

Bacteria Cellulose and Resin Stabilization in Densified Veneer

Ananto Nugroho^{1,*}, Triastuti², Fazhar Akbar²,
Sandi Sufiandi³ and Anne Zufliya Syahrial¹

¹Department of Metallurgical and Materials Engineering, Universitas Indonesia, Kampus Baru UI, Depok, West Java 16424, Indonesia

²Research Center for Biomass and Bioproducts, National Research and Innovation Agency (BRIN), Jl. Raya Bogor Km. 46, Cibinong 16911, Indonesia

³Directorate of Laboratory Management, Research Facilities, and Science and Technology Park, National Research and Innovation Agency (BRIN), Jl. Raya Bogor Km. 46, Cibinong 16911, Indonesia

(*Corresponding author: anne@metal.ui.ac.id)

Received: 25 November 2022, Revised: 7 January 2023, Accepted: 17 January 2023, Published: 23 January 2023

Abstract

Cellulose produced by fermentation of acetic acid bacteria has high tensile strength. Meanwhile, cellulose derived from wood, which is abundant in nature, has a limit in strength. In this work, delignified wood veneer was immersed in *Acetobacter xylinum* culture medium to self-assemble bacterial cellulose into wood pores. Then the process was continued with a heating press. It makes the material denser and causes hydrogen bonds to form between the cellulose fibers. This study observed the densified hybrid veneer for the period of bacterial fermentation and impregnation of resin stabilization in tensile strength and dynamic mechanical analysis (DMA). The densified hybrid veneer of bacterial cellulose with resin impregnation had the maximum tensile strength after 7 days of fermentation. The DMA test showed that a densified hybrid veneer of bacterial cellulose stabilized with resin has a good ability to store cyclic energy and a damping factor that increases with temperature.

Keywords: Wood, Natural fibers, Delignification, Hydrogen bonds, Tensile strength

Introduction

Cellulose, which includes natural polymers made of several repeating glucose chains to build very long linear chains, is the most significant component and skeleton in plants [1]. Cellulose has become essential in the development of polymeric materials and composites due to its unexpected specificity, amazing architecture, diversified reactivity, and utility [2]. Current environmental consciousness has resulted in the creation of renewable natural materials for use in a variety of areas. Wood is a natural material that is lightweight, robust, bendable, affordable, and renewable. However, as a natural product, wood also has some disadvantages, such as low mechanical strength, poor fire resistance, defects, and non-uniform growth. Several of its weaknesses may be mitigated by changing it during the compaction process, which changes its physical and mechanical qualities.

The densification is a common method to enhance the qualities of wood without using harmful chemicals. The density of wood increases during the densification process, which requires heat and pressure. One of the drawbacks of this densification method is that the fixation phase of densified wood is difficult to achieve. Densified wood tends to swell with time and ambient humidity. Densified can be fixed in a few ways, such as with rising steam, adhesive impregnation or heat treatment [3]. The simplest method for producing dense, strong wood is to remove the lignin during the early stages of densification [4]. Through the process of delignification and densification, water molecules could produce hydrogen bonding in wood nanofibers during hot pressing, affecting their morphology and physical properties [5]. The mechanical properties of densified wood increase by giving heat stress, but they will decrease if the heat is continuously elevated [6].

Cellulose derived from plants is one of the most abundant polymers in nature. In addition, cellulose can also be produced from bacterial fermentation. One of them is from a type of acetic acid bacteria such as *Acetobacter xylinum*. Cellulose produced from bacterial fermentation is pure and has a high strength. It was recently discovered that it has the capability to coat organic fibers with bacterial cellulose (BC). The BC pellicle that coats the natural fiber acts provides extra reinforcement to improve the mechanical strength [7]. The interaction between BC and plant cellulose is known to have the potential to form hydrogen bonds between cellulose chains [8]. Since cellulose chains are long and straight, they may be arranged near one

another in parallel. **Figure 1** shows that when cellulose chains are parallel, the hydroxyl (OH) groups on glucose monomers in different chains can be next to each other and link to make hydrogen bonds. BC is also able to increase the surface bond between polymer adhesives and natural fibers [9]. Previously, we discovered *Acetobacter xylinum* could enter the veneer cavity and form a pellicle in the culture medium [10]. The finished product is a densified hybrid veneer-BC with improved mechanical strength [11].

