Recyclable Grease-Proof Cellulose Nanocomposites with Enhanced Water Resistance for Food Serving Applications

Rakibul Hossain

The University of Maine

Mehdi Tajvidi (✉ mehdi.tajvidi@maine.edu)

University of Maine <https://orcid.org/0000-0002-3549-1220>

Douglas Bousfield

The University of Maine

Douglas J. Gardner

The University of Maine

Research Article

Keywords: cellulose nanomaterials, wood flour, food containers, recyclability, water resistance

Posted Date: February 22nd, 2022

DOI: <https://doi.org/10.21203/rs.3.rs-1277635/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Recyclable cellulose nanofibril (CNF) and lignin-containing cellulose nanofibril (LCNF) coated wood flour composites were fabricated using a vacuum-filtration process for food serving applications. The coated cellulose nanofibril composites had excellent mechanical, and oil, and grease barrier properties compared to a commercial container. However, the composites with both LCNF and CNF coating layers had poor performance in wet conditions compared to the commercial container. The addition of 1 wt.% aluminum sulfate (alum) to the CNF and LCNF coating layer significantly improved the water-resistance of the composites. CNF +1% alum coated composites had inferior water resistance and lower mechanical strength in wet conditions compared to the commercial container. However, the LCNF +1% alum coated composites had comparable water resistance and higher wet mechanical properties than the commercial container. The recyclability of the composites was assessed through the disintegration of the samples in water and subsequent reformation, and it was found that the composites were fully recyclable. The composites could fully retain their mechanical and excellent oil and grease barrier properties after each recycling level. These recyclable fully bio-based nanocomposites can be an eco-friendly alternative for currently used food container systems that use harmful chemicals.

Introduction

The worldwide production of plastics has ramped up from 1.5 million metric tons in 1950 to 359 million metric tons in 2017 (PlasticsEurope 2019). Plastics are generally produced from fossil fuel sources and therefore are not sustainable (Balat 2007). Most plastics are non-biodegradable and they cause catastrophic pollution to the environment as 79% of the plastic wastes ends up in landfills or the ocean (Zaman and Newman 2021). Moreover, 12% of plastic wastes are incinerated producing various greenhouse gases in the atmosphere which contributes to global warming (Jambeck et al. 2015; Geyer et al. 2017). The large production of plastics along with their low recyclability (9% of the total global plastic production) creates a huge adverse impact on the environment (Weber Macena et al. 2021). Plastic materials can break into micro-plastics and nano-plastics; these smaller particles can enter into the body of animals and create health issues (Rodrigues et al. 2019).

With the rising demand for 'fast-food' or ready-made foods and beverages, the use of single-use plastics is increasing at an exponential rate. Approximately 80% of the marine wastes are plastic wastes and out of them, 70% are single-use plastics such as disposable plates, bottles, straws, etc. (Korbelyiova et al. 2021). There is a growing concern about the negative environmental impacts of plastic pollution and many environmental agencies are limiting or planning to limit the use of single-use plastics (European Parliament 2018). To fulfill the demands of petrochemical-free disposable plates, containers, bottles, etc., food and packaging industries have begun to replace plastic disposables with bio-based materials such as wood, leaf, grass, maize, bagasse, etc. (Korbelyiova et al. 2021). Driven by the growing concern of the consumers about the environment in recent years, the market value of the plastic-free disposable plates is expected to grow at a compound annual growth rate of 5.6% to reach from 4.26 billion USD in 2020 to 5.96 billion USD in 2027 (Acumen Research and Consulting 2020; Gill et al. 2020).

Food containers made from bio-based materials such as lignocellulosic fibers have some eco-friendly properties such as biocompatibility, biodegradability, compostability, recyclability, renewability, etc. (Iewkittayakorn et al. 2020). Though pulp or paper-based containers have certain edges over plastic food containers in terms of their eco-friendly properties, properties like poor resistance to water, oil, and grease limit their use in various food contact applications (Tarrés et al. 2018). The most common approach to improve the water, oil, and grease barrier properties of paper plates is by applying a coating layer of plastic materials (Li and Rabnawaz 2018). Various plastic materials such as low-density polyethylene (LDPE), melamine, poly siloxanes, polylactic acid (PLA), per or poly-fluoroalkyl (PFA) polymers, higher alkanes, etc. are used to impart water and oil and grease resistance to paper plates (Verdes et al. 1999; Osann and Fasching 2008; Li and Rabnawaz 2018; Xing et al. 2018). These coatings impart some undesirable traits to the eco-friendly properties of pulp or paper-based containers and create hindrance in their biodegradability, recyclability, and compostability properties (Deshwal et al. 2019; Triantafillopoulos and Koukoulas 2020).

Recycling disposable food serving containers is essential to reduce the carbon footprint and achieve a circular economy (Deshwal et al. 2019). One of the major misconceptions about pulp and paper-based food containers is that they are recyclable. However, most paper-based food containers are coated with plastic layers that make them difficult to separate from the fibers and thus cannot be recycled easily in a standard recycling mill (Yuhui 2018; Al-Gharrawi et al. 2021). Another issue with recycling plastic-coated fiber-based food containers is the migration of harmful chemicals like PFAs, bisphenol A and S, phthalates, adipates, etc. to food (Deshwal et al. 2019; Wu et al. 2020). Plastic coatings with PFAs possess some serious health concerns and environmental hazards, for which their use is declining for direct food-contact applications (OECD 2020).

To preserve the inherent eco-friendly properties of bio-based food containers, various research has been conducted to impart water, grease, and oil barrier properties to pulp and paper-based containers using bio-based materials such as sodium alginate and gellem gum coating (Zhang et al. 2017), bi-layered coating of chitosan and beeswax (Zhang et al. 2014), bi-layered coating of shellac and starch composites (Khairuddin et al. 2019), cellulose nanofibrils and lignin-containing cellulose nanofibrils coating (Tayeb et al. 2020; Hossain et al. 2021). These bio-based coatings impart different degrees of grease and oil resistivity but as with most bio-based materials they are hydrophilic and have inferior water resistance properties when compared to petroleum-based coatings. It is essential to find coating methods for the pulp and paper-based containers which are recyclable and have considerable resistance against water, oil, and grease to be used for food-serving applications.

Cellulose nanofibrils (CNFs) and lignin-containing cellulose nanofibrils (LCNFs) are garnering considerable interest attributed to their excellent properties like non-toxicity, renewability, biodegradability, tunable chemistry, high aspect ratio, high mechanical strength, high stiffness, high grease, and oil resistance (Tayeb et al. 2018; Dhali et al. 2021; Hossain et al. 2021). Because of the abundance of primary and secondary hydroxyl groups in their structure, CNFs and LCNFs can form extensive hydrogen bonds between themselves and also with other lignocellulosic materials (Tayeb et al. 2018; Amini et al.

2020). CNFs and LCNFs can form strongly bonded composite systems by acting as a binder with lignocellulosic materials such as wood (Kojima et al. 2014; Amini et al. 2017; Diop et al. 2017a; Hossain et al. 2021), pulp (Fortea-Verdejo et al. 2016), and paper (Yousefi Shivyari et al. 2016). As the aspect ratios of CNFs and LCNFs are high, they have a low percolation threshold which enables them to form films with a very dense network with high resistance against oxygen, grease, and oil (Lavoine et al. 2012; Tayeb and Tajvidi 2019; Tayeb et al. 2020; Hasan et al. 2021; Fein et al. 2021).

The hydrophilic nature of cellulose nanomaterials limits their applications in humid conditions or water. Because of the abundance of hydroxyl groups in the structure of CNFs or LCNFs, water molecules get adsorbed on their surface resulting in the swelling of their films (Shimizu et al. 2016). From previous studies, it has been reported that CNF or LCNF neat films or barrier coatings on fiber-based materials cannot sufficiently decrease wetting or water absorption (Ferrer et al. 2012; Lavoine et al. 2014; Xu et al. 2016; Mazhari Mousavi et al. 2017; Yook et al. 2020). Adsorbing water molecules plasticize nanocellulose films by cleavage of intrafibrillar hydrogen bonds that are formed under dry conditions, which drastically decrease the mechanical strength of the films at wet conditions (Shimizu et al. 2016). It has been reported that LCNF films or barrier coatings had higher resistance to wetting and water absorption than the CNF ones attributable to the presence of hydrophobic lignin in their structure (Rojo et al. 2015; Tayeb et al. 2020; Hossain et al. 2021). Various methods have been tried to improve the water resistance of the nanocellulose films or barrier coatings like chemical modification (Rodionova et al. 2011; Yang et al. 2014; Peresin et al. 2017; Solala et al. 2018), Silylation (Zhang et al. 2015), adding neutral sizing agents like alkyl ketene dimer (AKD) (Goo et al. 2018), making composites with poly vinyl alcohol (Hakalahti et al. 2015), carboxymethyl cellulose (Pahimanolis et al. 2013), starch (Prakobna et al. 2015), and chitosan (Toivonen et al. 2015). Though these methods impart hydrophobicity to nanocellulose surfaces to various degrees, most of these methods are expensive, time-consuming, and not eco-friendly (Yook et al. 2020). Moreover, most of these methods often decrease the crystallinity of the nanocellulose films and thus decrease their mechanical properties (Shimizu et al. 2016).

