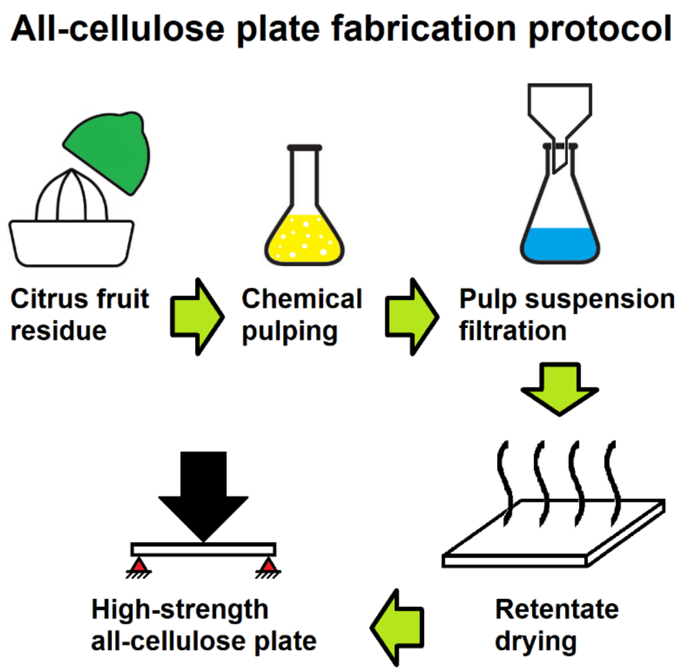
Molding of All-cellulose Plates Made of Cellulose Pulp Extracted from Citrus Fruit Residue

Antonio N. Nakagaito,[a,*] Hitoshi Takagi,[a] and Takumi Watanabe[b]

* Corresponding author: nakagaito@tokushima-u.ac.jp

DOI: 10.15376/biores.20.1.1577-1583

GRAPHICAL ABSTRACT



Molding of All-Cellulose Plates Made of Cellulose Pulp Extracted from Citrus Fruit Residue

Antonio N. Nakagaito ,[a,]* Hitoshi Takagi ,[a] and Takumi Watanabe [b]

Cellulose is photosynthesized by plants from carbon dioxide and water, and it is the most abundant organic compound available. It is present in the plant cells as structural component in the form of elementary fibrils known as nanofibers. Cellulose nanofibers can be easily extracted from parenchyma tissues of agricultural waste. Although thin sheets made of cellulose nanofibers can be readily obtained by a papermaking method, thicker plates are difficult to make. Here we propose a papermaking-like method to fabricate 1 to 2 mm-thick plates from citrus fruit residue-derived cellulose pulp initially having a solids content of about 1%. The protocol is simple, easy, requires affordable devices and relies on water evaporation to consolidate the fibrils by hydrogen bond interconnections. The pulp morphology seems to consist mostly of cellulose nanofibers and the bending strength and modulus of obtained plates reached 190 ± 30 MPa and 9.6 ± 1.5 GPa, respectively, values that approach those reported in a previous study that molded microfibrillated cellulose but relying on a complex process. This streamlined protocol could be groundwork for further studies aiming the difficult task of molding cellulosic materials.

DOI: 10.15376/biores.20.1.1577-1583

Keywords: All-cellulose plate; Cellulose pulp; Cellulose nanofiber; Citrus fruit; Papermaking

*Contact information: a: Graduate School of Technology, Industrial and Social Sciences, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima, Tokushima 770-8506, Japan; b: Graduate School of Advanced Technology and Science, Tokushima University, 2-1 Minamijosanjima-cho, Tokushima, Tokushima 770-8506, Japan; *Corresponding author: nakagaito@tokushima-u.ac.jp*

INTRODUCTION

Fruits and root vegetables are mostly made of parenchyma tissues. According to Gibson (2012), these are made of pressurized cells that are liquid-filled, closed-cell foams, polyhedral in shape, with thin cell walls consisting of a single layer formed by cellulose nanofibers (CNF) reinforcing a matrix of hemicelluloses, glycoproteins, and pectin. Cell walls of palm stems and trees are structures aimed at supporting the plants' own weight and coping with bending stresses caused by winds, whereas parenchyma cells are just intended to store liquids. The mechanical properties of the former are far higher than those of the latter, making parenchyma cells relatively easier to fibrillate into CNF. The CNF have mechanical properties comparable to those of aramid fibers (Gordon 1976), with great potential to be used in the fabrication of engineering materials.

