Enhancing wood performance using citric acid and whey ultrafiltration permeate: a promising approach

KERALTA Assira[1], CHAABENE Sahar[2], WINNINGER Jérémy[1], CHAMBERLAND Julien[3], LANDRY Véronic[1]

[1] Department of Wood and Forest Sciences, Renewable Materials Research Center, Université Laval, Quebec City, Canada, G1V 0A6.
[2] Institut National des Sciences Appliquées et de Technologie, 1080 Tunis Cedex, Tunisie.
[3] STELA Dairy Research Center, Institute of Nutrition and Functional Foods (INAF), Department of Food Science, Université Laval, Quebec City, Canada, G1V 0A6.
assira.keralta.1@ulaval.ca

Keywords: Wood modification, polyesterification, whey ultrafiltration permeate.

Context and objectives

Wood is increasingly valued for its environmental benefits, including carbon sequestration, recyclability, and aesthetic appeal. However, its hygroscopic nature limits its applications where stability and durability are critical. Traditional materials like concrete and steel, despite their environmental drawbacks, outperform wood in these areas. Wood's tendency to deform, crack, and degrade under varying humidity, exposure to microorganisms, and UV light necessitates effective treatment methods. One promising approach is polyesterification (Berube et al 2018, Kurkowiaw et al 2022), where wood is impregnated with acids and alcohols, and the esterification reaction is carried out in situ to densify wood cell wall. This study investigates an innovative application of whey ultrafiltration (UF) permeate, a dairy coproduct containing lactose and minerals (Baldasso et all 2011, Chamberland et al 2020) as a replacement for traditional alcohols used in this process. The goal is to leverage the abundance and biosourced nature of whey UF permeate to improve wood's dimensional stability and moisture resistance. Preliminary results indicate that polyesterified wood with citric acid and whey UF permeate exhibits significant improvements in these properties. Further research will focus on the wood's resistance to fungal attack and color stability under various conditions.

Materials and methods

Citric acid (CA) ≥99.5%, was purchased from Sigma Aldrich (Oakville, ON, Canada) and used as received. Whey UF permeate and lactose (>99.0%) powders were provided by Agropur (Longueuil, QC, Canada). Whey UF permeate contained 88% lactose, 5.8% ash, 2% non-protein nitrogen on a dry basis, and 4% w/w moisture. Trembling aspen (*Populus tremuloides L.*) wood was prepared by sawing solid wood pieces to the desired size as presented in Table 1. The samples were stored in a conditioning room (21 °C, 41% RH) before treatment.

Wood Treatment Process

After the formulation preparation, ten block wood samples were immersed in the formulation, and a weight was put on the top to maintain the samples immersed in the formulation. They underwent a dynamic vacuum at 50 mbar in a desiccator for 1 h; afterward, the vacuum was cut, and samples were maintained immersed in the formulation at atmospheric pressure and ambient temperature to absorb the formulation for 24 h. They were then removed from the formulation, and a paper was used to remove the excess solution. Samples were weighted, and their dimensions were measured. The treatment process is summarized in Fig. 1. The

formulation WUPAC consists of an aqueous mixture of CA and whey UF permeate with a total solid content of 596 g/L.

Table 1: Wood sample dimensions and sampling for the different tests performed.

Sample size (T × L × R) mm^3	Tests or analysis performed	Number of samples per treatment
25 × 25 × 10	Density, SU*, WGP*, CWB*, ASE*	10
4 × 4 × 2	Thermogravimetric analysis, infrared spectroscopy	2
50 × 50 × 10	Density profile	3
5 × 5 × 5	Sorption isotherms	2

SU*: solution uptake - WGP*: weight gain percentage - CWB*: Cell wall bulking - ASE*: Anti-swelling efficiency.