Aluminum sulfate or alum is one of the most important sizing agents in the history of papermaking. Alum-rosin size is widely prevalent in the paper industry to impart resistance to wetting and water absorption since the 1850s (Jablonsky et al. 2020). Alum is added to the pulp suspension as a wet-end additive during papermaking to act as a retention aid for anionic substances such as sizes, dyes, pigments, glue, and fillers (Kato et al. 2000). It is also used to accelerate drainage and reduce the tendency of pulp foaming during papermaking (Jablonsky et al. 2020). For its performance, low price, and wide availability, alum is termed the 'Papermaker's friend'. Alum can agglomerate the fibers together by acting as a coagulant and it can retain the smaller-sized fibers (fine fraction particles) on the larger fibers by electrostatic interaction between the cationic aluminum ion and anionic hydroxyl (OH^-) and carboxyl groups in pulp (Kato et al. 1998). There is no literature available to our knowledge about the utilization of alum as a sizing agent for improving the water-resistance of CNF or LCNF films or barrier coatings.

In our previous study, we utilized the binding and barrier properties of CNFs and LCNFs to fabricate multi-layer oil-resistant food serving containers using CNF or LCNF coated wood flour composites (Hossain et al. 2021). Compared with a commercial container, the produced multi-layer nanocellulose composites made with LCNFs as binder with maple wood particles (binder: wood particles ratio =30:70) at the base with LCNF or CNF coated top layer (40 g/m² coat weight) on a paper substrate had superior grease and oil resistance with a kit value 12 (highest possible) and had excellent mechanical and thermal properties to be used for food serving applications. However, the water resistance and recyclability of the produced nanocellulose composites were not investigated. For food serving applications, it is important to have a food container or plate with high water resistance and high wet flexural strength so that the plates do not leak, bend or break by absorbing water from the food materials. In this study, a food-serving container system was developed using LCNFs as a binder with wood flour (sawdust) and coated with LCNFs or CNFs and 1% alum to impart water, grease, and oil barrier properties. A comprehensive study was conducted on the surface morphology, mechanical, physical, and barrier properties of the coated composites to test the feasibility of utilizing this product for food serving applications and investigating the recyclability of these composites. The effect of the addition of alum on the physical, barrier, and mechanical properties of the nanocellulose composites was also investigated.

Materials And Methods

Materials

Three types of cellulose/lignocellulose nanomaterials were used in this study. CNF suspensions at 3 wt.% solids, 2.4% residual lignin, and 90% fines were produced by mechanical refining of bleached softwood kraft pulp (BKP) at the Process Development Center (PDC) of the University of Maine. LCNF suspensions at 3 wt.% solids, 10-15% residual lignin content with a kappa number 70-100, and 90% fines (Smook 2015) were produced from unbleached softwood kraft pulp (UBKP) at the PDC. The third material was the lignin-containing cellulose nanofibrils produced from recycled old corrugated containers (OCC) by a multi-step mechanical refining process denoted as LCNF-OCC. This material was produced at 3 wt.% solids and had 70% fines content and 16.7% residual lignin by weight (Amini et al. 2020). Fines content is defined as the percentage of fibrils with a length less than 200 µm and was measured using a MorFi Compact fiber analyzer (MorFi, Techpap Inc., Grenoble, France). The fibrillation process to produce LCNFs, CNFs, and LCNF-OCC at the PDC is documented elsewhere (Bilodeau & Paradis 2018).

The solids contents of the suspensions were measured using an Ohaus MB45 moisture analyzer (Ohaus Corporation, Parsippany, NJ). The 3 wt.% suspensions of LCNF-OCC, LCNFs, and CNFs were diluted to 2.0, 0.3, 0.3 wt.%, respectively before use by simply adding distilled water and mechanical stirring. The pH values of the suspensions were measured using a FiveEasyTM Plus pH meter (Mettler Toledo Rainin, Oakland, CA) and were 8.2 ± 0.4, 8.4 ± 0.3, and 9.1 ± 0.2 for LCNF-OCC, LCNF, and CNF suspensions, respectively. The particle size distributions of the LCNF-OCC, LCNF, and CNF suspensions with 70%, 90%, and 90% fines content, respectively were measured using a Malvern Mastersizer (Malvern Instruments,

Ltd., UK). Comparing the particle size distribution of the fibers, it was observed that the largest volume fraction of all fibers had mean particle size in the range of 10-200 μm (**Fig. S1**). The definition of fines content aligns with the particle size distribution of 90% fine LCNFs and CNFs as it can be observed that about 90% of the particles had lengths less than 200 μm . LCNF-OCC had more non-uniform particle size distribution than that of LCNFs and CNFs, and this can be attributed to the presence of different impurities like starch, inks, ash, adhesives, etc. present in the old corrugated containers (Yousefhashemi et al. 2019). At the same fines content, CNFs had a higher volume fraction of smaller particles than LCNFs (**Fig. S1**). A slight shift in the right in the particle size distribution of 70% fine LCNF-OCC indicates that this material had a larger particle size than the 90% fine LCNFs and CNFs. Lignetics (Louisville, CO) kindly supplied maple wood particles with a length of 1.0 ± 0.4 mm and an aspect ratio of 4.2 ± 2.1 at 9.5% moisture content. Liquid aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$) or alum was supplied as a 48.5 wt.% aqueous solution by Chemtrade Logistics Inc. (Ontario, Canada).

Fabrication process of coated nanocellulose composites

A schematic summary of the fabrication process of oil-resistant double-layered nanocellulose composite food serving plates with higher resistance to water absorption via vacuum-assisted filtration and hot pressing is given in Fig. 1. To prepare the base layer, the 2 wt.% LCNF-OCC suspensions were sonicated at 80% amplitude for 3 minutes using a Branson 450 Sonifier (Branson Ultrasonics Corporation, Danbury, CT). The ultrasound energy de-agglomerates the fibrils and homogeneously disperses the fibrils into the suspension (Hu et al. 2017). Maple wood particles were then added to the LCNF-OCC suspensions and mixed by mechanical stirring. The ratio of binder content (70% fine LCNF-OCC) to the maple wood particles was 30:70 by weight. The 0.3 wt.% LCNF or CNF suspension was used to prepare the top layer in the same process except for the addition of wood particles. One percent (by dry weight of CNFs or LCNFs) aluminum sulfate solution was added to the top layer suspensions and then mixed for 2 minutes at 2000 rpm with the help of a planetary mixer (Thinky 310, Thinky Corporation, Tokyo, Japan).

Vacuum filtration was used to produce samples. First, the base layer suspension was deposited on a polystyrene filter mesh of 40 μm pore size via a vacuum-assisted filtration method (Fig. 1.) The vacuum pressure was kept at 40 kPa for 3 minutes for the filtration of water. Once no more liquid water was filtered, the top layer suspension was deposited on the wet base layer. The total time for filtration of water was counted to the point when the time between two last drops of the filtrate exceeded 15 seconds. After the completion of filtration of water, the wet composite material was immediately removed from the filter mesh and placed between two sheets of filter paper, and the entire assembly was placed between two stainless steel plates. The steel plates along with the wet material were pressed (Carver Inc., Wabash, IN) at a temperature of 150°C at 1.5 MPa pressure in a hot press for 3 minutes. The moisture contents of wet and dried (hot pressed) composite material were $70 \pm 3\%$ and $2 \pm 0.5\%$, respectively. The basis weights of the base and top layer were 400 g/m^2 and 40 g/m^2 , respectively. By keeping the binder content the same and varying the top layer, nanocellulose composite materials were prepared in four formulations as LCNFs, LCNFs + 1% alum, CNFs, and CNFs + 1% alum as the top layer. Twenty samples of each formulation were prepared according to the process explained above. The samples were kept in a

conditioning room at $23 \pm 2^\circ\text{C}$ at $50 \pm 3\%$ RH for 24 hours before testing. The mass of the conditioned samples was measured using an analytical balance. The radius and thickness of the conditioned samples were measured using a Vernier caliper to determine volume. Density was calculated by dividing conditioned mass by volume.

Oil and grease resistance

The oil and grease resistance of the pre-conditioned nanocellulose composites were measured by standard 'KIT test' according to TAPPI T559cm-12 standard (TAPPI 1996). The test method involves placing a drop of reagent (oils with various viscosities) on the surface of the material from 13 mm height, which is then wiped off after 15 seconds using a cotton ball. If a dark stain is visible on the surface of the samples, then the test fails, and the absence of any spot is referred to as 'passed' kit value. Reagents consist of castor oil and two solvents (n-heptane and toluene), and their proportions are arranged in 1-12 levels according to the level of aggressiveness in penetrating the surface of the samples with kit values of 1 and 12 being the lowest and highest, respectively based on aggressiveness. The kit test was performed on the uncoated surface of five samples and coated surface of five samples of each formulation and a commercial container as control. An average kit number of five measurements was reported.

Water resistance

Water resistance of the nanocellulose composites was measured by the Cobb test by following a modified TAPPI T441 standard (Tappi 2009). The preconditioned samples were cut into an area of 77.8 cm^2 , weighed using an analytical balance, and fastened inside a Cobb tester with the coated surface facing up. A soft, non-absorbent rubber gasket of the same diameter as the test ring was used during the Cobb test to prevent leakage of water from the sides. 77.8 ml of deionized water was added to the Cobb tester for three test times, namely, 600 s, 1200 s, and 1800 s. Within $10 \pm 2\text{ s}$ of the expiration of the test, water was poured out from the Cobb tester, and samples were immediately placed between two blotting papers and pressed by a 10 kg roller to remove the residual water. The weight of the 'wet' sample was measured quickly where the difference between the dry and 'wet' weight gives the amount of water absorbed through the coated surface of the samples. Then water absorptiveness value (Cobb value) of the samples was calculated with Equation 1:

$$\text{Cobbvalue} \left(\frac{\text{g}}{\text{m}^2} \right) = \frac{\text{Weightofthe'wet'sample(g)} - \text{Weightoftheconditionedsample(g)}}{\text{Areaofthetestsurface} \left(\text{m}^2 \right)}$$

1

Cobb test was performed on the surface of five samples of each formulation as well as the commercial container. The amount of water absorbed was calculated to the nearest 0.01g.

