Self-Densified 3 mm-Thick All-(ligno)Cellulose Nanofiber Panel

Elmira Kaffashsaei

Gorgan University of Agricultural Sciences and Natural Resources

Hossein Yousefi (✉ hyousefi@gau.ac.ir)

Gorgan University of Agricultural Sciences and Natural Resources <https://orcid.org/0000-0002-4457-1345>

Takashi Nishino

Kobe University: Kobe Daigaku

Takuya Matsumoto

Kobe University: Kobe Daigaku

Mahdi Mashkour

Gorgan University of Agricultural Sciences and Natural Resources

Mehrab Madhoushi

Gorgan University of Agricultural Sciences and Natural Resources

---

Research Article

Keywords: Lignocellulose nanofiber, cellulose nanofiber, panel, self-densification

Posted Date: March 1st, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1283588/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License. [Read Full License](#)

Abstract

Al/lignocellulose nanofiber panel (LCNF-P) and *all*-cellulose nanofiber panel (CNF-P) with a nominal thickness of 3 mm were fabricated without adhesive or additive. To provide comparison, lignocellulose microfiber panel (LCMF-P) and cellulose microfiber panel (CMF-P) were also made. The pastes of nano- and micro-fibers were first cold pressed then dried with a mild drying condition in a vacuum oven at 60°C. Although the nominal target density of panels was 1 g/cm³ and a very mild pressure of 0.002 MPa (created by four paper clips) was employed during drying, the density of nano-panels increased to 1.3 g/cm³ thanks to their self-densification capability, while the density of micro-panels obtained around 0.8 g/cm³. X-ray diffraction test confirmed the laminate structure of all panels and also showed that lignin-containing panels had a lower crystallinity and crystallite size than those obtained from bleached fibers. FTIR test showed that the amount of lignin and hemicellulose in LCNF-P and LCMF-P were higher than those of CNF-P and CMF-P. TGA analysis did not show a distinctive difference among the initial onset temperature of specimens (around 270°C) and at 500°C the nano-panels showed higher char content compared to those of micro-panels. Long-term water absorption and thickness swelling tests demonstrated that nano-panels had a higher dimensional stability and less water absorption compared to those of micro-panels. Both the flexural and tensile strengths of LCNF-P (108 and 118 MPa respectively) and those of CNF-P (103 and 126 MPa respectively) were considerably higher than those of micro-panels.

1. Introduction

Wood is one of the most abundant sources of cellulose mainly in the form of cellulose nanostructures adhered by lignin and hemicellulose. Wood-based bio-nanocomposites have attracted considerable attention over the last two decades due to their promising properties, which include high mechanical and barrier properties, biodegradability, bio-renewability, wide variety and abundant raw materials, etc. (Berglund and Peijs 2010). Pure cellulose nanofibers (CNFs), produced from white wood pulp, are one of the wood derivatives which has received broad attention in the field of materials science and technology due to its wide applications and high physical and mechanical properties (Yousefi et al. 2018a). Brown wood pulp containing lignin and hemicellulose can be also downsized to lignin-containing nanofibers called lignocellulose nanofibers (LCNFs). In fact, LCNFs are composed of cellulose nanofibers impregnated with lignin and hemicellulose, which are an unpurified form of CNFs (Ferrer et al. 2012a; Hoeger et al. 2013).

The potential of energy saving, improvement in physical and mechanical properties and environmental issues has driven researchers across the world to compare LCNFs to CNFs in a variety of production techniques and applications. The rationale for the use of unbleached pulps, containing residual extractives, lignin, and hemicellulose, was that the materials can provide opportunities for production at higher yields and lower operational costs, with the potential benefits of some technical properties (Spence et al. 2010). LCNF production is cheaper than CNFs, because LCNF production does not require bleaching operations, so energy and chemical reagent consumption level is greatly reduced due to the elimination of the bleaching steps, so offer the advantage of higher yields and environmental burden by avoiding bleaching steps (Spence et al. 2010; Ferrer et al. 2012a; Hoeger et al. 2013). Spence et al. (2010) examined the amount of energy and chemicals used to produce lignocellulose and found that the LCNF product had many potential features for a variety of applications, including packaging. Moreover, lignin and hemicellulose which are naturally present in fibrils, also are a promising alternative for various applications due to the interesting properties conferred to the final material (Solala et al. 2019). The presence of lignin in the nanocomposite affects the morphology, crystallinity, thermal, physical and mechanical properties (Imani et al. 2019). In addition, the presence of lignin can regulate the polarity and hydrophobicity of cellulose, which can be considered for many applications, and in general we can say that LCNFs can be less polar and more hydrophobic than CNFs which allows better dispersion in non-polar media (Rojo et al. 2015). It has proven that the reinforcing effect of LCNFs for mechanical strength is similar to that of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-oxidized CNFs (Delgado-Aguilar et al. 2016). In addition, Rojo et al. (2015) showed that the presence of lignin in nanofibrils does not weaken the mechanical properties and it was comparable to those of products derived from fully bleached CNFs, while it might be expected that lignin weakened the hydrogen bonds between fibrils and thus reduces the amount of mechanical resistance. But, in fact the uniform distribution of lignin helps to transfer stress between fibrils and thus maintains mechanical resistance. A recent comprehensive study of lignin-containing composites also showed that films made of LCNFs did not reduce mechanical strength, because the lignin did not interfere with hydrogen bonding, as well as lignin substantially changed the interfacial free energy and increased hydrophobicity (Rojo et al. 2015). On the other hand, fibers containing lignin showed