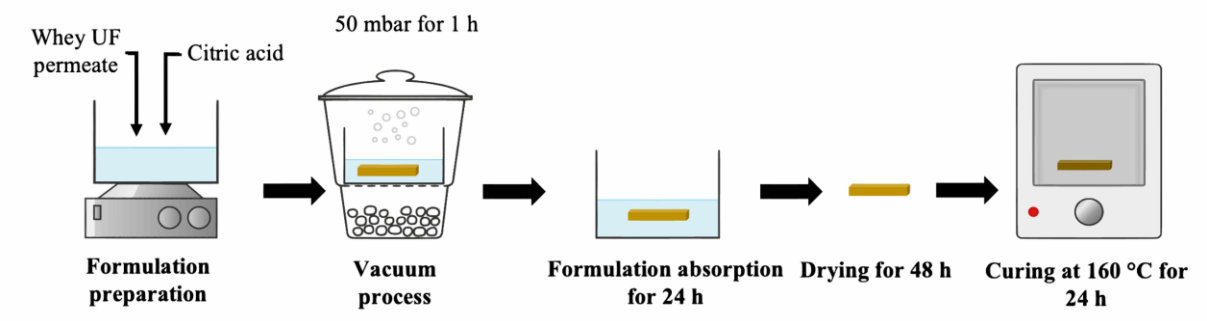

Fig. 1: Wood treatment process

Physical characterization of the wood samples

After the impregnation process, the penetration of the solution into the wood samples was assessed and presented as solution uptake (SU). The impregnation process was followed by a curing step at 160 °C. The rate of solids gained or lost by the sample was calculated and presented as weight gain percentage (WGP). The cell wall bulking (CWB) due to the formation of polymers in the cell wall and the anti-swelling efficiency (ASE), which is the gain in dimensional stability after treatment, were calculated and compared to samples treated with water alone. Mean and standard deviation were used to plot each of these physical properties.

The density profile was measured before and after treatment on the sample. An X-ray densitometer QPD-01X (Quintek Measurement Systems, Knoxville, TN, USA) was used to measure the density profile. The density was measured at intervals of 0.02 mm through the specimen's thickness in the radial direction. Three samples for each treatment were used, and the mean was used for the plot.

Chemical characterization of the wood samples

Fourier Transform Infrared (FTIR) spectroscopy analysis was conducted using the Invenio R spectrometer (Bruker, Billerica, MA, USA) to assess the effectiveness of the reaction inside wood. Spectra were recorded on the untreated samples, water-treated samples, and samples treated with the WUPCA formulation. Spectra were obtained by accumulating 32 scans in the 400 to 4000 cm^{-1} region with a resolution of 4 cm^{-1}. The OPUS software (Bruker, Billerica, MA, USA) was used to process the spectra.

Thermal characterization of the wood samples

Thermogravimetric analyses were performed using a TGA 851e (Mettler Toledo, Greifensee, Switzerland) to assess the thermal degradation of treated samples and the impact of curing

temperature on the thermal properties of the samples. The temperature was raised from 35 °C to 800 °C at a rate of 10 °C/min under a nitrogen flow of 100 mL/min. Each sample was tested two times.

Hygroscopic characterization

Sorption isotherm tests were conducted using a DVS Adventure water vapor sorption analyzer (Surface Measurement Systems, Allentown, USA) at 25 °C. The samples were first dried at 0% RH until the mass change of the specimen per minute (dm/dt) was <0.001% min^{-1} over a period of 10 min and then exposed to an RH of 95% for 720 min. This was done to limit the potential influence of the previous sorption history on the sorption isotherms, which has been observed when comparing multiple sorption cycles (Majka et al 2016). Afterwards, the samples were dried again at 0% RH before the RH was increased stepwise in the following sequence: 5, 15, 25, 35, 45, 55, 65, 75, 85, 95% RH (absorption curve), which was followed by a decrease to 0% RH in the reverse order (desorption curve). The RH in the analysis chamber was maintained until the sample's mass percentage varied by less than 0.0002% over 10 minutes or the step duration exceeded 24 h. The moisture content during adsorption and desorption cycles was plotted against the target RH. Two repetitions were performed on each type of sample.