Surface free energy

The surface free energy (SFE) of the coated surface of the nanocellulose composites and the top surface of commercial containers were measured by the double sessile method using a Krüss mobile surface analyzer (Krüss MSA, KRÜSS GmbH, Germany). In this method, the contact angle of two drops of liquid: one polar (water) and one non-polar (diiodomethane) are measured and surface free energy is calculated using the Owens, Wendt, Rabel, and Kaelble (OWRK) model (Owens and Wendt 1969; Kaelble 1970). The volume of the liquid drops was approximately 1 μL and contact angles were measured after 1 s of the drop on the surface. SFE of five preconditioned samples of each formulation and the commercial container was measured.

Microscopic analysis

For a better understanding of the surface morphology and configurations and arrangement of the coating layer of the nanocellulose composites, scanning electron microscopy (SEM) imaging was performed on the uncoated, coated surface and cross-sections of the composites with an Amray 1820 SEM (Amray Inc., New Bedford, MA). The samples were mounted on a specimen mount with double-sided carbon tape and then painted with conductive silver paint at the edges. The studied samples were sputter-coated with Au/Pd (23 nm) using a Cressington 108 sputter coater (Ted Pella Inc., Redding, CA). SEM was operated at an accelerating voltage of 10 kV and high-resolution images were obtained at different magnifications.

Energy-dispersive X-ray spectroscopy

To evaluate the distribution of aluminum on the surface and cross-section of the nanocellulose composites, energy-dispersive X-ray spectroscopy (EDS) was performed on the coated surface and cross-sections of the composites with an Amray 1820 SEM equipped with EDS (EDS, iXRF model 550i, Amray Inc., New Bedford, MA). Samples were mounted on a carbon specimen mount with double-sided carbon tape and painted with conducting carbon paint at the edges. Similar to SEM, samples were sputter-coated with Au/PD (23 nm) and EDS was operated at an accelerating voltage of 10 kV. In this study, the distributions of carbon, oxygen, and aluminum were obtained, and elemental mapping of Al was performed at 5000X magnification.

Fourier transform infrared spectroscopy

To identify the chemical functional groups and to investigate the formation of any new bond after the addition of alum to the top layer of CNF or LCNF coated composites, Fourier transform infrared spectroscopy (FTIR) was performed on the surface of the composites using a Perkin Elmer FTIR-attenuated total reflectance (ATR) spectrometer (Spectrum Two, PerkinElmer, Shelton, CT). Coated nanocellulose composites were placed on a diamond crystal with an ATR accessory. The spectra were collected in the absorbance mode with a resolution of 4 cm^{-1} . The data were obtained under an accumulation of 16 scans in the range of 450-4000 cm^{-1} .

Mechanical properties

To evaluate the mechanical properties of the nanocellulose composites and the commercial containers, flexural tests were performed on the samples using a 500 N load cell Instron mechanical testing machine

(Model 5942, Instron Instruments, Norwood, MA). Composites and commercial containers were cut into strips of 8 cm × 1.5 cm dimensions and a three-point bending test was performed on each of the strips to determine the flexural properties. Modulus of rupture (MOR), modulus of elasticity (MOE), and flexural strain values were determined from the stress-strain curve obtained from the flexural test. The span length was 60 mm and cross-head speed was maintained at 5 mm/min. 'Dry' flexural tests were conducted on the samples that were conditioned at 23 ± 2°C at 50 ± 3% RH for 24 hours. At least six samples of each formulation were used for the 'dry' flexural test.

'Wet' flexural tests were conducted on the samples that were used for the water absorptiveness test. Immediately after the completion of the water absorptiveness test (Cobb test) for 600 s, 1200 s, and 1800 s, samples were cut into strips of 8 cm × 1.5 cm dimensions and flexural tests were conducted on the 'wet' samples. The moisture content of the strips was measured using a moisture analyzer (Ohaus MB45 Corporation, Parsippany, NJ) immediately after completion of the flexural test. Modulus retention term (MRT) of the composites obtained from the 'wet' flexural test was calculated according to Equation 2:

$$\text{MRT}(\%) = \frac{\text{Modulus of elasticity at 'wet' condition}}{\text{Modulus of elasticity at 'dry' condition}} \times 100$$

2

At least six samples of each formulation at each water absorptiveness test time were used for the 'wet' flexural test.

Recyclability assessment

The hot pressed-dried nanocellulose composites with LCNFs at the top were recycled according to the process shown in Fig. 1. First, the composites were immersed in water at room temperature for 30 minutes. Then the materials were disintegrated using a kitchen blender (Waring Commercial, Conair LLC, Stamford, CT) at speed level 5 for 5 minutes to create a 2 wt.% suspension of the mixture of wood particles, LCNF-OCC and LCNFs. The remainder of the process was identical to the method described earlier. The nanocellulose composites were recycled up to five times and six samples were prepared for each (1,2,3 and 5) level of recycling.

The samples were kept in a conditioning room at 23 ± 2°C at 50 ± 3% RH for 24 hours before testing. Densities of the conditioned samples were measured according to the method described earlier. The length, width, and aspect ratio of the wood particles in each level of recycling were measured by using a particle size analyzer (Morphologi G3, Malvern Panalytical Ltd., Malvern, UK). Oil and grease resistance and mechanical properties of the recycled samples were evaluated using the same methods described above.

Statistical analysis

A one-way analysis of variance (ANOVA) was performed on the data obtained from flexural, surface free energy, water absorption (Cobb), and recyclability tests. To observe the significance of the difference

among group means, a Duncan's Multiple Range Test (DMRT) was then used as a post hoc test. All statistical analyses were performed at a 95% confidence level using IBM SPSS Statistics Version 23 (IBM Corp., Armonk, NY).

Results And Discussion

Surface morphology of the composites

SEM images of the uncoated and coated surfaces were taken at different magnifications for a better understanding of the surface morphology of the composites. The microscale pores and wood particles were visible in the SEM images of the uncoated composites (Fig. 2a). A much smoother surface was observed in the case of coated composites, and it is evident that the top layer of CNFs or LCNFs with a coat weight of 40 g/m² was sufficient to fill up the pores of the base layer as no wood particles or pores were noticeable on the SEM images of the coated composites (Fig. 2b, c, d, e). Such a non-porous structure is essential for imparting barrier properties to the composites as grease, oil and water can penetrate through porous surfaces (Yook et al. 2020). SEM images of CNF or LCNF top layer revealed micron-scale fibers with nanoscale fibrils attached to them and together they formed a tight network structure by agglomeration and entanglement, which is possible due to the intermolecular attraction (mostly hydrogen bonds and Van der Waals attraction) between the fibrils (Aulin et al. 2010). A similar observation was reported when a CNF or LCNF layer was coated on paper (Tayeb et al. 2020; Yook et al. 2020). The CNF or LCNF coated surfaces were slightly smoother with the addition of 1% alum (Fig. 2c, e). LCNF coated surfaces were much smoother than the CNF coated ones and this is because when the wet base layer with 70 ± 3% moisture content is hot pressed at 150°C for 3 minutes, lignin softens and act as a cementing agent between the fibrils and fills the void between them resulting in a smoother surface. Similar phenomena of reduced roughness of LCNF coated surface due to softening of lignin have been reported in other studies (Ferrer et al. 2012; Rojo et al. 2015; Tayeb et al. 2020).

SEM images of the cross-sections of the coated composites revealed coated layers of LCNFs and CNFs with a micron-scale thickness (Fig. 3). The top layer is compactly arranged with the base layer as no layer spacing was visible between the base and top layers. Like the surface of the uncoated composites, micron-scale pores were visible at the cross-sections of the base layer due to the absence of a coating layer. A layer-by-layer arrangement of the coating layer was observed at higher magnifications, and this is because the top layer was deposited on the base layer by the filtration of the LCNF or CNF suspensions over a time of several minutes which allowed the fibrils to be deposited in a swirling conformation with the principal axis in the plane of the film (Rojo et al. 2015). Such layer-by-layer arrangement of CNF or LCNF films has been reported in other studies (Ferrer et al. 2012; Rojo et al. 2015; Chen et al. 2018; Tayeb et al. 2020; Fein et al. 2021). One interesting observation was that there were some voids between the series of individual layers in the internal structure of both CNFs and LCNFs. It is possible that these inter-layer spacings were formed due to the passage of water vapor during drying of the wet composites by assuming that the surface is more densely packed than the center in the internal structure of the CNF

coated layer. As the wet mat was dried at high temperature and by applying pressure in the z-direction, water evaporates in the easiest path i.e., in the x-y directions of the fibril layers as z-direction is blocked by a more densely packed CNF network at the surface. It has been reported that for CNF films prepared by vacuum filtration followed by restrained drying, the surface skin layer was more densely packed than the core, thus it is easier for the water vapor to pass through the core than through the surface (Fein et al. 2021).