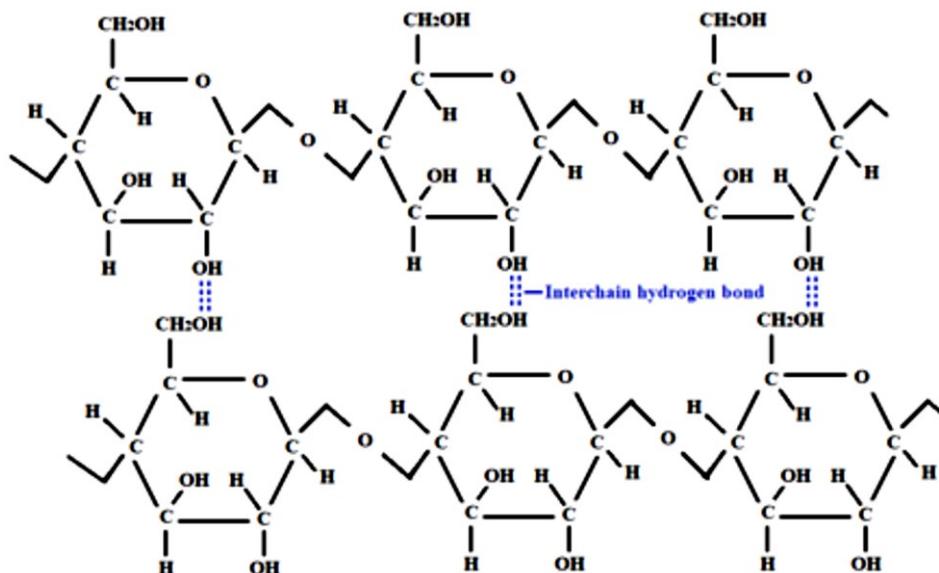


Figure 1 Intermolecular hydrogen bonds.

Elastic deformation occurs during microfiber, recovery to original shape is possible. Set-recovery can be attributed to cellulose macromolecules elastic strain energy release [12]. In contrast, spring-back is a wood's natural response to reduce the pressures produced by a process. After a load that caused the deformation was removed, the spring-back effect swiftly took place, leading to an instant set-recovery in the wood [13]. A hygroscopic nature of wood causes a densified wood to revert its original shape. Due to the free hydroxyl groups in cellulose, it binds to water extremely readily. As the wood's size increases over time in humid places, its strength decreases. The solution to this issue is to stabilize the wood by impregnating it with resin. To get into the wood pores, a stable resin with low viscosity and high vacuum strength is needed. Hydroxypropyl methacrylate is the major ingredient of stable resin, a polar monomer capable of enhancing wood's dimensional [14]. As a result, the originality of this work is that the endeavor to replace wood fiber with bacterial cellulose reinforcement and stabilize compaction veneer with resin impregnation has never been done previously. In this case, the results of the modification research will be used to make and use hybrid materials that can absorb ballistic energy [15].

The dynamic load will have an impact on the wood during use and application. Therefore, understanding and investigating the behavior of densified wood under periodic stress is critical. A dynamic mechanical analyzer (DMA) is a method for determining the thermo-mechanical characteristics of material under dynamic stress [16]. Results from DMA can characterize morphology and adsorption as a result of frequency, duration, load, or a set of parameters. This research creates delignification veneer using BC in the culture medium to be densified and then stabilized with resin. This technique was utilized to enhance the physical and mechanical properties of veneer. The capacity of bacteria to enter veneer pores was observed, measured and shown using a digital microscope. A tensile test determined the veneer's mechanical strength. DMA was used to find out how dynamic load affects the stored modulus (E') and damper factor (\tan) of veneer hybrids like the thermal rose.

Materials and methods

This research utilized 2.3 mm wood veneer. A 15-year old Platinum teak tree (*Tectona grandis L.f.*) is harvested and processed for veneer. All specimens used were devoid of noticeable knots and crack. The sample is then cut into a size of $100 \times 100 \text{ mm}^2$. Another material used in the study is a bacterial starter. The bacterial starter contains millions of *Acetobacter xylinum* cells needed to produce BC in the culture medium. *Acetobacter xylinum* is a gram-negative bacterium. This acetic acid bacteria can polymerize glucose into cellulose strands [17]. The starter was purchased from the Biotechno Store Collection in liquid form.

Wood delignification is required to remove lignin and hemicellulose. The veneer sample is delignified by boiling it in a 1 M NaOH solution in beaker glass at 90 °C for 90 minutes [10,11]. After that, it was washed with water. By soaking the wood for 24 hours in water, any residual NaOH solution and other contaminants were eliminated. Next, it was cleaned until there were no significant impurities.

