WFs, WF-PF and CNF-WF laminate (LAM) examined via DMA (black) and MTS (red) in axial direction (circle) [(a) – (c)] and in transverse direction (square) [(d) – (f)].

of the WF due to the weak strength in this direction. There are two main mechanisms for property improvements: the PF resin modification and the addition of the CNF films. The influence of temperature due to PF resin curing were found to be minimal (Figures 3 and 4). The crosslinking of the PF resin between the formaldehyde and phenol moieties including also the hydroxyl groups on the cellulose surfaces (WF or CNF) are effective after PF resin coating of WFs. In the transverse direction, the CNF films have higher E and σ_t than the WF and act as reinforcement layers and contribute to LAM-T with superior properties. However, in the axial direction these forces are not effective.

Laminate properties and laminated plate theory (LPT)

The elastic modulus of the CNF-WF laminate in the axial (E_x) and the transverse (E_y) direction was predicted by the LPT. For computing the A_{ij} (Eq. 3) of the laminate, several

of the input variables measured from DMA or MTS testing methods were used in the Eq. (4). For the isotropic CNF films, $t_{CNF}=10\ \mu\text{m}$, $E^{CNF}=17\ \text{GPa}$ ($E_x^{CNF}=E_y^{CNF}$; based on CNF-LRh), and $\nu_{xy}^{CNF}=\nu_{yx}^{CNF}=0.25$ (assumed) were applied. For the wood flake, $t_{WF}=500\ \mu\text{m}$, $E_x^{WF}=10.5\ \text{GPa}$ (E of WF-Ah from DMA) or $6.5\ \text{GPa}$ (E of WF-Ah from MTS), $E_y^{WF}=0.6\ \text{GPa}$ (WF-Th), $\nu_{xy}^{WF}=0.374$ [Forest Products Laboratory (U.S.) 1999], and $\nu_{yx}^{WF}=0.022$ [Forest Products Laboratory (U.S.) 1999]. G_{xy}^w was ignored during the calculation because these components did not influence the E of the laminate. The calculated elastic moduli (E_x and E_y) based on the LPT are close to experimental measurements. With $E_x^{CNF}=10.5\ \text{GPa}$ (from DMA) in the laminate calculations, the computed $E_x=10.8\ \text{GPa}$ and $E_y=1.3\ \text{GPa}$ are similar to the DMA measurements of $E_x=13\ \text{GPa}$ (LAM-A) and $E_y=1.9\ \text{GPa}$ (LAM-T), respectively. If $E_x^{WF}=6.5\ \text{GPa}$ (from MTS) was the basis, then the calculated $E_x=6.9\ \text{GPa}$ is close to the $E_x=5.8\ \text{GPa}$ (LAM-A) measured from the MTS. Recall that E in the transverse direction could not be measured

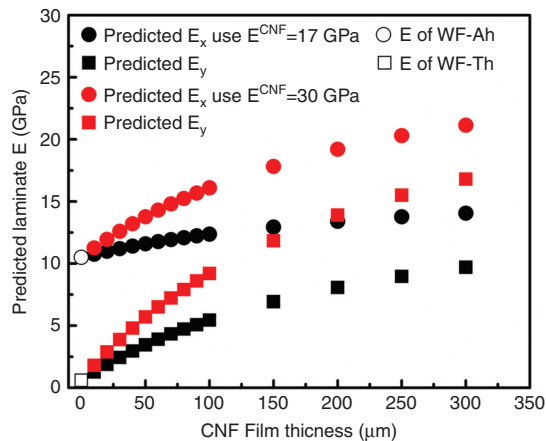


Figure 6 Graph of the predicted elastic modulus (filled symbols) of the CNF-WF laminate in transverse (E_y , squares) and axial (E_x , circles) directions with changing the thickness of the CNF film and with two different elastic modulus of CNF films [black ($E^{CNF}=17$ GPa), red ($E^{CNF}=30$ GPa)]. The prediction was calculated based on the laminated plate theory and DMA experiments. The initial elastic modulus (empty symbols) of WFs in axial (WF-Ah, square) and in transverse (WF-Th, square) directions are also indicated in this graph.

from MTS because of the test specimen's size restrictions, but the LPT predicted value was $E_y=1.3$ GPa. The variance between experimental results and theoretical prediction was below $\sim 30\%$. Contributions to this variance might come from not accounting for the PF layer that bonds the CNF films to the WF in the LPT, as well as the natural defects of WF.

LPT is also utilized for investigating the role of laminate configuration (e.g., CNF film thickness, and the E of CNF) on the predicted laminate stiffness. Figure 6 shows the predicted E_x and E_y of the CNF-WF laminate as a function of CNF film thickness (10–300 μm) for a fixed WF thickness ($t_{WF}=500$ μm) and $E_x^{WF}=10.5$ GPa (from DMA). When increasing CNF film thickness, both E_x and E_y became larger, with a greater increase in transverse direction. For 100 μm CNF film reinforcement, $E^{CNF}=17$ GPa, the WF stiffness in the transverse directions increased from 1 GPa to $E_x \approx 6$ GPa for the laminate. However, in the axial direction there was slight enhancement of E from WF (10.5 GPa) to laminate ($E_x \approx 12$ GPa). By increasing E^{CNF} from 17 to 30 GPa (e.g., $E^{CNF}=30$ GPa, which might be applicable for certain bacterial cellulose films, Watanabe et al. 1998),

the laminate properties improve more in E_x and E_y . Interestingly, the degree of anisotropy in E (e.g., transverse vs. axial direction) in the laminates decreased with stiffer CNF reinforcement (via increases in E^{CNF} and film thickness). For example, E anisotropy (axial/transverse) for WF is ~ 10 , while for the CNF-WF laminate with 100 μm CNF film thickness and $E^{CNF}=30$ GPa, the E anisotropy (E_x/E_y)=1.8.

Conclusions

Continuous wrinkle-free cellulose nanofibril (CNF) films were produced that had elastic moduli of $E=14$ –17 GPa, tensile strength of $\sigma_f=130$ –200 MPa, and strain to failure of $\varepsilon_f=0.8$ –1.6%. A lamination procedure was developed to make CNF-wood flake (WF) laminates. The results show that lamination increases the tensile properties of WF. The E and σ_f of WF in the transverse direction improved by reinforcement via lamination resulting in 200–300% increase in E and σ_f of laminate (LAM-T) as compared to the WF. However, in the WF axial direction the property enhancement was limited. The strengthening mechanism is attributable to a combined effect of the presence of CNF film together with PF crosslinking. Laminated plate theory (LPT) is useful for calculating the theoretical elastic moduli reinforcement resulting from the lamination. Predictions were $\sim 30\%$ lower than the experimental results, which were attributed to the fact that the presence of PF resin layer and WF modification were not considered in the LPT calculations. Overall, it was shown that the lamination of CNF films onto wood flakes has a strengthening and stiffening effect, particularly in the weak transverse direction.

Acknowledgments: The authors would like to thank the US Forest Service-Forest Products Laboratory (FPL) for funding this project (Grant number 09-JV-1111137-151). We are grateful for Rick Reiner and Zhiyong Cai from the FPL for providing the CNF suspensions and wood flakes, respectively.

Received April 29, 2013; accepted August 27, 2013; previously published online September 21, 2013

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