EDS mapping was conducted to gain insight into the distribution of aluminum on the surface and cross-section of the coated composites (Fig. 4) as a measure for the retained alum as well as its distribution. From the EDS spectrum, it is seen that the major constituents of all the samples were carbon and oxygen (**Fig. S3**). As expected, no traces of aluminum were seen in the LCNF and CNF coated surfaces when alum was not added (Fig. 4a, c) whereas the retention of aluminum on the surface of composites coated with LCNFs or CNFs with 1% alum can be confirmed from EDS analysis (Fig. 4b, d). From cross-section images, it can be noted that aluminum is mostly deposited on the top layer where there were minute traces of aluminum in the base layer (Fig. 4e, f). There is no literature available to the author's knowledge which elucidates the adsorption mechanism of aluminum at LCNF or CNF surface. However, the retention mechanism of aluminum species on fine fractions (smaller length fiber) of cellulose during alkaline papermaking can clarify the mechanism of adsorption of aluminum on the LCNF or CNF surface. The retention of aluminum on the fiber surface is dependent on the pH of the pulp suspensions, alum concentration, and the presence of other chemical species (Rojas and Hubbe 2004). It has been reported that in alkaline conditions, retention of alum on fine fractions of cellulose fiber follows mainly two mechanisms; one mechanism is that multivalent cationic aluminum species are adsorbed on fine fractions mostly by the electrostatic interaction with carboxyl groups (Budd and Herrington 1989; Kato et al. 2000). Another mechanism of alum retention is that aluminum flocs are formed by the reaction between OH^- ions and aluminum species in the pulp suspension which is adsorbed on the fine fractions by being trapped during filtration (Kato et al. 1999; Kato. et al. 2000). From FTIR analysis it can be confirmed that no new bond was formed on the CNF or LCNF surface after the addition of alum and it is expected as there is a negligible amount of carboxyl group present in the CNF or LCNF surface (**Fig. S2**). From FTIR analysis it can also be confirmed that the adsorption mechanism of aluminum on the CNF of LCNF surface is not a chemical interaction but a physical one (**Fig. S2**). The pH of the LCNF and CNF suspensions were 8.4 ± 0.3 , and 9.1 ± 0.2 respectively. At pH above 5.5 and equilibrium conditions, all aluminum species that originate from alum react with OH^- groups present in the CNF or LCNF suspensions to form aluminum flocs and the retention of aluminum species at the CNF or LCNF surface may be attributed to the physical entrapment of aluminum flocs in the fibers during the filtration process. In addition, cationic aluminum flocs may become adsorbed on the fibril surface by hydrogen bonding or Van der Waals interaction with the OH^- groups present (Ohno 1999).

Chemical and surface characterization

The FTIR absorption spectra of the coating layer of LCNFs and CNFs with and without the addition of 1% alum ranging from 4000 to 450 cm^{-1} are presented in **Fig. S2**. All the spectra were normalized by taking C-O at 1055 cm^{-1} as the reference peak. Both LCNFs and CNFs exhibited similar peaks including 3330 cm^{-1} (intermolecular O-H band), 2900 cm^{-1} ($-\text{CH}_2-$ stretching vibration), 1632 cm^{-1} (oxygen-containing group of C-O and O-H), 1435 cm^{-1} ($-\text{CH}_2-$ bending vibration), 1390 cm^{-1} ($-\text{CH}-$ vibration) and 1055 cm^{-1} (stretching vibration of C-O) (Chen et al. 2018; do Lago et al. 2021). However, the LCNF coating layer exhibited a peak at 1610 cm^{-1} which is absent in the CNF coating layer due to the stretching vibration of the C=C bond present in the phenyl group of lignin (Chen et al. 2018). The ratios of O-H and C-O were calculated from the FTIR spectra and the values for LCNFs and CNFs were 0.35 and 0.39, respectively. Such a decrease in the ratio of O-H and C-O suggests that there are more available hydroxyl groups on the surface of CNF samples than LCNF ones (Diop et al. 2017b). The FTIR spectra of the LCNF and CNF materials with and without the addition of alum were identical which indicates that there were no new bonds as a result of alum addition.

Surface properties of the composites

Table 1

Water contact angles, diiodomethane contact angles, grease resistance (Kit number), surface free energy, and its components for the surface of the produced composites ^{*}.

Coating material	Water contact angle (°)	Diiodomethane contact angle(°)	Surface free Energy (mN/m)	Dispersive surface energy (mN/m)	Polar surface energy (mN/m)	Grease resistance (Kit No)
LCNFs	43.4 (14%)	44.1 (18%)	60.5 (14%)	37.5 (11%)	23.0 (18%)	12
LCNFs + 1% alum	47.5 (10%)	41.0 (24%)	58.9 (15%)	39.1 (13%)	19.8 (19%)	12
CNFs	30.3 (26%)	45.8 (17%)	67.3 (15%)	36.6 (11%)	30.8 (20%)	12
CNFs + 1% alum	32.6 (24%)	52.2 (10%)	64.8 (14%)	33.0 (9.3%)	31.7 (19%)	12
*Values in parenthesis are coefficients of variation (CV%).						

To gain insight into the barrier properties of the composites, surface free energies (SFE) were determined as SFE of solid is a characteristic parameter that has a strong effect on wetting and adsorption of water, oil, and grease (Rojo et al. 2015). SFE and their polar and dispersive components along with the contact angle values of the coated composites are presented in Table 1. Water contact angle (WCA) values of all

nanocellulose coated composites were less than 90°, suggesting their hydrophilic property attributable to the presence of exposed hydroxyl groups at the CNF or LCNF surface (Yook et al. 2020). The WCA values of the LCNF coated composites were higher (43.4 ± 6.2)° than the CNF coated ones (30.3 ± 7.9)° and this can be attributed to the presence of lignin which increases the hydrophobicity of the LCNF coated surface (Ferrer et al. 2012; Rojo et al. 2015; Tyagi et al. 2021). Lignin in its native state is more hydrophobic than cellulose and it can shield accessible hydroxyl groups present at the fibril surface, thereby preventing them from forming hydrogen bonds with water molecules (Rojo et al. 2015; Chen et al. 2018). From FTIR analysis it was seen that the ratio of O-H and C-C was higher for CNF coated composites (0.39) than the LCNF-coated ones (0.35) which suggests that the number of exposed hydroxyl groups at the LCNF surface is less than those on the CNF surface (**Fig S2**) (Ghasemi et al. 2017). The SFE of the CNF-coated composites was slightly higher than that of LCNF-coated ones as lignin present in LCNFs decreases the polar components of SFE (Hossain et al. 2021). There was no change in the WCA and SFE values with the addition of 1% alum for both CNF and LCNF coated composites. From these observations, it is understood that the addition of alum to the CNF or LCNF coating layer does not have any effect on providing resistance to wetting by liquid water.

Water resistance

For food serving applications, it is essential to have plates or containers that can hold water/wet food for a long time without leaking. Water absorption values (Cobb values) of the coated composites at different times are given in Fig. 5a. For all coated composites and commercial containers (C.C.), Cobb values increased with the increase of time which is expected as more water can penetrate through them with increased time. For each time level of 600 s, 1200 s, and 1800 s, the water absorption values of CNF coated composites were significantly higher compared to LCNF coated ones. However, Cobb values of C.C. (at all-time levels) were still significantly lower than the CNF- and LCNF-coated composites which indicate their higher water resistance than the coated composites. The addition of 1% alum reduced the Cobb values of both CNF and LCNF coated composites but even the reduced Cobb values of CNF + 1% alum coated composites were higher than LCNF-coated composites. However, LCNF-coated composites with 1% alum had the highest water resistance among all the other formulations with Cobb values slightly higher than the commercial container at all-time levels.

A schematic representation of the mechanism of water absorption in the coated composites is given in Fig. 5b. The layered structure of CNFs or LCNFs (as observed from surface and cross-section SEM images) may help in understanding the water absorption property of the coated composites. Water can be absorbed by coated composites as adsorbed water molecules can plasticize nanocellulose films by cleavage of intrafibrillar hydrogen bonds and penetrate the surface (Shimizu et al. 2016). As observed from the WCA values, both LCNF and CNF coated surfaces were hydrophilic ($WCA < 90^\circ$), and thus they cannot resist the penetration of water through the pores by capillary action. Water can penetrate the surface of CNFs or LCNFs easily, but it needs to travel through a tortuous path formed by the layered arrangement of the CNF or LCNF coating layer to reach the base layer (Fig. 5b). Because of tortuosity, water must take a longer path to pass through the top layer and thus it reduces the intra-fiber flow rate of

water molecules. Once it reaches the base layer it can traverse the other side of composites easily attributable to the presence of many pores (as observed from SEM images). For CNF-coated composites, it was observed that water did not leak from the other side of the composites at 600 s and 1200 s, but it did for 1800 s test time. No leakage was observed for the LCNF coated composites for any of the test times. Lower water absorption values of LCNF coated composites than CNF ones can be attributed to the hydrophobic nature of lignin. Lignin can shield the water molecules from forming hydrogen bonds with hydroxyl groups and thus it can reduce water penetration (Nair and Yan 2015). Besides, the softening temperature of softwood and hardwood lignin is reduced to less than 50°C at or above 20% moisture content (Börcsök and Pásztor 2020). During hot pressing of the wet mat at 150 °C with 70 ± 3% moisture content, lignin softens and acts as a glue to fill the voids between the fibrils resulting in a much more densely packed and smoother structure (Jiang et al. 2019). Consequently, the flow rate of water molecules through the LCNF layer is slow compared to CNF ones attributable to the filling up of the voids between the fibrils.