improved water interaction and fibrillation at a moderate lignin level of 13% (Spence et al. 2010; Ferrer et al. 2012a). Rojo et al. (2015) also showed that increasing the amount of lignin reduces the diameter of fibrils during fibrillation, which is associated with the radical scavenging ability of the lignin that results in better cell wall deconstruction.

When we talk about wood-based composites and panels, we cannot ignore the issue of the polymer binders and adhesives used to hold them together. Different kind of resins such as polyester resin, phenolic resin, vinyl ester resin, epoxy resin and other binders and adhesives like melamine formaldehyde, urea formaldehyde, melamine-urea formaldehydes, phenol formaldehyde and methylene diphenyl diisocyanates are the most common binders and adhesives used in wood-based composites and panels (McDevitt and Grigsby 2014). In the recent years, there have been many concerns about adhesives and binders that pose serious environmental hazards (McDevitt and Grigsby 2014). The debate and challenges related to the depletion of non-renewable resource and environmental issues have increased in recent decades. One of the main environmental hazards that is very dangerous to health, is the emission of formaldehyde during board production and service life in wood composite materials due to the high toxicity of this substance. Negative environmental effects of synthetic adhesives, not only endangering human health, but also pose a threat to nearby community because of the release of volatiles and other wastes. For example, toluene, one of the solvents, is VOCs used as carrier fluids in conventional heat-melt adhesives, which is very dangerous from an environmental point of view and causes a lot of damage to health. Moreover, composites and panels made from thermoset adhesives severely limit the recyclability and reuse of fibers. On the other hand, in the recent years, very strict rules have been applied regarding the use of these adhesives in the manufacture of wood composites, so that all these cases together encourage scientists and industrialists to use environmentally friendly adhesive materials in the manufacture of wood composites. Wood adhesives from renewable raw materials can be a considerable and eco-friendly alternative to synthetic adhesives and the use of these renewable micro/nano materials becomes the new trend of adhesives (McDevitt and Grigsby 2014; Yang and Rosentrater 2015). Kojima et al. (2013) investigated the binding capacity of LCNFs in resin free *α*-lignocellulosic fiberboard of wood flour and observed improvements in physical and mechanical properties of the boards (Kojima et al. 2013). LCNFs have been used with the role of adhesives and binders in the production of medium density fiberboards (Diop et al. 2017) and in fabricating wood-flour boards (Kojima et al. 2013). In these studies, it was concluded that, when LCNFs are used as glue and binders in the fabrication of boards, the flexural strength and internal bonding of the board increase significantly (Kojima et al. 2013). Also, Yousefi et al., (2018) introduced a thick board made entirely from cellulose nanofibers with no adhesive or additive whose tensile and flexural strength were reported to be 85 MPa and 162 MPa, respectively.

Herein, we made *α*-lignocellulose nanofibers panel (LCNF-P) and *α*-cellulose nanofiber panel (CNF-P) with a nominal thickness of 3 mm through a wet process to make LCNF/CNF mats and subsequently drying in a vacuum oven with a very mild pressure created by paper clips. No adhesive/additive and no conventional hot press was used to make LCNF/CNF panels. Panels made from lignocellulose microfibers (LCMFs) and cellulose microfibers (CMFs) were used as controls. In addition, we discussed about the concept of self-densification of (ligno) cellulose nanofibers. The self-densification capability is mostly seen in nanostructures in which the structure is densified without using high pressure. From an economic point of view, the elimination of hot pressing step strongly affects the cost of the final product, because hot pressing step possesses high energy consumption (Wei et al. 2016).

2. Experimental

2.1. Materials

The particles of paulownia fortunei (cultivated in Gorgan, Iran) prepared from a wood saw mill (Gorgan, Iran) was used as the raw material in this study. Sodium hydroxide and sodium sulfite (Na₂SO₃), sodium hypochlorite (NaClO) and hydrogen peroxide (H₂O₂) (Merck Co., Germany) are purchased without further purification.

2.2. Methods

Figure 1 shows the general route and different products fabricated in this study. To produce CNFs, water slurry with 1 wt% cellulose fibers was passed three times through a disk grinder (MKCA6-2; Masuko Sangyo Co., Ltd., Japan) at 840 rpm, during which the gap between stator and rotator disks was set to be ~ 300 μm. The gel concentration was carried out using centrifuging (Sigma KS centrifuge apparatus (Sigma Co., Germany) at 14000 rpm for 30 min.