Results and discussion

Physical properties

Fig. 2 presents the SU of water (used as reference) and WUPCA formulation by trembling aspen samples. WUPCA formulation was absorbed as much as water by the samples, even it is quite higher than the absorption of water (Fig. 2a). This difference in solution uptake between water and WUPCA is explained by the difference in oven-dry density. Samples impregnated with water were quite denser than those impregnated with WUPCA formulation (Fig. 2b). After curing at 160 °C following the impregnation process, samples impregnated with water had a weight loss of around 1%, which could be attributed to the leaching of extractives by hot water. Samples treated by WUPCA had a gain weight percentage of around 40%, which corresponds to the amount of solids components formed between whey UF permeate and CA (Fig. 2a). This could be seen in the density; samples treated with water had almost the same density. In contrast, samples treated with WUPCA gained in density after the treatment due to the products formed in wood between CA and whey UF permeate.

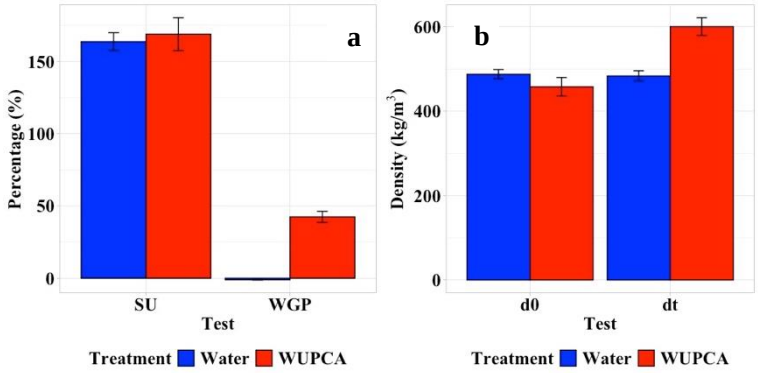

Fig. 2: Comparison of the solution uptake (SU) and weight gain percentage (WGP) (a) and density of water-treated and WUPCA-treated samples.

The density profile presented in the Fig. 3 showed that the treatment was almost homogeneous throughout the entire thickness of the samples. The density profile remained the same after the treatment with water, showing that the curing temperature did not affect the wood density throughout its entire thickness.

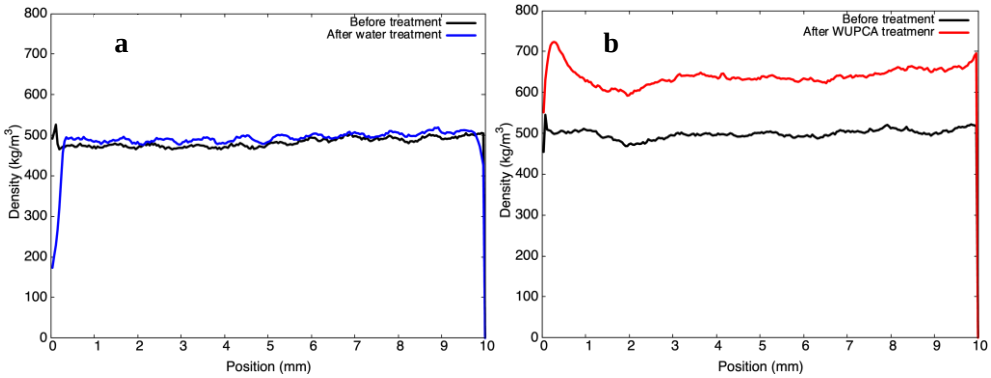

Fig. 3: Comparison of the density profile before and after treatment for water-treated (a) and WUPCA-treated (b) samples.

Chemical composition changes

Untreated, water-treated, and WUPCA-treated samples were analyzed by FTIR and presented in Fig. 4. Firstly, the bands of the main wood components (cellulose, hemicellulose, and lignin) did not change, meaning that the curing temperature did not affect these polymers, and the WL observed could be definitively attributed to the loss of extractives. For WUPCA-treated samples, there is a deep increase in the band intensity at 1733 cm^{-1} assigned to C=O esters, meaning that CA and the lactose in whey UF permeate reacted together in wood. There is also a decrease in the band intensity at 3320 cm^{-1} assigned to OH, meaning there might be a reaction between OH groups of wood and CA.