For a better understanding of the mechanism of water absorption through the LCNF or CNF coated composites, neat films of the top layer and the base layer were prepared separately by following the method described in Fig. 1. A water absorption test was conducted on the neat CNF or LCNF films with and without the addition of 1% alum for 1800 s. The Cobb values of the neat films followed the same trend of the composites with LCNFs +1% alum presenting the least Cobb value and CNFs exhibiting the highest one. Interestingly, it was observed that water leaked to the other side of the neat CNF films but there was no leakage for the LCNF + 1% alum one. The water absorption test failed for the uncoated composites as water could easily penetrate the uncoated surface in less than 5 s and leak from the other side. These observations corroborate our hypothesis that the water-resistance of the coated composites is mainly attributable to the tortuous passage of water through the dense top coating layer.

The Cobb values decreased for both LCNF and CNF coated composites when 1% alum was added. From FTIR analysis it was observed that no new covalent bond was formed on the CNF or LCNF surface with the addition of alum (**Fig. S2**). An increase in water resistance with the addition of alum to the coated surface can be attributed to the electrostatic interaction between adsorbed cationic aluminum species and the hydroxyl groups present on the fibril surface. Because of the presence of a multi-valent positive charge, alum can bring the fibrils together by reducing the repulsive forces between them in aqueous suspensions (Rojas and Hubbe 2004). This property can also help to explain the reduction in filtration time due to the addition of alum. It was observed that during the preparation of the wet composites via vacuum filtration, the filtration time was reduced by ~ 45% for both CNF and LCNF suspensions when alum was added. Decrease in filtration time can be attributed to the property of alum to bring the fine fibrils together as fine fibrils may block the pores of the filter mesh or drainage passage of the wet mat during filtration. When the fibrils in LCNF and CNF suspension are closer together, fibrils are more closely packed as a result of increased hydrogen bond formation and van der Waal's attraction force between them. Because of the formation of more hydrogen bonds, the charge density attributable to hydroxyl groups is expected to decrease which provides fewer sites for water molecules to form hydrogen bonds and thus lowers inter-fiber diffusion of water (Ferrer et al. 2012). To prove this hypothesis, cast films of

CNFs, LCNFs with and without the addition of 1% alum were prepared in a petri dish and allowed to dry in a vacuum hood for 48 hours. It was observed that the density of the CNF and LCNF films increased by 8 ± 0.3 and $11 \pm 1.4\%$ respectively with the addition of 1% alum. An increase in density of CNF and LCNF films means they are more compactly arranged attributable to extensive hydrogen bond formation between the fibrils (Tayeb et al. 2018). The flow rate of water molecules is expected to decrease because of the increase of density in the top layer with the addition of alum. With the increase of density, the number of pores per volume in which water can be absorbed decreases, resulting in lower water absorption values (Amini et al. 2017). Further study is needed to elucidate factors affecting the water adsorption of CNF or LCNF coated surface in the presence of alum, however, this is beyond the scope of this research.

Oil and grease resistance

All the coated composites exhibited excellent oil and grease resistance and all of them passed kit value 12 (the maximum possible) (Table 1). However, uncoated composites had very poor oil and grease resistance and could not even pass kit no. 1. Such excellent resistance to oil and grease can be attributed to the dense, tight network structure formed by the fibrils attributable to the extensive hydrogen bonding between them (Tayeb et al. 2020; Fein et al. 2021). As observed from SEM images, coated composites had no visible pores through which oil or grease can penetrate. It has been reported that the oil and grease resistance of the nanocellulose films increases with the decrease of air permeability (Aulin et al. 2010). The porosity of CNF or LCNF films can be correlated with air resistance as high air resistance means dense films with low porosity (Tyagi et al. 2021). The air resistance of our coated composites could not be measured as they had a very tight structure with air resistance values below the measurement limit of the Gurley Densometer. Such tight structures of CNF- and LCNF-coated composites with low porosity impart excellent oil and grease barrier properties to the coated composites. As discussed earlier, the layered arrangement of the CNF or LCNF top layer creates a tortuous path for the passage of water which is also true in the case of the oil and grease pathways (Hossain et al. 2021). Besides, the intrinsic hydrophilicity and hydrogen bonds have been reported to be responsible for such excellent oil and grease resistance property of CNFs (Aulin et al. 2010; Hubbe et al. 2017). As expected, LCNF or CNF-coated composites with 1% alum also had excellent grease and oil resistance with kit no. 12 as the addition of alum is expected to make the LCNF or CNF layer even tighter.

Mechanical properties

Table 2

Modulus of rupture (MOR), modulus of elasticity (MOE), flexural strain (%), and the density of the composites and the commercial container (C.C.).

Core binder material	Core binder content (%)	Top layer material	MOR (MPa)	MOE (MPa)	Flexural strain (%)	Density (g/cm ³)
70% fine LCNF- OCC	30	LCNFs	13.1 (16%)	2055 (17%)	0.88 (7.9%)	0.73 (4.8%)
		LCNFs + 1% alum	12.7 (7.3%)	1984 (12%)	0.88 (11%)	0.75 (4.7%)
		CNFs	14.9 (9.2%)	2223 (11%)	0.92 (12%)	0.76 (3.7%)
		CNFs + 1% alum	12.6 (15%)	2025 (18%)	1.02 (12%)	0.76 (6.6%)
Commercial container (C.C)			9.70 (4.7%)	1208 (9.3%)	1.06 (8.8%)	0.57 (6.8%)
*Values in parenthesis are coefficients of variation (CV%).						

The produced composites should have sufficient mechanical strength in both 'dry' and 'wet' conditions to be used for food serving applications. The modulus of rupture (MOR), modulus of elasticity (MOE), and flexural strain values obtained from the flexural test of the preconditioned samples and their density values are presented in Table 2. The density values of the composites were in the range 0.73 – 0.76 g /cm³ and from the ANOVA test, it was found out that the density values were not statistically different for all formulations (p-value >0.05). It is seen from Table 2 that all composites had significantly higher MOR (12.7 -14.9 MPa) and MOE values (1984 - 2055 MPa) compared to the C.C. disregarding the type of coating layer. Such excellent mechanical properties of the composites can be attributed to the binding property of 70%-fine LCNF-OCC with lignocellulosic materials as they can form numerous hydrogen bonds with the wood particles and the fibrils themselves to form a strongly bonded composite system (Tayeb et al. 2018; Amini et al. 2020; Hossain et al. 2021). MOR and MOE values of the composites with all formulations were not statistically different (p-value >0.05) from each other which suggests that the coating layer did not have any statistically significant effect on the flexural properties of the composites. This is possible as the coating layer (40 g/m²) was too thin compared to the total basis weight of the composites (440 g/m²).

It is essential to have a food serving container with high wet flexural properties so that they do not leak, bend, or break by absorbing water from the food materials. MOR and MOE values obtained from the 'wet' flexural test of the composites after absorption of water for different times are presented in Fig. 6. Comparing Table 2 with Fig. 6, it was observed that the MOR and MOE values of the C.C. decreased by ~71% and ~76% respectively after absorbing water for 600 s but they remained unchanged at longer times. On the contrary, it was observed that the MOR and MOE values of the composites continued to decrease with the increase of water absorption time (Fig. 6). The wet flexural properties of the composites

can be correlated with the water absorption values as the moisture content (MC%) of the composites were highest for CNF coated composites and lowest for LCNF + 1% alum coated composites (Fig. 7a). Aligned with the Cobb values, MC% of the composites decreased for both CNF- and LCNF-coated composites with the addition of 1% alum. For wet flexural properties of the composites, the MOR vs MC% followed a power law trend where 70% of the MOR variations could be explained by MC%. Similarly, the MOE vs. MC% followed a logarithmic relation where 67% of the MOE variations could be attributed to MC%. (Fig. 7b, c). This is expected as the mechanical properties of the nanocellulose films are directly proportional to the inter-fibril hydrogen bonds of the films (Nair et al. 2014). With the increase of water absorption of the composites, more hydrogen bonds between the fibrils break and are replaced with hydrogen bonds between water and the hydroxyl groups of the fibrils (Nair and Yan 2015). This leads to swelling of the fibers which deteriorates the mechanical properties of the composites (Aulin et al. 2009). Besides, cleavage of intrafibrillar hydrogen bond because of an increase of MC% is expected to disrupt the three-dimensional bonding effect of the LCNF or CNF films which may also be responsible for the deterioration of mechanical properties (Hossen et al. 2018).

For 600 s of water absorption, the MOR and MOE values of all the coated composites decreased to various extents compared to the 'dry' flexural properties but still, the values were higher than the commercial container. For the 1200 s, the MOR and MOE values decreased furthermore due to cleavage of more hydrogen bonds due to absorption of more water and as a result, the CNF and the CNF + 1% alum coated composites had statistically similar flexural properties to that of the C.C. while the LCNF and the LCNF + 1% alum samples had comparatively higher values. For 1800 s, the flexural properties drastically reduced for the CNF and CNF +1% alum coated composites while LCNF-coated ones had statistically the same strength and modulus to C.C. As seen from the Cobb values, water absorption was the lowest for LCNF + 1% alum coated composites and as a result, they had higher MOR values compared to the C.C. even after 1800 s of water absorption. Their MOE values were statistically equal to the C.C. for the same time of water absorption.