In-situ BC self-assembly is carried out in culture medium. The composition of the culture medium for 1 L of coconut water was 5 % white sugar, 1 % acetic acid, and 0.1 % urea. Strain the old coconut water and boil it on the stove. Then, decrease the heat together with gradually add the acetic acid at pH 4. After Mixing sugar with urea, the solution was stirred, and it was boiled on low heat for 15 minutes. Next, inserting BC into veneer cavity. First, it was put in a plastic box, then the box was filled with hot media until it was saturated. To avoid infection, quickly cover it with paper. Before adding 10 mL of starting of bacteria to 1 L of culture solution, the temperature must reach 30 °C. To avoid contamination from the air, starter bacteria should be put into the culture medium immediately. The fermentation took 5, 6, 7, and 8 days at room temperature (28 - 30 °C). The veneer and BC might be harvested to make a hybrid veneer.

First, harvesting and cleaning of wood veneer, then this hybrid veneer was dried and cured to 30 - 35 %. At a temperature of 135 °C, a hot press densified the veneer using 10 MPa in pressure with gradually increasing 2.5 MPa every 15 minutes for 60 minutes. These methods resulted in a veneer that was densified and had a density of 1.18 - 1.23 g/cm³. After densifying, it is resin stabilized. This process used a tube with a vacuum pressure of 50 cm Hg for 30 minutes and the impregnation method. Then, it got 60 minutes of high-pressure air from a compressor. This study uses a stabilized resin type, namely hydroxypropyl methacrylate-based stabilizer resin (Stick Fast®).

A tensile strength test was measured to analyze the mechanical strength of densified veneer. This research compares the tensile strength of the natural teak veneer (NV), densified veneer-BC (DVB), and densified veneer-BC-stabilized (DVB-S) made with 5, 6, 7, and 8 days of fermentation. All of tensile strength specimens were 100 mm in length and 10 mm wide, and there were 6 replicates [18]. A universal testing machine (SHIMADZU, AGS-X-10 kN) was used to evaluate tensile strength at 0.6 mm/minute in speed. Perkin Elmer DMA 8000 was utilized to analyze dynamic mechanical. **Figure 2** shows the veneer's dimensions, 10 mm in width and 40 mm in length, with a clamping range of 6.5 mm in the center. The specimens were heated at 20 to 250 °C at a rate of 5 °C/minute. In addition, the strain pressure was 0.01 mm at a constant frequency of 1 Hz.

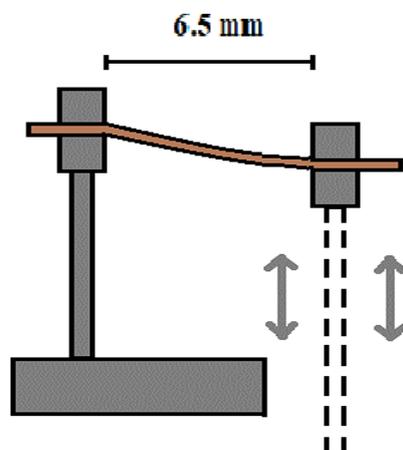


Figure 2 Single-cantilever DMA bending mode.

Results and discussion

After the delignification process, bacterial cells can penetrate the veneer wood pores up to a thickness of 2.3 mm, as shown in **Figure 3(a)**. Using the ImageJ software, the diameter of the wood pore structure is about 0.12 - 0.35 mm. The diameter of an *Acetobacter xylinum* is smaller than the size of wood pores, so penetration can occur. These bacteria have a width of 0.5 - 1 µm and a length of 2 - 10 µm, while the bacteria make cellulose fibers 30 - 80 nm in width. Natural fiber, which is hydrophilic and rough, is optimal for plant growth including *Acetobacter xylinum* [19]. Wherever the wood veneer was soaked in culture media, the fulfillment of BC happened. BC and veneer fibers interact strongly because cellulose has a great connection to each other and other materials with hydroxyl groups [20]. *Acetobacter xylinum* is an aerobic

bacteria that needs oxygen [21]. This explains why BC can fill and cover the wood pores, and it occurs more near the veneer surface. The hybrid veneer was impregnated, then placed in an oven at 95 °C for 60 minutes, covered in aluminum foil. The heating process is carried out to accelerate the hardening of the resin. This procedure bonded the resin to the veneer's fibers and keeps it stable, as shown in **Figure 3(b)**.