The largest fruit produce in the world is citrus (Mahato *et al.* 2020). About half of the citrus fruit's weight becomes waste after juice extraction (Marino *et al.* 2015). The dry residue, comprised mostly of parenchyma tissue, contains low amounts of lignin (3 to 5%) but high pectin (up to 25%), hemicelluloses, and cellulose (up to 20%) (Marino *et al.* 2018). Other than serving as animal feed or composting, such residues could be burnt for heat, but incineration has small energetic advantage due to the high moisture content. Therefore, fruit residue could be used as raw material for CNF isolation, adding value to an otherwise underutilized material.

Biocomposites consisting of petroleum-based matrixes reinforced with natural fibers have been studied and produced for a long time due to environmental impact advantages over traditional composites. However, they have weaknesses such as limited recyclability and biodegradability, in addition to poor interfacial bonding due to the hydrophilic nature of plant fibers embedded in hydrophobic polymers. As a possible solution, all-cellulose composites have been considered lately. For their fabrication, there are some approaches such as embedding cellulosic fibers in dissolved cellulose, which is coagulated to become the matrix phase, as first proposed by Nishino *et al.* (2004). Another way is by selective dissolution of the surface of fibers to adhere and consolidate the fibers after cellulose regeneration (Nishino and Arimoto 2007). More recently, there have been many attempts to obtain all-cellulose materials by compression molding of partially fibrillated fibers without dissolution, using only water and no chemicals (Nilsson *et al.* 2010, 2012; Arevalo and Peijs 2016; Pintiaux *et al.* 2019; Abou-Yousef and Kamel 2023). Some of these reports suggest that fibrillation of cellulose have positive effects on the mechanical properties of the molded materials. Hence, an alternative method to make all-cellulose materials would be the consolidation of CNF by hydrogen bond formation driven by water, in a concept resembling papermaking.

Although papers are easily fabricated from CNF, making thick plates has been hardly investigated. One of the few attempts used a laborious and time-consuming protocol to mold microfibrillated cellulose, but obtained a material with 250 MPa of strength and 16 GPa of modulus in bending (Yano and Nakahara 2004). Here we aimed to extract CNF from citrus fruit residue to make all-cellulose plates using a much more straightforward process similar to papermaking. Molded materials achieved a bending strength and modulus around 200 MPa and 9 GPa, respectively. The molding of all-cellulose materials still has limitations such as the complexity of processes that demands special facilities, the excessive molding time, and the shape inaccuracies of molded parts that make them unsuitable for mass production. This study provides a further step towards the molding of all-cellulose plates by a straightforward and less costly means that eventually could become a method scalable at an industrial level.

EXPERIMENTAL

Materials

Two morphologies of cellulose were used. Commercially available microfibrillated cellulose tradename Celish KY100G (Daicel Miraizu Ltd., Japan) and cellulose pulp extracted from residue of citrus fruit sudachi (*Citrus sudachi*).

Chemicals used for pulping of fruit residues consisted of sodium chlorite and acetic acid purchased from Kanto Chemical Co., Inc., Japan, in addition to hydrochloric acid and potassium hydroxide from FUJIFILM Wako Pure Chemical Corporation, Japan.

Isolation of Cellulose Pulp from Citrus Fruit

The first step consisted of bleaching by immersing 300 g of wet residue (20 wt% of solid content) in 1.5 L of distilled water containing 10 g of sodium chlorite and 2 mL of acetic acid at 75 °C. The same amount of chemicals was added twice more after each hour, for a total of three hours of treatment. In the next step, pectin depolymerization was performed by cooking the material in 2 L of aqueous solution of 0.18 wt% hydrochloric acid at 120 °C (under a pressure of 100 kPa) for two h, based on a method proposed by Hiasa *et al.* (2014). The last step consisted of removing hemicelluloses by immersion in 1.5 L of 6 wt% potassium hydroxide aqueous solution at 80°C for two h. Materials were washed through filtration after each treatment step to remove residual chemicals.

All-cellulose Plate Fabrication

Preliminary experiments to make all-cellulose plates were carried out using commercial CNF tradename Celish with a homemade metal mold, to determine the best molding parameters such as CNF paste moisture content and drying temperature. A vacuum filtration apparatus was especially fabricated to dewater 1 wt.% CNF aqueous suspension to form pre-molded hydrogels. Drying of hydrogels were accomplished using a hot plate.