The modulus retention term (MRT) of the composites and the commercial container is shown in Fig. 7d. For 600 s, it is seen that all coated composites retained similar modulus values compared to the C.C. while for the 1200s and 1800 s, CNF, and CNF +1% alum coated composites had lower retention of modulus compared to the LCNF, LCNF + 1% alum coated ones and the C.C. Composites with LCNFs + 1% alum and the C.C showed no statistical difference in MRT for either 1200 s or 1800 s of water absorption. From the wet flexural test, it can be concluded that LCNF +1% alum coated composites had better performance than C.C in wet conditions for all test times. All other coated composites had lower performance than the C.C when they were allowed to absorb water for 1800 s. Statistically significant (p -value<0.05) relationships were established between both MOR and MOE and the moisture content of the samples when samples from all formulations were pooled together (Fig. 7b, c) indicating that the reduction of MOR and MOE can be estimated knowing the samples, moisture content and thereby time to lose certain percentage of the properties can be estimated.

Recyclability assessment

Mechanical and oil and grease resistance properties of the composites were chosen as the probing factor for recyclability assessment. After each recycle time, the recycled product must have the required mechanical and barrier properties to be used for food serving applications. It is seen from Fig. 8a that the density of the composites had a positive linear relationship with the recycling level ($y = 0.0229x - 0.6302$) with $R^2 = 0.65$. During the recycling process, the total mass of the container (including the base composite layer and the top LCNF coating) was reused to constitute the new base layer which was then coated with fresh LCNFs on top. Therefore, the actual binder content in the base layer would increase upon recycling. The presence of more binder results in more inter and intra-fibril connection by the formation of hydrogen bonds, resulting in a more compact structure (Amini et al. 2017) and therefore higher density. The MOR and MOE values followed a positive linear relationship with the density of the composites where 72% of the MOR and 80% of the MOE variations could be explained by density (Fig. 8a, b). To eliminate the effect of density, the MOR and MOE values of the recycled composites were normalized with density and presented in Fig. 8d, e. It was observed that the MOR and MOE values significantly increased after two recycling levels. Previously, we had found that when 70%-fine LCNF-OCC was used as a binder with wood particles, the flexural properties of the composites increased when the binder content was increased by 10% (Hossain et al. 2021). During recycling, the binder content increased by 6.4% due to the mixing of top layer LCNFs with the base layer LCNF-OCC and the wood particles. For two recycling levels, the binder content increased by more than 10% (12.8%), and the MOR and MOE values of the composites increased accordingly. Thus, it aligns with our previous findings that the mechanical properties increase with the increase of binder content by 10%. At certain binder content, it is expected that the 70%-fine LCNF-OCC and 90%-fine LCNFs can form a percolating network by connecting the fibrils by hydrogen bonds to form a continuous structure (Tajvidi et al. 2016; Hossain et al. 2021). This percolating network can hold the wood particles together to form a strongly bonded composite structure.

Particle size and particle size distribution of LCNF binders are also a contributing factor to the mechanical properties of the composites. From particle size distribution analysis, it was seen that the 90%-fine LCNFs had a comparatively smaller particle size compared to the 70%-fine LCNF-OCC (**Fig S1**). Smaller particle sizes have a higher surface area which aids in the formation of more hydrogen bonds with the fibrils themselves and the wood particles resulting in higher mechanical properties (Kojima et al. 2013; Tayeb et al. 2018). To confirm the effect of binder type and quality, composites were made by replacing the 70%-fine LCNF-OCC with 90%-fine LCNFs (UBKP) at the same binder content with the same coating layer in the same process as mentioned in Fig. 1. It was seen that the MOR and MOE values were 19% and 17.5% higher for these composites.

We also investigated whether the wood particle size had any effect on the mechanical properties of the composites upon recycling. SEM images, length, width, and aspect ratio of the wood particles at each level of recycling are presented in Fig. 9. It can be observed from Fig. 9 that the aspect ratio of the wood particles remained the same for un-recycled and all recycled times which indicates that the shear force of the blender did not change the aspect ratio of the wood particles during recycling. It is also evident from

the particle size analysis that the particle size of wood particles did not have any effect on the mechanical properties of the composites. Therefore, we can conclude that the main reason for the increased mechanical performance of composite containers upon recycling was due to the increased portion of higher quality binder.

Composites at all levels of recycling had excellent oil and grease resistance with kit no. 12. This is because a fresh layer of LCNFs was deposited on the base layer after each level of recycling (Fig. 1). The recycled composites had the same mechanism of oil and grease resistance as fresh composites. From the mechanical and oil and grease resistance test of the recycled composites, it can be concluded that the composites were recyclable, and they could retain their mechanical and barrier properties after each recycling level to be used for food serving applications.

Conclusions

LCNF- and CNF-coated composites made with 70%-fine LCNF-OCC at 30% binder content with wood particles had excellent mechanical, oil, and grease resistance properties to be used for food serving applications. Water resistance of the composites was improved with the addition of 1% alum to the LCNF or CNF coating layer. Compared to the commercial container, LCNF +1% alum coated composites exhibited almost equal water resistance but the CNF +1% alum coated ones had inferior water resistance. 'Dry' mechanical properties of all the coated composites were higher than that of commercial containers. The mechanical properties of the CNF +1% alum coated composites were poor in wet condition compared to the commercial containers while the LCNF +1% coated ones had better performance. Composites were recyclable and they could retain their excellent barrier properties against grease and oil after recycling. The mechanical properties of the recycled composites increased after two-level recycling due to the increase in binder content. Considering the excellent barrier and mechanical properties, it can be concluded that the LCNF + 1% alum coated composites with 70% fine LCNF-OCC as binder with wood particles can be used for food serving applications in both wet and dry conditions.

Abbreviations

CNF, cellulose nanofibril; LCNF, lignin-containing cellulose nanofibril; LDPE, low-density polyethylene; PLA, polylactic acid; PFA, per or poly-fluoroalkyl; AKD, alkyl ketene dimer; BKP, bleached kraft pulp, UBKP, unbleached kraft pulp; OCC, old corrugated container; SFE, surface free energy; SEM, scanning electron microscope; EDS, energy-dispersive X-ray spectroscopy, FTIR, Fourier transform infrared spectroscopy; ATR, attenuated total reflectance; MOE, modulus of elasticity; MOR, modulus of rupture; MRT, modulus retention term; ANOVA, analysis of variance; DMRT, Duncan's multiple range test;

Declarations

Funding

This work was supported by USDA Agricultural Research Service (ARS) [Project # 58-0204-6-003].

Conflict of Interest

The authors have no conflict of interests for this article.

Informed Consent

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Ethical Approval

This study does not involve any human or animal subjects.

References

1. Acumen Research and Consulting (2020) Disposable Plates Market Analysis
<https://www.acumenresearchandconsulting.com>
2. Al-Gharrawi MZ, Wang J, Bousfield DW (2021) Improving recycling of polyethylene-coated paperboard with a nanofibrillated cellulose layer. *BioResources* 16:3285–3297
3. Amini E, Hafez I, Tajvidi M, Bousfield DW (2020) Cellulose and lignocellulose nanofibril suspensions and films: A comparison. *Carbohydr Polym* 250:117011.
<https://doi.org/10.1016/j.carbpol.2020.117011>
4. Amini E, Tajvidi M, Gardner DJ, Bousfield DW (2017) Utilization of cellulose nanofibrils as a binder for particleboard manufacture. *BioResources* 12:4093–4110.
<https://doi.org/10.15376/biores.12.2.4093-4110>
5. Aulin C, Ahok S, Josefsson P, et al (2009) Nanoscale cellulose films with different crystallinities and mesostructures - Their surface properties and interaction with water. *Langmuir* 25:7675–7685.
<https://doi.org/10.1021/la900323n>
6. Aulin C, Gällstedt M, Lindström T (2010) Oxygen and oil barrier properties of microfibrillated cellulose films and coatings. *Cellulose* 17:559–574. <https://doi.org/10.1007/s10570-009-9393-y>
7. Balat M (2007) Status of fossil energy resources: A global perspective. *Energy Sources, Part B Econ Plan Policy* 2:31–47. <https://doi.org/10.1080/15567240500400895>
8. Bilodeau & Paradis (2018) U.S. Patent No. 9,988,762. Washington, DC: U.S. Patent and Trademark Office.
9. Böröcsök Z, Pásztor Z (2020) The role of lignin in wood working processes using elevated temperatures: an abbreviated literature survey. *Eur J Wood Wood Prod.*
<https://doi.org/10.1007/s00107-020-01637-3>