Figure 2 shows a simple schematic and real photo of hand-made cold pre-pressing system used to make LCNF/CNF mats prior to drying. The pre-pressing apparatus was mainly composed of a piston and cylinder made from poly-ethylene surrounded by an iron frame. To dewater LCNF/CNF gels, a steel screen with mesh size of 500 was used at the top of the cylinder to keep the CNFs inside the cylinder while allowing the water to drain out. First, 393 g of gel (6 wt%) containing 23.55 g dry-based LCNFs/CNFs was put in the cold press machine and then gradually pressed to dewater and cast, resulting in a LCNF/CNF mats. This process ended when no water withdrawal was seen from the cold pressed mat. The LCNF/CNF mats were then dried in a vacuum oven at 60°C for 12 h to make LCNF/CNF-board. Four paper clips were used to keep the LCNF/CNF mat inside a pair of 11×11 cm glass sheets which provided an effective pressure of 0.002 MPa which is very low pressure value compare to that of provide in conventional hot pressing system (3–5 MPa) of wood-based panels. The LCMFs and CMFs were also employed to make LCMF-P and CMF-P using the same fabrication method to allow comparison of the results.

2.3. Measurements

The apparent density of specimens was calculated through equations below:(Sadatnezhad et al. 2017)

$$D = m / v$$

1

where D is density of specimen (g/cm³), m is the mass of specimen (g) and v is the volume (cm³).

A field emission scanning electron microscopy (FE-SEM; JSM-6700F; JEOL, Tokyo, Japan) at an accelerating voltage of 5 kV was used to observe specimens at micro- and nano-scales. All specimens were dried in a vacuum and deposited with platinum/palladium (Osmium coater; Neoc-Pro MEIWAFOSS Co., LTD. Tokyo, Japan). The diameters of 100 micro and nanofibers were measured on micrographs using ImageJ software.

X-ray diffraction measurements were carried out using a Rigaku RINT-2000 at 40 kV and 20 mA in the range of $2\theta = 5-40^\circ$ at a scanning speed of 1.2 $^\circ$ /min. The crystallinity index (Xcr) was evaluated using the following equation.(Segal et al. 1959)

$$CrI = 100(I-I_a)/I(2)$$

where I is the diffraction intensity assigned to the 200 reflection of cellulose fiber which is typically in the range of 21° to 23° , I_a is the intensity measured at 2θ of 18° to 21° where the maximum occurs in a diffractogram for lignin, hemicellulose and non-crystalline cellulose.

The crystallite size of cellulose was estimated by Scherrer's equation (Scherrer 1918).

$$D = 0.9\lambda/\beta\cos\theta(3)$$

where D is the crystallite size, λ is the X-ray wavelength (0.15418nm), θ is the diffraction angle for the (200) plane, and β is the full width at half maximum.

The crystallite orientation (π) was determined by the following equation for the azimuthal profile of the 200 reflection.(Nishino et al. 2004; Kasai et al. 2005)

$$\pi = 180-H/180(4)$$

where H is the full width at the half maximum along the Debye-Scherrer ring.

A Fourier transform infrared spectrophotometer (SHIMADZU, Ltd., Spectrum IRTracer-100 FT-IR System) was used for the determination of the chemical composition of each sample. The dried (under a vacuum oven at 40°C for 48 h) samples were dispersed into KBr pellets. The prepared samples were measured at a range between 4000 and 400 cm⁻¹ with 2 cm⁻¹ resolutions for 10 times accumulation.

Thermal degradation behavior of specimens was evaluated using thermogravimetric analysis (TGA, Thermo plus EVO Ⅱ TG8121, Rigaku Co., Japan). The thermograms were run under a nitrogen atmosphere at a heating rate of 10 °C/min from 30 to 500 °C with Al pan.

To study the long-term water absorption (WA) and thickness swelling (TS), 10×10mm square specimens of nano- and micro-panels were immersed in distilled water from 0.1 h (6 min) to 240 h at room temperature. The amount of WA and TS was calculated using the following equations:

$$WA(t) = (W_t - W_o) / W_o \quad (5)$$

where $W(t)$ is the weight of specimen at immersion time t and W_o is the vacuum dried weight.

$$TS(t) = (T_t - T_o) / T_o \quad (6)$$

where $T(t)$ is the thickness of specimen at immersion time t and T_o is the vacuum dried thicknesses.

The flexural test of the specimens was performed in a Universal Testing Machine (AG-X plus, Shimadzu Co., Japan). The nominal dimension of specimens was 60×10×3 mm. The length of support span and load speed were 24 mm and 1 mm/min, respectively. Flexural strength, modulus of elasticity (MOE) and strain at break were calculated.

The tensile test of the specimens was carried out using a tensile tester (AG-X plus, Shimadzu Co., Japan) at room temperature. The specimens were trimmed to the size of 40 mm long and 4 mm wide. The load cell and crosshead speed were 1000 N and 1 mm/min, respectively. For the reliable data, the tensile test of five samples prepared under each condition, were performed and their results were averaged. Tensile strength, Young's modulus (E) and strain at break were calculated.