Bending Test

Test pieces 60 mm-long, 10 mm-wide, and 1 to 2 mm-thick were cut and dried at 105 °C for 1 h just before testing. Three-point bending tests at a cross-head speed of 1 mm/min were performed with an AUTOGRAPH AG-X plus (Shimadzu Corporation, Japan). The span was set so that the span to thickness ratio was 16, regardless of sample thickness. For each sample, 4 to 5 replicates were tested.

Scanning Electron Microscopy

Celish and sudachi residue-derived pulp suspensions at 0.01 wt.% concentrations were dropped on silicon Si substrates and let to dry. Celish was suspended in water, while sudachi pulp was suspended in ethanol to minimize fibril aggregations during drying. All samples were coated with osmium to avoid charging during observations. Micrographs were taken by a field emission scanning electron microscope S-4700 (Hitachi High-Tech Corp., Japan).

RESULTS AND DISCUSSION

As a proof of concept, about 100 g of Celish aqueous paste (fiber content of 10 wt%) was poured inside a rectangular mold (89 mm long, 78 mm wide) and oven-dried, while applying a constant pressure of 13 kPa on top of the mold lid to avoid warping. The lid was perforated to allow the proper leakage of water vapor. Samples were dried at 70 °C for 30 h, 105 °C for 24 h, and 115 °C for 20 h which delivered plates with bending strengths/moduli of 90 ± 6 MPa/5.6 ± 0.6 GPa, 106 ± 7 MPa/8.0 ± 0.2 GPa, 103 ± 16 MPa/8.1 ± 0.2 GPa, respectively. Bending properties increased with drying temperature, especially above 100 °C, but were far below those by Yano and Nakahara (2004) who reported bending strength/modulus of 250 MPa/16 GPa. Their samples reached a density of around 1.5 g/cm^3, while in this study it stayed at around 1.23 g/cm^3, and small cavities inside the sample were visible. Pre-compression of the paste at 1 MPa before drying increased density to 1.36 g/cm^3, resulting in bending strength/modulus of 130 ± 10 MPa/8 ± 1 GPa. A larger pre-compression of 5 MPa did not deliver further improvement. Next, the starting CNF paste had the fiber contents adjusted to 2, 3, 5, and 10 wt% by addition of water. The bending strengths/moduli were noticeably higher for plates molded from the most diluted pastes, at 179 ± 15 MPa/9.0 ± 0.5 GPa and 190 ± 12 MPa/9.6 ± 1.7 GPa for 2 and 3 wt% fiber contents, respectively. This was possibly due to the capillary forces of excess water drawing the nanofibers together, interconnecting them by a larger number of hydrogen bonds and increasing density. Based on these preliminary experiments, a vacuum filtration apparatus was fabricated with a built-in metal mold for posterior drying of the retentate under compression. The contraption is depicted in Fig. 1(a). The upper part made of transparent acrylic is connected to a metal mold (Fig. 1(b)) that would hold the retentate after dewatering. Filtration is aided by negative pressure formed in the acrylic box at the base, connected to a vacuum pump. After dewatering, the pre-molded retentate was carefully removed together with the metal mold and set on a hot plate to dry (Fig. 2(a)). Pre-molded retentates were dried at temperatures of 80 °C, 90 °C, and 105 °C for 24 h applying a pressure of about 16 kPa on top, resulting in samples with bending strengths/moduli of 136 ± 14 MPa/5.2 ± 0.5 GPa, 167 ± 13 MPa/7.7 ± 0.7 GPa, and 166 ± 9 MPa/7.8 ± 0.4 GPa, respectively. Similar to the preliminary experiments, temperatures over 100 °C delivered the highest mechanical properties.