10. Budd J, Herrington TM (1989) The adsorption of aluminium from aqueous solution by cellulose fibres. *Colloids and Surfaces* 41:363–384. [https://doi.org/https://doi.org/10.1016/0166-6622\(89\)80066-6](https://doi.org/https://doi.org/10.1016/0166-6622(89)80066-6)
11. Chen Y, Fan D, Han Y, et al (2018) Effect of high residual lignin on the properties of cellulose nanofibrils/films. *Cellulose* 25:6421–6431. <https://doi.org/10.1007/s10570-018-2006-x>
12. Deshwal GK, Panjagari NR, Alam T (2019) An overview of paper and paper based food packaging materials: health safety and environmental concerns. *J. Food Sci. Technol.* 56:4391–4403
13. Dhali K, Ghasemlou M, Daver F, et al (2021) A review of nanocellulose as a new material towards environmental sustainability. *Sci Total Environ* 775:145871. <https://doi.org/10.1016/j.scitotenv.2021.145871>
14. Diop CIK, Tajvidi M, Bilodeau MA, et al (2017a) Evaluation of the incorporation of lignocellulose nanofibrils as sustainable adhesive replacement in medium density fiberboards. *Ind Crops Prod* 109:27–36. <https://doi.org/10.1016/j.indcrop.2017.08.004>
15. Diop CIK, Tajvidi M, Bilodeau MA, et al (2017b) Isolation of lignocellulose nanofibrils (LCNF) and application as adhesive replacement in wood composites: example of fiberboard. *Cellulose* 24:3037–3050. <https://doi.org/10.1007/s10570-017-1320-z>
16. do Lago RC, de Oliveira ALM, de Amorim dos Santos A, et al (2021) Addition of wheat straw nanofibrils to improve the mechanical and barrier properties of cassava starch-based bionanocomposites. *Ind Crops Prod* 170:. <https://doi.org/10.1016/j.indcrop.2021.113816>
17. European Parliament (2018) Plastic oceans: MEPs back EU ban on throwaway plastics by 2021 [Press Release]. *Eur Parliam News Press room* 30–33
18. Fein K, Bousfield DW, Gramlich WM (2021) Processing Effects on Structure, Strength, and Barrier Properties of Refiner-Produced Cellulose Nanofibril Layers. *ACS Appl Polym Mater* 3:3666–3678. <https://doi.org/10.1021/acsapm.1c00620>
19. Ferrer A, Quintana E, Filpponen I, et al (2012) Effect of residual lignin and heteropolysaccharides in nanofibrillar cellulose and nanopaper from wood fibers. *Cellulose* 19:2179–2193. <https://doi.org/10.1007/s10570-012-9788-z>
20. Fortea-Verdejo M, Lee K-Y, Zimmermann T, Bismarck A (2016) Upgrading flax nonwovens: Nanocellulose as binder to produce rigid and robust flax fibre preforms. *Compos Part A Appl Sci Manuf* 83:63–71. <https://doi.org/https://doi.org/10.1016/j.compositesa.2015.11.021>
21. Geyer R, Jambeck JR, Law KL (2017) Production, use, and fate of all plastics ever made. *Sci Adv* 3:25–29. <https://doi.org/10.1126/sciadv.1700782>
22. Ghasemi S, Tajvidi M, Bousfield DW, et al (2017) Dry-spun neat cellulose nanofibril filaments: Influence of drying temperature and nanofibril structure on filament properties. *Polymers (Basel)*. 9
23. Gill MB, Jensen KL, Lambert DM, et al (2020) Consumer preferences for eco-friendly attributes in disposable dinnerware. *Resour Conserv Recycl* 161:104965. <https://doi.org/10.1016/j.resconrec.2020.104965>

24. Goo S, Park H, Yook S, et al (2018) Preparation of Hydrophobized Cellulose Nanofibril Film with High Strength Using AKD TT - Preparation of Hydrophobized Cellulose Nanofibril Film with High Strength Using AKD. *J Korea Tech Assoc Pulp Pap Ind* 50:34–41.
<https://doi.org/10.7584/JKTAPPI.2018.12.50.6.34>
25. Hakalahti M, Salminen A, Seppälä J, et al (2015) Effect of interfibrillar PVA bridging on water stability and mechanical properties of TEMPO/NaClO₂ oxidized cellulosic nanofibril films. *Carbohydr Polym* 126:78–82. <https://doi.org/https://doi.org/10.1016/j.carbpol.2015.03.007>
26. Hasan I, Wang J, Tajvidi M (2021) Tuning physical, mechanical and barrier properties of cellulose nanofibril films through film drying techniques coupled with thermal compression. *Cellulose*.
<https://doi.org/10.1007/s10570-021-04269-9>
27. Hossain R, Tajvidi M, Bousfield D, Gardner DJ (2021) Multi-layer oil-resistant food serving containers made using cellulose nanofiber coated wood flour composites. *Carbohydr Polym* 267:118221.
<https://doi.org/10.1016/j.carbpol.2021.118221>
28. Hossen MR, Dadoo N, Holomakoff DG, et al (2018) Wet stable and mechanically robust cellulose nanofibrils (CNF) based hydrogel. *Polymer (Guildf)* 151:231–241.
<https://doi.org/https://doi.org/10.1016/j.polymer.2018.07.016>
29. Hu Z, Zhai R, Li J, et al (2017) Preparation and Characterization of Nanofibrillated Cellulose from Bamboo Fiber via Ultrasonication Assisted by Repulsive Effect. *Int J Polym Sci* 2017:9850814.
<https://doi.org/10.1155/2017/9850814>
30. Hubbe MA, Ferrer A, Tyagi P, et al (2017) Nanocellulose in thin films, coatings, and plies for packaging applications: A review. *BioResources* 12:2143–2233.
<https://doi.org/10.15376/biores.12.1.2143-2233>
31. Iewkittayakorn J, Khunthongkaew P, Wongnoipla Y, et al (2020) Biodegradable plates made of pineapple leaf pulp with biocoatings to improve water resistance. *J Mater Res Technol* 9:5056–5066.
<https://doi.org/10.1016/j.jmrt.2020.03.023>
32. Jablonsky M, Šima J, Lelovsky M (2020) Considerations on factors influencing the degradation of cellulose in alum-rosin sized paper. *Carbohydr Polym* 245:.
<https://doi.org/10.1016/j.carbpol.2020.116534>
33. Jambeck JR, Geyer R, Wilcox C, et al (2015) Plastic waste inputs from land into the ocean. *Science (80-)* 347:768 LP – 771. <https://doi.org/10.1126/science.1260352>
34. Jiang, Liu X, Yang Q, et al (2019) Effects of residual lignin on composition, structure and properties of mechanically defibrillated cellulose fibrils and films. *Cellulose* 26:1577–1593.
<https://doi.org/10.1007/s10570-018-02229-4>
35. Kaelble DH (1970) Dispersion-Polar Surface Tension Properties of Organic Solids. *J Adhes* 2:66–81.
<https://doi.org/10.1080/0021846708544582>
36. Kato., Isogai A, Onabe F (2000) Intrafiber distribution of aluminum components in alum-treated handsheets. *J Wood Sci* 46:75–78. <https://doi.org/10.1007/BF00779557>

37. Kato, Isogai A, Onabe F (2000) Studies on interactions between aluminum compounds and cellulosic fibers in water by means of ²⁷Al-NMR. *J Wood Sci* 46:310–316.
<https://doi.org/10.1007/BF00766222>
38. Kato, Isogai A, Onabe F (1999) Factors influencing retention behavior of aluminum compounds on handsheets. *J Wood Sci* 45:154–160. <https://doi.org/10.1007/BF01192333>
39. Kato M, Isogai A, Onabe F (1998) Adsorption behavior of aluminum compounds on pulp fibers at wet-end. *J Wood Sci* 44:361–368. <https://doi.org/10.1007/BF01130448>
40. Khairuddin, Purnawan C, Aningtyas S (2019) Preparation and properties of paper coating based bilayer of starch and shellac composites. *J Phys Conf Ser* 1153:. <https://doi.org/10.1088/1742-6596/1153/1/012092>
41. Kojima Y, Isa A, Kobori H, et al (2014) Evaluation of binding effects in wood flour board containing ligno-cellulose nanofibers. *Materials (Basel)* 6:6853–6864. <https://doi.org/10.3390/ma7096853>
42. 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>
43. Korbelyiova L, Malefors C, Lalander C, et al (2021) Paper vs leaf: Carbon footprint of single-use plates made from renewable materials. *Sustain Prod Consum* 25:77–90.
<https://doi.org/10.1016/j.spc.2020.08.004>
44. Lavoine N, Bras J, Desloges I (2014) Mechanical and barrier properties of cardboard and 3D packaging coated with microfibrillated cellulose. *J Appl Polym Sci* 131:1–11.
<https://doi.org/10.1002/app.40106>
45. Lavoine N, Desloges I, Dufresne A, Bras J (2012) Microfibrillated cellulose - Its barrier properties and applications in cellulosic materials: A review. *Carbohydr Polym* 90:735–764.
<https://doi.org/10.1016/j.carbpol.2012.05.026>
46. Li Z, Rabnawaz M (2018) Fabrication of Food-Safe Water-Resistant Paper Coatings Using a Melamine Primer and Polysiloxane Outer Layer. *ACS Omega* 3:11909–11916
47. Mazhari Mousavi SM, Afra E, Tajvidi M, et al (2017) Cellulose nanofiber/carboxymethyl cellulose blends as an efficient coating to improve the structure and barrier properties of paperboard. *Cellulose* 24:3001–3014. <https://doi.org/10.1007/s10570-017-1299-5>
48. Nair SS, Yan N (2015) Effect of high residual lignin on the thermal stability of nanofibrils and its enhanced mechanical performance in aqueous environments. *Cellulose* 22:3137–3150.
<https://doi.org/10.1007/s10570-015-0737-5>
49. Nair SS, Zhu JY, Deng Y, Ragauskas AJ (2014) Characterization of cellulose nanofibrillation by micro grinding. *J Nanoparticle Res* 16:. <https://doi.org/10.1007/s11051-014-2349-7>
50. OECD (2020) PFASs and Alternatives in Food Packaging (Paper and Paperboard) Report on the Commercial Availability and Current Uses. 1–65
51. Ohno K (1999) Retention behavior of size and aluminum components in handsheets prepared in rosin soap size-alum systems. *J Wood Sci* 45:238–244. <https://doi.org/10.1007/BF01177732>