3. Results And Discussion

Figure 3 shows the photos of samples made in this study including a) LCNF-P, b) CNF-P, c) LCMF-P and d) CMF-P. Also, Table 1 presents the nominal and real dimensional and density values of panels. The color of LCMF-P and CMF-P is light brown and white, respectively, but in case of LCNF-P and CNF-P both samples converted to darker colors compared to the micro-panel ones. This is because of the effect of hydro-thermal treatment of the panels happened within drying step. As presented in Table 1, the nominal and real diameter of the micro-panels were the same, while in case of nano-panels the real diameter values were less than those of nominal ones and those of micro-panels. In case of thickness and volume, the corresponding real values for micro-panels were higher than those of nominal ones, but for nano-panels the real values of thickness were lower than those of nominal ones. These resulted in higher real density values of nano-panels compared to nominal ones (1 g/cm³) and lower real density values of micro-panels compared to nominal ones (1 g/cm³). This is meaning the real density of LCNF-P (1.33 g/cm³) and CNF-P (1.35 g/cm³) increased by +33% and +35% respectively compared to the nominal one. Also, the real density of LCMF-P (0.79 g/cm³) and CMF-P (0.81 g/cm³) decreased by -21% and -19% respectively compared to the nominal one. These facts are attributed to the greater compressibility of LCNFs/CNFs and their smaller dimensions compared to those of LCMFs/CMFs, which readily sealed the tiny pores; hence, the volume of void decreased and density increased. Also, since the pressure (0.002 MPa) provided at drying step originated from just 4 paper clips, it was not enough to collapse LCMFs/CMFs to get the nominal density, while in case of nano-panels it was concluded that self-densification or self-tightening happened during vacuum drying. In fact, the self-densification is due to the in-plane and out-of-plane shrinkage of nano-panels. This phenomenon is attributed to the nanostructure network of LCNFs/CNFs with high tiny porosity and high specific surface and bonding area as well as high aspect ratio and entanglements of LCNFs/CNFs. During drying, water molecules came out of the tremendous amount of tiny voids in the nanostructure network creating high capillary forces (Nakagaito and Yano 2005); thus, highly flexible nanofibers were brought closer together and the self-interactions of LCNFs/CNFs were created through the formation of hydrogen bonds. This resulted in self-densification of the nano-panels with no extra press pressure (Yousefi et al. 2018a; Li et al. 2020).

Table 1
Nominal and real dimensional and density values of panels.

Samples	Nominal diameter (cm)	Real diameter (cm)	Nominal thickness (cm)	Real thickness (cm)	Nominal volume (cm ³)	Real Volume (cm ³)	Dry mass (g)	Nominal density (g/cm ³)	Real density (g/cm ³)	Density changes (%)
LCNF-P	10	8.95	0.3	0.282	23.55	17.73	23.55	1	1.33	+ 33
CNF-P	10	8.9	0.3	0.28	23.55	17.41	23.55	1	1.35	+ 35
LCMF-P	10	10	0.3	0.38	23.55	29.83	23.55	1	0.79	-21
CMF-P	10	10	0.3	0.37	23.55	29.045	23.55	1	0.81	-19

Figure 4. depicts the FE-SEM micrographs from surface of LCNF-P, CNF-P, LCMF-P and CMF-P. The average diameters of LCNFs and CNFs obtained were 18 ± 7 nm and 27 ± 8 nm, respectively. The corresponding values for LCMFs and CMFs obtained were 28 ± 7 μ m and 28 ± 8 μ m respectively. The average diameters of LCNFs and CNFs were within the real nanoscale (1-100 nm), but those of LCNFs were averagely lower than that of CNFs. These results are compatible with the literature where it emphasized that due to the radical scavenging ability of lignin which induce the stability of the radicals during the mechanical defibrillation, as unbleached pulp is used as a starting material and lignin is not removed, the possibility of attraction between the fibrils decrease, favoring the separation of the fibers. The stabilization of free radicals promote the reduction of fibrils diameters together with the increase of lignin/hemicellulose content increase the repulsion among the fibrils. Consequently, a reduction of the crosslink and a better defibrillation of the samples could be expected and smaller fibrils diameters are obtained at lignin/hemicellulose-containing fibers (Solala et al. 2019).

Figure 5. shows a) X-ray diffraction profiles of the specimens and their crystallinity and crystallite size and b) X-ray diffraction photographs and π -value of the diffraction for the 200 reflection along the Debye-Scherrer ring. The X-ray was irradiated to the edge and through of the specimens, which were parallel and perpendicular of the surface, respectively.