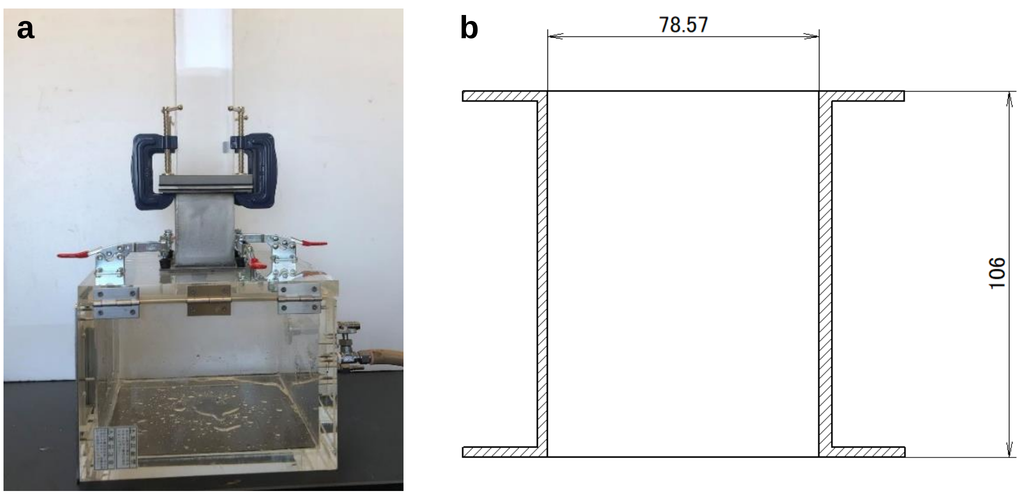


Fig. 1. Vacuum filtration apparatus (a) and the cross-sectional view of the metal mold (b)

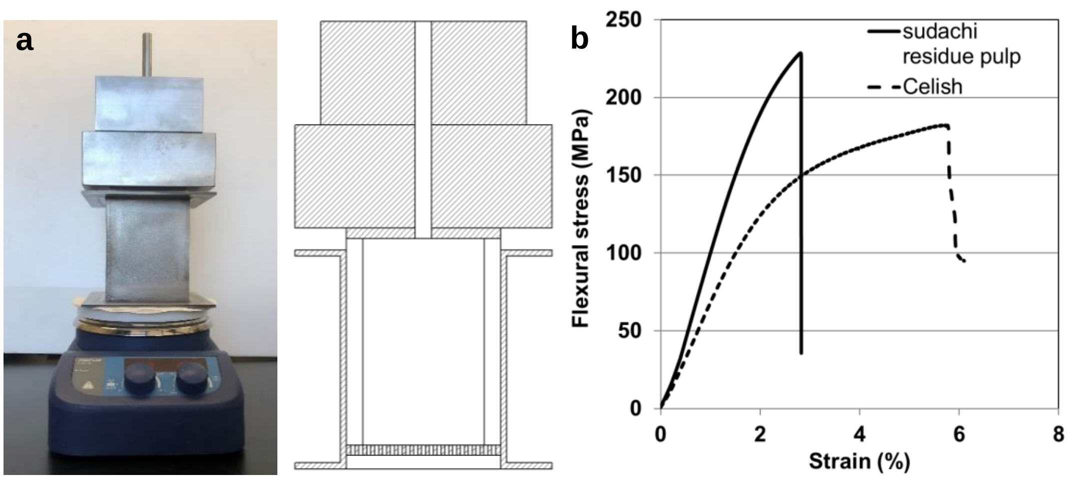


Fig. 2. Cellulose molding by vacuum filtration and hot-plate drying (a) and typical bending stress-strain curves of commercial Celish and sudachi residue-derived pulp plates (b)

When pulp extracted from sudachi citrus fruit residue was molded by the same filtration pre-forming and drying (Fig. 2(a)), the bending strength/modulus achieved 190 ± 30 MPa/9.6 ± 1.5 GPa, surpassing the values obtained with Celish, as depicted by the stress-strain curves shown in Fig. 2(b). The molding from sudachi pulp aqueous paste gave similar results at 221 ± 15 MPa/9.5 ± 0.9 GPa of bending strength/modulus. These values were still lower than those reported by Yano and Nakahara (2004) at 250 MPa/16 GPa of bending strength/modulus, but relatively close values were accomplished by a simpler fabrication method and by using pulp extracted from agricultural residue. Ultrasonication of sudachi pulp did not improve the mechanical properties of the obtained plates, indicating that the pulp itself already had a CNF morphology, as observed by electron microscopy.

Table 1 summarizes the mechanical properties of all-cellulose materials fabricated by thermo-compression. The material obtained in the present study showed values on a par with those based on cellulose from different sources. The bending modulus was relatively low, but the higher bending strength might be caused by the finer morphology of the parenchyma cell-derived cellulose. The higher molding pressures used in other studies might have contributed to lower strength due to reduction of average molar mass of cellulose, as noted by Nilsson *et al.* (2010).