52. Osann R, Fasching MM (2008) (12) Patent Application Publication (10) Pub . No .: US 2008 / 0225123 A1 Patent Application Publication. Priv Point Contain Sm Card 1:11–14
53. Owens DK, Wendt RC (1969) Estimation of the surface free energy of polymers. *J Appl Polym Sci* 13:1741–1747. <https://doi.org/https://doi.org/10.1002/app.1969.070130815>
54. Pahimanolis N, Salminen A, Penttilä PA, et al (2013) Nanofibrillated cellulose/carboxymethyl cellulose composite with improved wet strength. *Cellulose* 20:1459–1468. <https://doi.org/10.1007/s10570-013-9923-5>
55. Peresin MS, Kammiovirta K, Heikkinen H, et al (2017) Understanding the mechanisms of oxygen diffusion through surface functionalized nanocellulose films. *Carbohydr Polym* 174:309–317. <https://doi.org/https://doi.org/10.1016/j.carbpol.2017.06.066>
56. PlasticsEurope (2019) *Plastics - the Facts 2019*. 14, 35
57. Prakobna K, Galland S, Berglund LA (2015) High-Performance and Moisture-Stable Cellulose–Starch Nanocomposites Based on Bioinspired Core–Shell Nanofibers. *Biomacromolecules* 16:904–912. <https://doi.org/10.1021/bm5018194>
58. Rodionova G, Lenes M, Eriksen Ø, Gregersen Ø (2011) Surface chemical modification of microfibrillated cellulose: improvement of barrier properties for packaging applications. *Cellulose* 18:127–134. <https://doi.org/10.1007/s10570-010-9474-y>
59. Rodrigues MO, Abrantes N, Gonçalves FJM, et al (2019) Impacts of plastic products used in daily life on the environment and human health: What is known? *Environ Toxicol Pharmacol* 72:103239. <https://doi.org/10.1016/j.etap.2019.103239>
60. Rojas OJ, Hubbe MA (2004) The dispersion science of papermaking. *J Dispers Sci Technol* 25:713–732. <https://doi.org/10.1081/DIS-200035485>
61. 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>
62. Shimizu M, Saito T, Isogai A (2016) Water-resistant and high oxygen-barrier nanocellulose films with interfibrillar cross-linkages formed through multivalent metal ions. *J Memb Sci* 500:1–7. <https://doi.org/10.1016/j.memsci.2015.11.002>
63. Smook GA (2015) *Handbook for pulp and paper technologists* smook pdf
64. Solala I, Bordes R, Larsson A (2018) Water vapor mass transport across nanofibrillated cellulose films: effect of surface hydrophobization. *Cellulose* 25:347–356. <https://doi.org/10.1007/s10570-017-1608-z>
65. Tajvidi M, Gardner DJ, Bousfield DW (2016) Cellulose nanomaterials as binders: Laminate and particulate systems. *J Renew Mater* 4:365–376. <https://doi.org/10.7569/JRM.2016.634103>
66. Tappi (2009) Water absorptiveness of sized (non-bibulous) paper , paperboard , and corrugated fiberboard (Cobb test). Tappi 1–6
67. TAPPI (1996) Grease resistance test for paper and paperboard

68. Tarrés Q, Oliver-Ortega H, Ferreira PJ, et al (2018) Towards a new generation of functional fiber-based packaging: cellulose nanofibers for improved barrier, mechanical and surface properties. *Cellulose* 25:683–695. <https://doi.org/10.1007/s10570-017-1572-7>
69. Tayeb AH, Amini E, Ghasemi S, Tajvidi M (2018) Cellulose nanomaterials-binding properties and applications: A review. *Molecules* 23:1–24. <https://doi.org/10.3390/molecules23102684>
70. Tayeb AH, Tajvidi M (2019) Sustainable Barrier System via Self-Assembly of Colloidal Montmorillonite and Cross-linking Resins on Nanocellulose Interfaces. *ACS Appl Mater Interfaces* 11:1604–1615. <https://doi.org/10.1021/acsami.8b16659>
71. Tayeb AH, Tajvidi M, Bousfield D (2020) Paper-based oil barrier packaging using lignin-containing cellulose nanofibrils. *Molecules* 25:. <https://doi.org/10.3390/molecules25061344>
72. Toivonen MS, Kurki-Suonio S, Schacher FH, et al (2015) Water-Resistant, Transparent Hybrid Nanopaper by Physical Cross-Linking with Chitosan. *Biomacromolecules* 16:1062–1071. <https://doi.org/10.1021/acs.biomac.5b00145>
73. Triantafillopoulos N, Koukoulas AA (2020) The Future of Single-use Paper Coffee Cups: Current Progress and Outlook. *BioResources* 15:7260–7287. <https://doi.org/10.15376/BIORES.15.3.TRIANTAFILLOPOULOS>
74. Tyagi P, Gutierrez JN, Nathani V, et al (2021) Hydrothermal and mechanically generated hemp hurd nanofibers for sustainable barrier coatings/films. *Ind Crops Prod* 168:113582. <https://doi.org/10.1016/j.indcrop.2021.113582>
75. Verdes RP, Pak SS, Data RUSA, et al (1999) United States Patent (19)
76. Weber Macena M, Carvalho R, Cruz-Lopes LP, Guiné RPF (2021) Plastic Food Packaging: Perceptions and Attitudes of Portuguese Consumers about Environmental Impact and Recycling. *Sustainability* 13:. <https://doi.org/10.3390/su13179953>
77. Wu A, March L, Zheng X, et al (2020) Enhanced Reader.pdf. *Nature* 388:1–14
78. Xing C, He T, Peng Y, Li R (2018) Synthesis and characterization of poly(methyl methacrylate)/polysiloxane composites and their coating properties . *J. Appl. Polym. Sci.* 135:46358-n/a
79. Xu Y, Kuang Y, Salminen P, Chen G (2016) The influence of nano-fibrillated cellulose as a coating component in paper coating. *BioResources* 11:4342–4352. <https://doi.org/10.15376/biores.11.2.4342-4352>
80. Yang Q, Takeuchi M, Saito T, Isogai A (2014) Formation of Nanosized Islands of Dialkyl β -Ketoester Bonds for Efficient Hydrophobization of a Cellulose Film Surface. *Langmuir* 30:8109–8118. <https://doi.org/10.1021/la501706t>
81. Yook S, Park H, Park H, et al (2020) Barrier coatings with various types of cellulose nanofibrils and their barrier properties. *Cellulose* 5:. <https://doi.org/10.1007/s10570-020-03061-5>
82. Yousefhashemi SM, Khosravani A, Yousefi H (2019) Isolation of lignocellulose nanofiber from recycled old corrugated container and its interaction with cationic starch–nanosilica combination to make paperboard. *Cellulose* 26:7207–7221. <https://doi.org/10.1007/s10570-019-02562-2>

83. Yousefi Shivyari N, Tajvidi M, Bousfield DW, Gardner DJ (2016) Production and Characterization of Laminates of Paper and Cellulose Nanofibrils. ACS Appl Mater Interfaces 8:25520–25528.
<https://doi.org/10.1021/acsami.6b07655>
84. Yuhui M (2018) Problems and Resolutions in Dealing with Waste Disposable Paper Cups. Sci Prog 101:1–7. <https://doi.org/10.3184/003685017X15129981721365>
85. Zaman A, Newman P (2021) Plastics: are they part of the zero-waste agenda or the toxic-waste agenda? Sustain Earth 4:. <https://doi.org/10.1186/s42055-021-00043-8>
86. Zhang N, Xu J, Gao X, et al (2017) Factors affecting water resistance of alginate/gellan blend films on paper cups for hot drinks. Carbohydr Polym 156:435–442.
<https://doi.org/10.1016/j.carbpol.2016.08.101>
87. Zhang W, Xiao H, Qian L (2014) Enhanced water vapour barrier and grease resistance of paper bilayer-coated with chitosan and beeswax. Carbohydr Polym 101:401–406.
<https://doi.org/10.1016/j.carbpol.2013.09.097>
88. Zhang Z, Tingaut P, Rentsch D, et al (2015) Controlled Silylation of Nanofibrillated Cellulose in Water: Reinforcement of a Model Polydimethylsiloxane Network. ChemSusChem 8:2681–2690

Figures

Figure 1

Schematic summary of the fabrication and recycling process of oil-resistant 2-layered nanocellulose composite food serving plates with higher resistance to water absorption.

Figure 2

Surface SEM images of a) uncoated composite, b) LCNF coated, c) LCNF coated + 1% alum, d) CNF coated and e) CNF coated + 1% alum composites at different magnifications.

Figure 3

SEM images of the cross-sections of the coated composites with a) LCNFs and b) CNFs at different magnifications.

Figure 4

EDS mapping of aluminum (red dots have been manually enlarged for enhanced visibility) of the surface of coated composites with a) LCNFs, b) LCNFs + 1% alum, c) CNFs, d) CNFs + 1% alum, and SEM of the corresponding cross-sections of the coated composites with e) CNFs + 1% alum, and f) LCNFs + 1% alum.

Figure 5

a) Water absorption values (Cobb values) of the produced composites and Commercial containers (C.C.) at different times, and **b)** a schematic representation of the mechanism of water absorption through the coated composites.

Figure 6

MOR and MOE values of the coated composites and the commercial container after absorption of water for different water contact times.

Figure 7

a) Moisture content (%) of the coated composites and the commercial container after water absorption for different times, b) MOR vs moisture content, c) MOE vs moisture content of the coated composites and d) modulus retention term (%) of the coated composites and the commercial container after water absorption for different times.

Figure 8

Effect of recycling times on the mechanical properties of the composite containers: a) linear increase in density as a function of recycle times; b and c) the relationships between density and MOR and MOE; d and e) normalized MOR and MOE as a function of recycle times.

Figure 9

a) SEM images of wood particles, and b) length, width, and aspect ratio of wood particles after each recycle level.