The diffraction profiles of the specimens showed typical peaks at $2\theta = 15^\circ$, 16° , 22.5° , and 35° of cellulose I_β. Among the chemical compounds of wood, cellulose is made of crystals; so it shows peaks in the XRD graph, but the other components, including lignin and hemicellulose, are amorphous polymers which have a broad peak at 2θ of $18-21^\circ$ (Nishino et al. 2004; Yousefi et al. 2018b). The crystallinity of LCNF-P, CNF-P, LCMF-P and CMF-P obtained were 60, 63, 67, 70 percent, respectively. The corresponding crystallite size obtained were 4.5, 4.6, 5.3, 5.5 nm, respectively. Since lignin and hemicellulose are not crystalline polymers, the specimens containing such materials (LCNF-P and LCMF-P) showed less crystallinity index. The crystallinity and crystallite size of nanofiber panels apparently decreased compared with those of microfiber panels. These are due to high shear and pressure forces during grinding, which causes partially the cleavage of the crystallites and the increase of the non-crystalline part (Yousefi et al. 2010).

In the case of Fig. 5b, the photos were generated due to the X-ray irradiation to the edge (parallel to the surface) and through (perpendicular to the surface) of specimens. The Debye-Scherrer rings in the through-irradiated specimens showed a constant equatorial distribution scattering intensity with a π -value of zero. This corresponds to random in-plane distribution of the micro- and nano-fibers which is in agreement with FE-SEM micrograph as shown in Fig. 4. In case of edge-irradiated specimens, they presented a not constant equatorial distribution scattering intensity. Because of this, the π -value of LCNF-P, CNF-P, LCMF-P and CMF-P obtained were 50, 55, 62 and 58 percent, respectively. This result confirmed the laminate structure of panels. However, the diffraction pattern of the nano-panels became slightly diffuse, resulted in less π -value in such specimens. This is attributed to the fact that nano-panels possesses less crystallinity compared to that of micro-panels. In addition, the nanofibers containing crystals were separately positioned in nano-panels while the crystals of microfibers in micro-panels were naturally packed in the parallel direction; hence positively affected on the π -value of micro-panels in edge direction.

Figure 6 shows the FTIR spectra of specimens including LCNF-P, CNF-P, LCMF-P and CMF-P. The absorbance peak at 895 cm^{-1} is associated with the C-C stretching (Huang et al. 2016). The peaks at 1105 and 1034 cm^{-1} correspond to C-OH stretching (Huang et al. 2016) and C-O stretching vibration of lignin and polysaccharides (Huang et al. 2016). The absorbance peak appearing at 1165 cm^{-1} is the result of C-O-C stretching due to the presence of the pyranose ring on the cellulose fiber structure. The band

located in the 1243 cm^{-1} assigned to the stretching vibrations of C-O in xylene and syringyl ring in lignin and hemicellulose (Pandey and Pitman 2003; Huang et al. 2016; Moosavinejad et al. 2019), which was strong in the LCNF-P and LCMF-P, while significantly decreased in the spectra of CNF-P and CMF-P. The absorption peaks at 1322 , 1378 and 1436 cm^{-1} are the result of CH₂, C-H, and O-H deformations, respectively (Huang et al. 2016). The band appeared at 1464 cm^{-1} is assigned to asymmetric bending of CH₃ of lignin (Moosavinejad et al. 2019). The band at 1508 cm^{-1} is attributed to the stretching vibration in the C = C of aromatic structure (Gelbrich et al. 2012; Pucetaite 2012; Moosavinejad et al. 2019). There is an absorbance peak at 1595 cm^{-1} corresponding to the aromatic skeletal vibrations together with C = O stretching (Huang et al. 2016; Moosavinejad et al. 2019). All these three aforementioned bands attributed to lignin were clearly seen in the spectra of lignin-containing panels including LCNF-P and LCMF-P while significantly weakened in CNF-P and CMF-P. The peak located between 2800 and 2900 cm^{-1} correspond to C-H stretching due to aliphatic and aromatic structures (Huang et al. 2016; Moosavinejad et al. 2019). Finally, the absorption peak corresponding to the aromatic and aliphatic O-H stretching vibrations was seen around 3327 cm^{-1} (Huang et al. 2016; Moosavinejad et al. 2019). Based on FTIR results, it can be drawn that the amount of lignin and hemicellulose in LCNF-P and LCMF-P significantly higher than those of CNF-P and CMF-P. This is clearly attributed to the bleaching process, through which the lignin and hemicellulose content decreased. Also, it can be inferred that the spectra of LCMFs with LCNFs and CMFs with CNFs had high similarity confirming no chemical changes occurred within mechanical treatment of disk grinder.