Hot compression acts as linkage for nanocellulose during the densification process in both dry and wet conditions. The veneer's water content is not immediately wasted when the sample is densified by heat for 60 min. The veneer had a moisture content around 1 and 4 %. After the veneer has dried in the oven for 2 hours at 70 °C, the residual moisture in the veneer can be evaporated. When submerged in water, the veneer will recover to 75 - 85 % of its previous size. Then it was recompressed under dried conditions. After heat compression treatment, it is expected that the mechanical properties will be better and approach the fixed shape

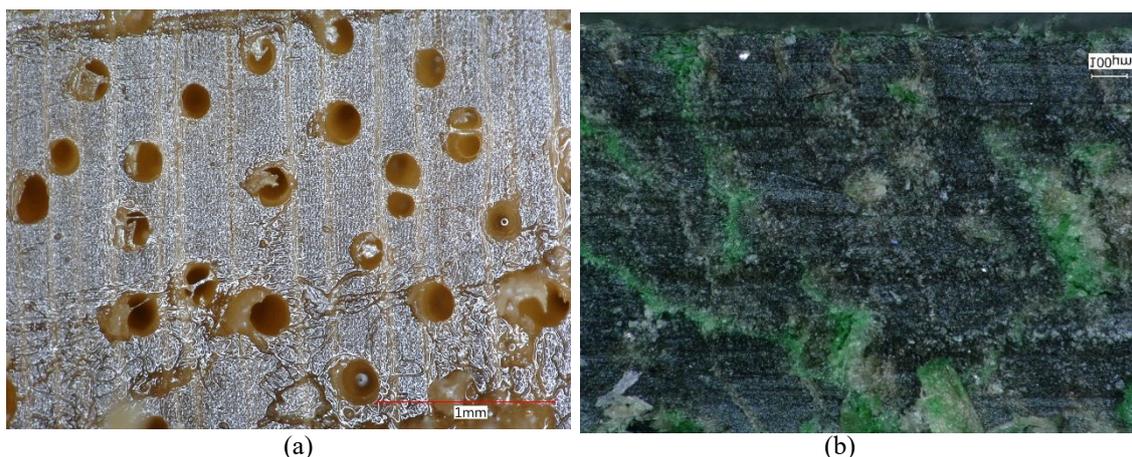


Figure 3 Cross-sectional hybrid veneer microscopy (a) BC self-assembled in veneer pores. (b) Green coloring pigment showed resin after densification and impregnation.

Table 1 indicates that densified veneer (DV) had a 40.50 % higher tensile strength than natural veneer (NV). The veneer modulus of elasticity rose up to 108.60 %. The delignification degraded lignin. As a result, it is easy to create veneer that is heavier than natural wood. The mechanical strength of the cellulose molecule chain increase with hydrogen bonds density and interaction. **Table 1** demonstrates that BC-reinforced hybrid veneer had higher tensile strength and modulus of elasticity. This indicates that BC acts as a reinforcement to enhance the densified veneer's mechanical properties. BC and natural fiber cellulose both have hydroxyl chains. These hydroxyl chains interact strongly with densification. This interaction has an impact on increasing the hydrogen bonds formation [22]. The tensile strength of densified veneer-BC by fermentation for 5 days (DVB-5) was the highest. When compared to natural veneer, tensile strength increases by up to 81.38 % and modulus of elasticity increases by up to 156.63 %. At 6, 7, and 8 days of fermentation, there was a small decrease in the mechanical strength.

Table 1 Physical and mechanical properties of hybrid veneer.

Sample	Density (g/cm ³)	Tensile Strength (MPa)	Modulus Elasticity (MPa)
NV	0.62	78.92 ± 14.31	5741.24 ± 575.88
DV	1.00	110.89 ± 20.50	11976.59 ± 885.84
DVB-5	1.18	143.15 ± 49.55	14733.97 ± 1666.49
DVB-6	1.18	138.78 ± 39.11	14203.52 ± 709.96
DVB-7	1.19	131.39 ± 27.53	14660.00 ± 1019.07
DVB-8	1.23	124.07 ± 49.29	12477.96 ± 720.20
DV-S	1.17	129.38 ± 25.78	10757.11 ± 1290.83
DVB-5-S	1.20	154.63 ± 54.92	10935.34 ± 975.71
DVB-6-S	1.20	162.18 ± 34.46	11479.73 ± 717.16
DVB-7-S	1.22	163.85 ± 30.04	11176.88 ± 675.41
DVB-8-S	1.21	128.97 ± 16.05	10979.93 ± 1222.98