Table 1. Comparison of Mechanical Properties of Compression Molded Materials from Different Cellulose Sources

Reference studies	Cellulose source	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)
Nilsson *et al.* 2010	Softwood pulp	-	-	11 ± 1.3	76 ± 10
Nilsson *et al.* 2010	Hardwood pulp	-	-	12.6 ± 2.4	65.3 ± 4
Arevalo and Peijs 2016	Refined flax fibers	17 ± 1.8	120 ± 5	-	-
Pintiaux *et al.* (2019)	Cellulose powder	8.1	70.1	1.9	31.1
Abou-Yousef and Kamel (2023)	Refined bagasse	-	-	38	>2
Present study	Citrus fruit CNF	9.6 ± 1.5	190 ± 30	-	-

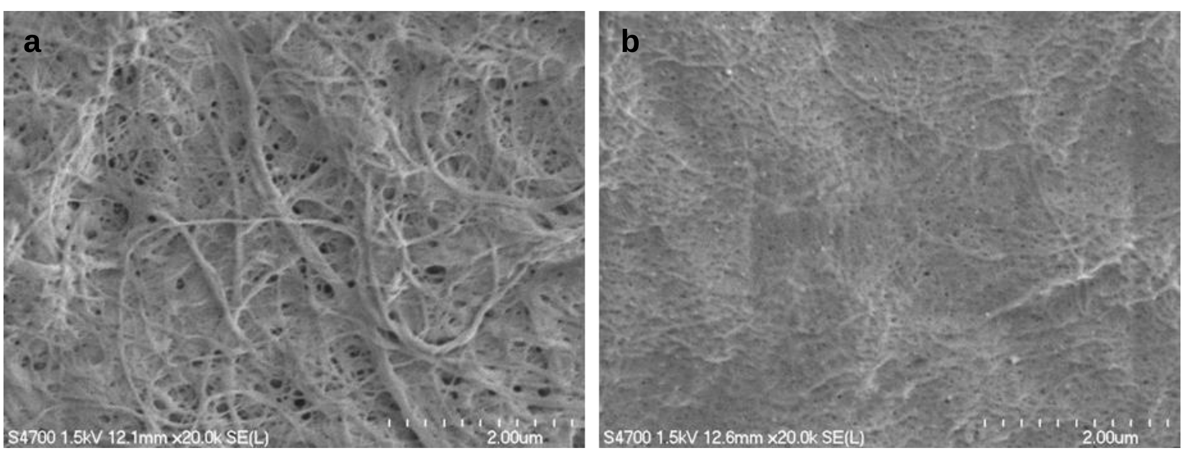


Fig. 3. Scanning electron micrographs of Celish (a) and sudachi residue-derived pulp (b) compared at the same magnification

Figure 3 compares the morphologies of commercial Celish and sudachi residue-derived pulp. Celish consists of a wide distribution of fibril diameters, from nanofibers to thicker fibril bundles, while sudachi pulp is comprised of more homogeneous and finer nanofibers. The number of hydrogen bond interconnections is proportional to the exposed surface hydroxyl groups made available by the fine morphology, resulting in stronger molded materials. But this morphology of enhanced hydrophilic area also slows down dewatering, resulting in extended filtration times depending on the initial water content. This limitation needs to be addressed. Further studies are being carried out to shorten the filtration times.

Even though the present study focused on molding plates made of cellulose extracted from fruit residue, the concept of adding value to agricultural waste should be considered from a broader perspective. For instance, the proposed use of ground pistachio shell as a filler in paper (Lee *et al.* 2024), delivering similar performance to the traditional ground calcium carbonate, suggests that other cellulosic sources might present a similar potential in papermaking. The possibility of using fibrillated cellulose morphologies as fillers or coatings in paper could deliver other properties beyond just mechanical strength. This would be particularly beneficial to the field of packaging (Hubbe *et al.* 2017).

CONCLUSIONS

1. This study demonstrates the possibility of molding high-strength/modulus all-cellulose plates by an uncomplicated method that relies solely on water to bridge the cellulose fibrils through hydrogen bond interconnections. Similar to paper, there is no need of adhesives or chemicals for fibril consolidation.
2. The molded products can be made from cellulose pulp extracted from agricultural residue, especially fruits and root vegetables that are mostly comprised of parenchyma tissue. The cellulose sources are inexpensive and the fibrillation of the pulp is not required.
3. The only reservation concerns the long times required to filter aqueous suspensions of cellulose nanofibers (CNF).

ACKNOWLEDGMENTS

The authors thank Tokushima Prefecture Agriculture, Forestry, and Fisheries Technology Support Center for supplying sudachi citrus fruit residue for this study.