Figure 7 shows the thermogravimetric (TGA) traces for micro- and nano-panels. The weight of specimens decreased slightly at low temperatures due to the removal of water. The decomposition-onset temperatures of all specimens were almost the same and ranged from 265 to $270\text{ }^{\circ}\text{C}$. A next degradation phase occurring between 270 to $370\text{ }^{\circ}\text{C}$ was attributed to the thermal depolymerization of hemicellulose and the breakdown of the glycosidic linkage of cellulose (Jose et al. 2014). Within this step, those specimens with less crystallinity index showed more rapid degradation rate. The removal of lignin in CNFs could explain its higher stability than its unbleached counterparts. Mostashari and Moafi (2007), stated that the initial decomposition of the cellulosic component takes place mostly in the amorphous regions. The removal of lignin by bleaching treatments was believed to increase the degree of crystallinity of cellulose, leading to higher thermal resistance (Jonoobi et al. 2009). The average char content of micro-panels (18%) were considerably lower than those of nano-panels (around 30%), mainly because of low crystallinity index of nano-panels compared to those of micro-panels, judging from Fig. 5.

Figure 8 depicts long term a) water absorption (WA) and b) thickness swelling (TS) of the specimens. The WA and TS values of the nano-panels and micro-panels increased with immersion time in water, and reached a plateau within 48 h. There are considerable significant differences between the WA values of nano-panels compared to the corresponding values of micro-panels. For example, the WA and TS values of the LCNF-P and CNF-P obtained after 24 h immersion time were 45% and 65%, respectively, while the corresponding values for the LCMF-P and CMF-P were 144% and 154%, respectively.

The WA and TS of micro-panels increased rapidly with initial immersion time (below 5 min) while the rapid increase in WA and TS of nano-panels occurred within 1 to 24 h. In comparison to micro-panels, the nano-panels had a more densified and consolidated structure with less pores, resulting in less capillary forces to uptake water. Also, the nano-panels consists a highly entangled nanofibrillated components with a higher specific surface and bonding area, resulting in less TS compared to the micro-panels. The WA and TS values of CNF-P were slightly higher than those of LCNF-P. From a molecular interaction point of view, lignin can control water contents and shield the free accessible hydroxyl group to prevent the formation of hydrogen bonding with water molecules, resulting in the reduction of WA (Spence et al. 2010; Horseman et al. 2017). However, this result did not repeat in cases of WA and TS values of LCMF-P and CMF-P as the WA and TS values were prominently affected by the porosity of the panels' structure rather than lignin content.

Figure 9. shows the mechanical properties of specimens including a) flexural strength, b) flexural modulus, c) strain at break of flexural test, d) tensile strength, e) Young's modulus and f) strain at break of tensile test. The flexural strengths of LCNF-P (108 MPa) and CNF-P (103 MPa) were considerably higher than those of LCMF-P (17.8 MPa) and CMF-P (13.4 MPa). In the case of flexural modulus and strain at break a similar results obtained. In case of tensile test, LCNF-P and CNF-P showed highest tensile strength of 118 MPa and 126 MPa, respectively while those corresponding values of LCMF-P and CMF-P were 14.3 and 13.5 MPa, respectively. The mechanical properties of LCNF-P and CNF-P did not show significant difference. Also, the mechanical properties of LCMF-P and CMF-P did not show significant difference. But as it was seen, the mechanical properties of nano-panels as

nanostructures dramatically increased compared to those of micro-panels. This is because the fiber diameter decreased from a micro-scale to a nano-scale resulting in higher specific surface and bonding area, higher aspect ratio as well as higher nanofiber entanglements and board density. Therefore, the nano-panels obtained a consolidated structure, and its mechanical properties were superior to those of the micro-panels. Also, microfibers possess several structural defect points such as fiber lumen, pits, etc. (Henriksson et al. 2008; Berglund and Peijs 2010; Sehaqui et al. 2011a, b; Yousefi et al. 2013). Although nano-panels showed high deflection under flexural and tensile forces it broke suddenly, while micro-panels broke more gradually.

4. Conclusions

The panels of pure lignocellulose nanofibers (LCNFs) and cellulose nanofibers (CNFs) were made through cold pre-press apparatus to dewater LCNF/CNF gels and then dried at vacuum oven with a very low pressure of 0.002 MPa to get a very high density of around 1.3 g/cm³, thanks to the self-densification properties. The flexural test was also carried out thanks to the high thickness of the nano-panels. The flexural and tensile properties of nano-panels were much higher than those of micro-panels (LCMF-P and CMF-P). Because of the above mentioned promising properties of LCNF-P and CNF-P, they can support future generations of green advanced materials in a wide variety of applications including aerospace, sporting equipment, building, automotive, defense, etc.

Declarations

Acknowledgments

E. K. would like to acknowledge the financial support of the Iranian Ministry of Sciences, Researches and Technology. Nano Novin Polymer Co. (Iran) is also thanked for its kind cooperation of nanofibers production.