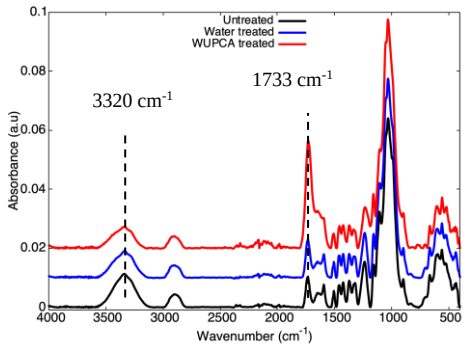

Fig. 4: FTIR spectra comparison of untreated, water-treated, and WUPCA-treated samples.

Thermal properties investigation

The initial pyrolysis temperature remains unchanged with water treatment. However, a decrease in the initial pyrolysis temperature is observed following WUPCA treatment (Fig. 5a). Additionally, the residual mass after analysis at 800 °C is higher for WUPCA-treated samples, while untreated and water-treated samples exhibit the same residual mass as untreated wood. This could be attributed to the presence of other components in whey UF permeate, particularly minerals, which may lower the initial pyrolysis temperature by accelerating the dehydration process and promoting the formation of a significant amount of char (Hagen et al 2009).

Hygroscopic behavior of wood samples

Fig. 6 shows the sorption isotherms of untreated, water-treated, and WUPCA-treated samples. All isotherms exhibited a type II pattern, which is typical for wood (Niemz et al 2023, Anwar et al 2021). However, the WUPCA-treated samples demonstrated lower sorption across the entire hygroscopic range compared to the untreated samples. This reduction is likely due to the occupation of absorption sites in the wood by the products formed between citric acid (CA) and lactose in the whey UF permeate. For the water-treated samples, there was a slight decrease in

adsorption, possibly due to the removal of some hydrophilic extractives during the heat treatment.

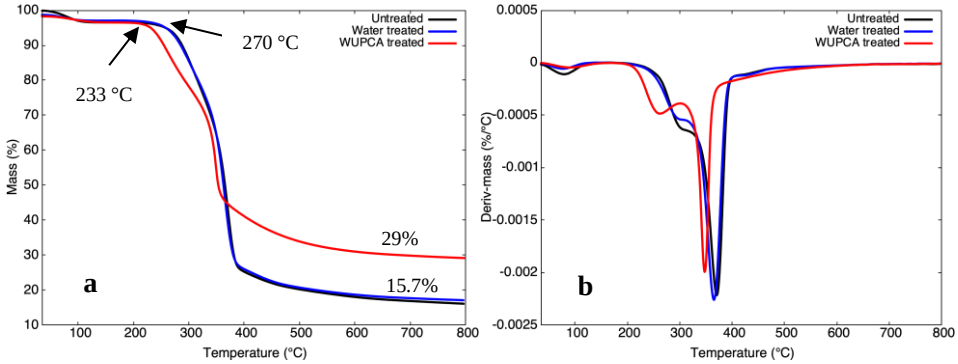

Fig. 5: Comparison of the thermogravimetric analysis (a) and its derivative (b) of untreated, water-treated, and WUPCA-treated samples.

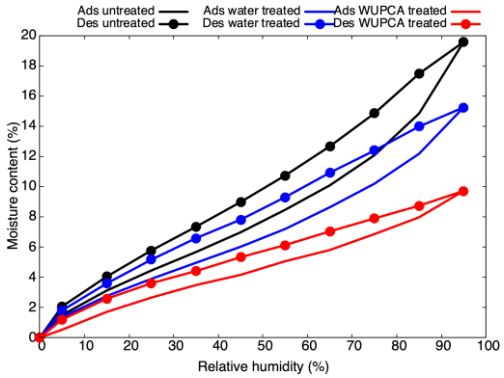

Fig. 6: Comparison of sorption isotherms of untreated, water-treated, and WUPCA-treated samples.