REFERENCES CITED

Abou-Yousef, H., and Kamel, S. (2023). “Physico-mechanical properties of all-cellulose composites prepared by different approaches from micro-fibrillated bagasse pulp fibers,” *Mater. Today Commun.* 35, article 105672. DOI: 10.1016/j.mtcomm.2023.105672

Arevalo, R., and Peijs, T. (2016). “Binderless all-cellulose fibreboard from microfibrillated lignocellulosic natural fibres,” *Compos. Part A – Appl. S.* 83, 38-46. DOI: 1016/j.compositesa.2015.11.027

Gibson, L. J. (2012). “The hierarchical structure and mechanics of plant materials,” *J. R. Soc. Interface* 9(76), 2749-2766. DOI: 10.1098/rsif.2012.0341

Gordon, J. E. (1976). *The New Science of Strong Materials*, Princeton University Press, Princeton, NJ, USA

Hiasa, S., Iwamoto, S., Endo, T., and Edashige, Y. (2014). "Isolation of cellulose nanofibrils from mandarin (*Citrus unshiu*) peel waste," *Ind. Crop. Prod.* 62, 280-285. DOI: 10.1016/j.indcrop.2014.08.007

Hubbe, M. A., Ferrer, A., Tyagi, P., Yin, Y., Salas, C., Pal, L., and Rojas, O. (2017). "Nanocellulose in thin films, coatings, and plies for packaging applications: A review," *BioResources* 12(1), 2143-2233. DOI: 10.15376/biores.12.1.2143-2233

Lee, J.-H., Fereidooni, L., Morais, A. R. C., Shiflett, M. B., Hubbe, M. A., and Venditti, R. A. (2024). "Valorization of food processing waste: Utilization of pistachio shell as a renewable papermaking filler for paperboard," *Ind. Crop. Prod.* 218, article 118810. DOI: 10.1016/j.indcrop.2024.118810

Mahato, N., Sharma, K., Sinha, M., Baral, E. R., Koteswararao, R., Dhyani, A., Cho, M. H., and Cho, S. (2020). "Bio-sorbents, industrially important chemicals and novel materials from citrus processing waste as a sustainable and renewable bioresource: A review," *Adv. Res.* 23, 61-82. DOI: 10.1016/j.jare.2020.01.007

Marino, M., da Silva, L. L., Duran, N., Tasic, L. (2015). "Enhanced materials from nature: Nanocellulose from citrus waste," *Molecules* 29, 5908-5923. DOI: 10.3390/molecules20045908

Marino, M. A., Rezende, C. A., and Tasic, L. (2018). "A multistep mild process for preparation of nanocellulose from orange bagasse," *Cellulose* 25, 5739-5750. DOI: 10.1007/s10570-018-1977-y

Nilsson, H., Galland, S., Larsson, P. T., Gamstedt, E. K., Nishino, T., Berglund, L. A., and Iversen, T. (2010). "A non-solvent approach for high-stiffness all-cellulose biocomposites based on pure wood cellulose," *Compos. Sci. Technol.* 70, 1704-1712. DOI: 10.1016/j.compscitech.2010.06.016

Nilsson, H., Galland, S., Larsson, P. T., Gamstedt, E. K., and Iversen, T. (2012). "Compression molded wood pulp biocomposites: A study of hemicellulose influence on cellulose supramolecular structure and material properties," *Cellulose* 19, 751-760. DOI: 10.1007/s10570-012-9688-2

Nishino, T., Matsuda, I., and Hirao, K. (2004). "All-cellulose composite," *Macromolecules* 37(20), 7683-7687. DOI: 10.1021/ma049300h

Nishino, T., and Arimoto, N. (2007). "All-cellulose composite prepared by selective dissolving of fiber surface," *Biomacromolecules* 8(9), 2712-2716. DOI: 10.1021/bm0703416

Pintiaux, T., Heuls, M., Vandenbossche, V., Murphy, T., Wuhrer, R., Castignolles, P., Gaborieau, M., and Rouilly, A. (2019). "Cellulose consolidation under high-pressure and high-temperature uniaxial compression," *Cellulose* 26, 2941-2954. DOI: 10.1007/s10570-019-02273-8

Yano, Y., and Nakahara, S. (2004). "Bio-composites produced from plant microfiber bundles with a nanometer unit web-like network," *J. Mater. Sci.* 39, 1635-1638.

Article submitted: July 5, 2024; Peer review completed: August 1, 2024; Revised version received: December 5, 2024; Accepted: December 11, 2024; Published: December 18, 2024.
DOI: 10.15376/biores.20.1.1577-1583