References

1. Berglund L a., Peijs T (2010) Cellulose Biocomposites—From Bulk Moldings to Nanostructured Systems. *MRS Bull* 35:201–207. <https://doi.org/10.1557/mrs2010.652>
2. Delgado-Aguilar M, González I, Tarrés Q, et al (2016) The key role of lignin in the production of low-cost lignocellulosic nanofibres for papermaking applications. *Ind Crops Prod* 86:295–300. <https://doi.org/10.1016/J.INDCROP.2016.04.010>
3. Diop CIK, Tajvidi M, Bilodeau MA, et al (2017) Evaluation of the incorporation of lignocellulose nanofibrils as sustainable adhesive replacement in medium density fiberboards. *Ind Crops Prod* 109:. <https://doi.org/10.1016/j.indcrop.2017.08.004>
4. Ferrer A, Quintana E, Filpponen I, et al (2012a) Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellulose* 19:2179–2193
5. Ferrer A, Quintana E, Filpponen I, et al (2012b) Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellul* 2012 196 19:2179–2193. <https://doi.org/10.1007/S10570-012-9788-Z>
6. Gelbrich J, Mai C, Militz H (2012) Evaluation of bacterial wood degradation by Fourier Transform Infrared (FTIR) measurements. *J Cult Herit*. <https://doi.org/10.1016/j.culher.2012.03.003>
7. Henriksson M, Berglund LA, Isaksson P, et al (2008) Cellulose nanopaper structures of high toughness. *Biomacromolecules* 9:1579–1585. <https://doi.org/10.1021/bm800038n>
8. Hoeger IC, Nair SS, Ragauskas AJ, et al (2013) Mechanical deconstruction of lignocellulose cell walls and their enzymatic saccharification. *Cellul* 2013 202 20:807–818. <https://doi.org/10.1007/S10570-013-9867-9>
9. Horseman T, Tajvidi M, Diop CIK, Gardner DJ (2017) Preparation and property assessment of neat lignocellulose nanofibrils (LCNF) and their composite films. *Cellul* 2017 246 24:2455–2468. <https://doi.org/10.1007/S10570-017-1266-1>
10. Huang Y, Wang Z, Wang L, et al (2016) Analysis of Lignin Aromatic Structure in Wood Fractions Based on IR Spectroscopy. <http://dx.doi.org/101080/0277381320161179325> 36:377–382. <https://doi.org/10.1080/02773813.2016.1179325>
11. Imani M, Ghasemian A, Dehghani-Firouzabadi MR, et al (2019) Coupling Nanofibril Lateral Size and Residual Lignin to Tailor the Properties of Lignocellulose Films. *Adv Mater Interfaces* 6:1900770. <https://doi.org/10.1002/ADMI.201900770>

12. Jonoobi M, Harun J, Shakeri A, et al (2009) CHEMICAL COMPOSITION, CRYSTALLINITY, AND THERMAL DEGRADATION OF BLEACHED AND UNBLEACHED KENAF BAST (*Hibiscus cannabinus*) PULP AND NANOFIBERS. *BioResources* 4:626–639
13. Jose CC, Lovely M, Sabu T (2014) REVIEW OF RECENT RESEARCH IN NANO CELLULOSE PREPARATION FROM DIFFERENT LIGNOCELLULOSIC FIBERS. *undefined*
14. Kasai N, Kakudo M, Kasai N, Eroglu S., Toprak S., Urgan O, MD, Ozge E. Onur, MD, Arzu Denizbasi, MD, Haldun Akoglu, MD, Cigdem Ozpolat, MD, Ebru Akoglu M (2005) X-ray diffraction by macromolecules
15. Kojima Y, Minamino J, Isa A, et al (2013) Binding effect of cellulose nanofibers in wood flour board. *J Wood Sci* 59:396–401. <https://doi.org/10.1007/S10086-013-1348-0/FIGURES/5>
16. Li K, Wang S, Chen H, et al (2020) Self-Densification of Highly Mesoporous Wood Structure into a Strong and Transparent Film. *Adv Mater*. <https://doi.org/10.1002/adma.202003653>
17. McDevitt JE, Grigsby WJ (2014) Life Cycle Assessment of Bio- and Petro-Chemical Adhesives Used in Fiberboard Production. *J Polym Environ* 2014 224 22:537–544. <https://doi.org/10.1007/S10924-014-0677-4>
18. Moosavinejad SM, Madhoushi M, Vakili M, Rasouli D (2019) Evaluation of degradation in chemical compounds of wood in historical buildings using Ft-Ir And Ft-Raman vibrational spectroscopy. *Maderas Cienc y Tecnol*. <https://doi.org/10.4067/S0718-221X2019005000310>
19. Nakagaito AN, Yano H (2005) Novel high-strength biocomposites based on microfibrillated cellulose having nano-order-unit web-like network structure. *Appl Phys A Mater Sci Process* 80:155–159. <https://doi.org/10.1007/s00339-003-2225-2>
20. Nishino T, Matsuda I, Hirao K (2004) All-cellulose composite. *Macromolecules* 37:7683–7687. <https://doi.org/10.1021/ma049300h>
21. Pandey KK, Pitman AJ (2003) FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. *Int Biodeterior Biodegrad* 52:151–160. [https://doi.org/10.1016/S0964-8305\(03\)00052-0](https://doi.org/10.1016/S0964-8305(03)00052-0)
22. Pucetaite M (2012) Archaeological wood from the Swedish warship Vasa studied by infrared microscopy. Lund university Press, Sweden, pp 16
23. Rojo E, Peresin MS, Sampson WW, et al (2015) Comprehensive elucidation of the effect of residual lignin on the physical, barrier, mechanical and surface properties of nanocellulose films. *Green Chem* 17:1853–1866. <https://doi.org/10.1039/C4GC02398F>
24. Sadatnezhad SH, Khazaeian A, Sandberg D, Tabarsa T (2017) Continuous surface densification of wood: A new concept for large-scale industrial processing. *BioResources*. <https://doi.org/10.15376/biores.12.2.3122-3132>
25. Scherrer P (1918) Bestimmung der Grösse und der inneren Struktur von Kolloidteilchen mittels Röntgenstrahlen. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Math Klasse* 1918:98–100. <https://doi.org/10.1007/978-3-662-33915-2>
26. Segal L, Creely JJ, Martin AE, Conrad CM (1959) An Empirical Method for Estimating the Degree of Crystallinity of Native Cellulose Using the X-Ray Diffractometer. *Text Res J* 29:786–794. <https://doi.org/10.1177/004051755902901003>
27. Sehaqui H, Allais M, Zhou Q, Berglund LA (2011a) Wood cellulose biocomposites with fibrous structures at micro- and nanoscale. *Compos Sci Technol* 71:382–387. <https://doi.org/10.1016/j.compscitech.2010.12.007>
28. Sehaqui H, Zhou Q, Ikkala O, Berglund LA (2011b) Strong and tough cellulose nanopaper with high specific surface area and porosity. *Biomacromolecules* 12:3638–3644. <https://doi.org/10.1021/bm2008907>
29. Solala I, Iglesias MC, Peresin MS (2019) On the potential of lignin-containing cellulose nanofibrils (LCNFs): a review on properties and applications. *Cellul* 2019 274 27:1853–1877. <https://doi.org/10.1007/S10570-019-02899-8>
30. Spence KL, Venditti RA, Habibi Y, et al (2010) The effect of chemical composition on microfibrillar cellulose films from wood pulps: Mechanical processing and physical properties. *Bioresour Technol* 101:5961–5968. <https://doi.org/10.1016/J.BIORTECH.2010.02.104>
31. Wei P, Rao X, Yang J, et al (2016) Hot Pressing of Wood-Based Composites: A Review. *For Prod J* 66:419–427. <https://doi.org/10.13073/FPJ-D-15-00047>
32. Yang M, Rosentrater KA (2015) Environmental effects and economic analysis of adhesives: a review of life cycle assessment (LCA) and techno-economic analysis (TEA). *Am Soc Agric Biol Eng Annu Int Meet* 2015 5:1-