Expected results

- There was a notable increase in density throughout the entire thickness of the samples. This density increase is expected to enhance the mechanical properties of the wood, as many wood mechanical properties are proportional to density.
- The moisture content of the wood was significantly reduced across the entire hygroscopic range after treatment, suggesting improved resistance to fungal attack. Previous studies have shown that wood's resistance to fungi is related to its ability to exclude moisture after treatment (Thybring Emile Engelund 2009).
- Long-term stability and durability of the treated samples are anticipated, owing to the stability of the compounds formed within the wood."

Conclusion and perspectives

This study shows the potential of whey UF permeate in enhancing wood properties. The lactose in whey UF permeate can react with citric acid inside trembling aspen wood, resulting in a higher densification of the cell wall. The cell wall bulking leads to an increase in density through the entire wood thickness and a deep increase of the dimensional stability. Most importantly, there is also a deep decrease in the moisture content of treated wood compared to untreated during the sorption isotherm test. This process offers substantial benefits for both the dairy and wood industries in Quebec and Canada. This process also presents a promising opportunity to add value to the primary co-products of the dairy industry, while simultaneously enabling the development of innovative wood products.

Acknowledgments

We would like to thank the Fonds de Recherche du Québec – Nature et Technologie (FRQNT) and the Natural Sciences and Engineering Research Council of Canada (NSERC) for funding this project through the NOVA program. We would also like to thank all the technicians and members of the Renewable Materials Research Center.

References

Berube M-A, Schorr D, Ball R J, Landry V, Blanchet P (2018) Determination of In Situ Esterification Parameters of Citric Acid-Glycerol Based Polymers for Wood Impregnation, Journal of Polymers and the Environment, 26(3), 970–979.

Kurkowiak K, Mayer A K, Emmerich L, Militz H (2022) Investigations of the Chemical Distribution in Sorbitol and Citric Acid (SorCA) Treated Wood—Development of a Quality Control Method on the Basis of Electromagnetic Radiation, Forests, 13(2), 151.

Baldasso C, Barros T C, Tessaro I C (2011) Concentration and Purification of Whey Proteins by Ultrafiltration, Desalination, 278(1–3), 381–386.

Chamberland J, Bouyer A, Benoit S, Provault C, Bérubé A, Doyen A, Pouliot Y (2022) Efficiency Assessment of Water Reclamation Processes in Milk Protein Concentrate Manufacturing Plants: A Predictive Analysis, Journal of Food Engineering, 272. 109811.

Majka J, Czajkowski L, Olek W (2016) Effects of Cyclic Changes in Relative Humidity on the Sorption Hysteresis of Thermally Modified Spruce Wood, BioResources, 11, 5265–5275.

Hagen M, Hereid J, Delichatsios M A, Zhang J, Bakirtzis D (2009) Flammability Assessment of Fire-Retarded Nordic Spruce Wood Using Thermogravimetric Analyses and Cone Calorimetry, Fire Safety Journal, 44(8), 1053–1066.

Niemz P, Teischinger A, Sandberg D, (2023) Springer Handbook of Wood Science and Technology; Eds.; Springer Handbooks; Springer International Publishing: cham, 2069 p.

Anwar Uyup M K, Sahari S H, Jalaludin Z, Husain H, Lee S H, Yusoh A S (2021) Water Vapour Sorption Behaviour and Physico-Mechanical Properties of Methyl Methacrylate (MMA)- and MMA–Styrene-Modified Batai (Paraserianthes Falcataria) Wood, Holzforschung, 75(5), 444–451.

Thybring, E. E (2013) The Decay Resistance of Modified Wood Influenced by Moisture Exclusion and Swelling Reduction, International Biodeterioration & Biodegradation, 82, 87–95.