33. Yousefi, Azad S, Mashkour M, Khazaeian A (2018a) Cellulose nanofiber board. Carbohydr Polym 187:133–139.
<https://doi.org/10.1016/j.carbpol.2018.01.081>
34. Yousefi H, Azari V, Khazaeian A (2018b) Direct mechanical production of wood nanofibers from raw wood microparticles with no chemical treatment. Ind Crops Prod. <https://doi.org/10.1016/j.indcrop.2018.02.020>
35. Yousefi H, Faezipour M, Hedjazi S, et al (2013) Comparative study of paper and nanopaper properties prepared from bacterial cellulose nanofibers and fibers/ground cellulose nanofibers of canola straw. Ind Crops Prod 43:732–737.
<https://doi.org/10.1016/j.indcrop.2012.08.030>
36. Yousefi H, Nishino T, Faezipour M, et al (2010) All-cellulose nanocomposite made from nanofibrillated cellulose. Adv Compos Lett 19:190–195

Figures

Figure 1

The general route of making *a*ll-lignocellulose nanofiber panel (LCNF-P), *a*ll-cellulose nanofiber panel (CNF-P), together with those fabricated from lignocellulose microfibers (LCMF-P) and cellulose microfibers (CMF-P).

Figure 2

a) Schematic design and b) real picture of handmade cold pre-pressing apparatus used in this study.

Figure 3

Photos of specimens: a) LCNF-P, b) CNF-P, c) LCMF-P and d) CMF-P.

Figure 4

a) FE-SEM from surface of LCNF-P, b) CNF-P, c) LCMF-P, d) CMF-P

Figure 5

a) X-ray diffraction profiles of the specimens and their crystallinity and crystallite size and b) X-ray diffraction photographs and π -value of the diffraction for the 200 reflection along the Debye-Scherrer ring. π is crystallite orientation value.

Figure 6

The FTIR spectra of the specimens.

Figure 7

Thermogravimetric (TGA) traces for specimens.

Figure 8
a) Long-term water absorption and b) thickness swelling of LCNF-P, CNF-P, LCMF-P and CMF-P.

Figure 9

The mechanical properties of specimens including: a) flexural strength, b) flexural modulus, c) strain at break of flexural test, d) tensile strength, e) Young's modulus and f) strain at break of tensile test.