Table 1 shows that densified veneer-stabilized (DV-S) has a higher density with an increase in tensile strength of about 16.67 % when compared to densified veneer (DV). However, the modulus of elasticity of the veneers decreased by about -10.18 %. The low-molecular weight resin in the cell wall worked as a plasticizer and softened the cell wall, lowering its elastic modulus [23]. **Table 1** shows the tensile strength increases in densified veneer-BC-stabilized (DVB-S). This indicates that BC was able to absorb resin and also act as a reinforcement to increase the mechanical strength. BC on natural fibers enhanced their surface bonding with polymer adhesives [9]. The tensile strength of densified veneer-BC-stabilized by fermentation for 7 days (DVB-7-S) was the highest. When compared to densified veneer (DV), tensile strength increases by up to 47.76 %, but the modulus of elasticity decreases by about -6.68 %. A small decrease in tensile strength occurred in the 8-day fermentation period. This is due to the abundance of BC, which makes the veneer more easily attracted to water and moisture. The adsorbed water acts as a plasticizer, which disrupts the hydrogen bonds between molecules and affects the mechanical strength [24].

Figure 4 illustrates the relation between temperature and storage modulus and the responses of the densified veneer-stabilized (DV-S) and densified veneer-BC-stabilized (DVB-S). Because of the increased chain mobility of the wall's polymeric component, all samples' storage modulus decrease with the heating temperature. Meanwhile, the densified veneer-BC-stabilized (DVB-S) had greater initial storage modulus than the densified veneer-stabilized (DV-S). The densified veneer-BC-stabilized by fermentation for 7 days (DVB-7-S) had the highest storage modulus. Every DVB-S has the same response level and storage modulus as the preceding layer, including tensile strength. BC has strong hydrogen bonds and is more crystalline. The crystalline area worked as a physical cross-linker similar to a filler particle to raise the storage modulus. This showed that BC was important for improving and keeping the storage modulus in veneer as the heating temperature increased.

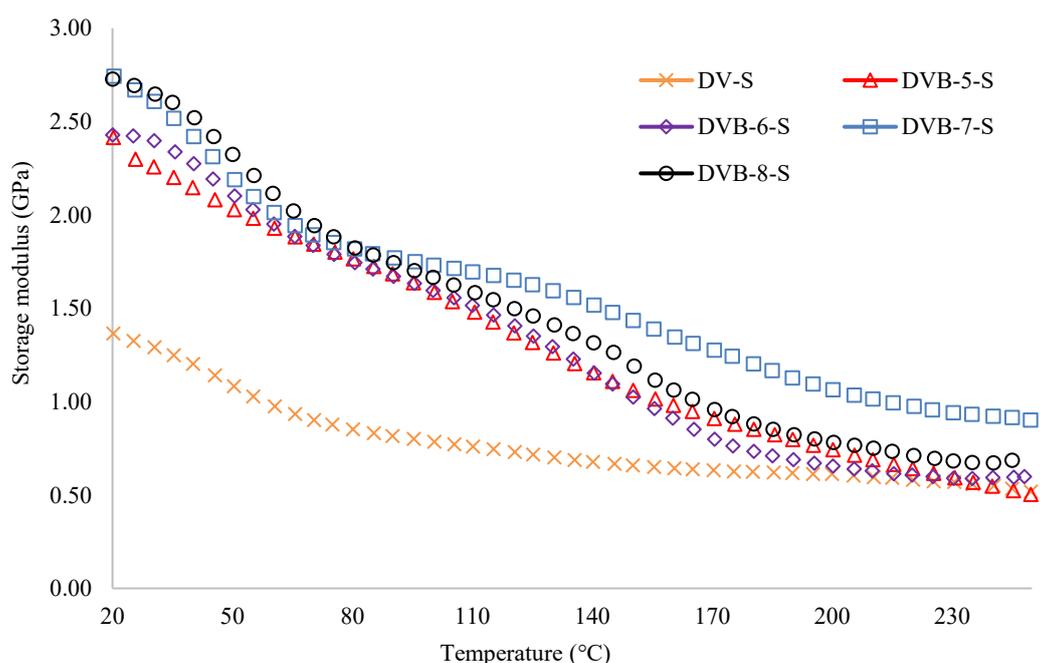


Figure 4 Effect of temperature to storage modulus.

Figure 5 represents the influence of temperature and $\tan \delta$ on damping behavior for all veneers. As heating temperatures rises, the absorb energy reduced. DV-S has a lower damping capability, while DVB-S has a higher damping capability and is stable up to 150 °C. If we look closely, the damping factor of all DVB-S has the same value for characteristics below 115 °. After reaching 115 °C, the damping response of each treatment changed. The DVB-7S seems to be the outlier, having the lowest damping factor above 115 °C. All veneer samples subjected to DMA were identified as polymeric, glassy behavior happened at 25 to 60 °C and a glass transition happened at 60 - 150 °C. The DMA test on wood and composite veneer was compatible with this temperature range [25].

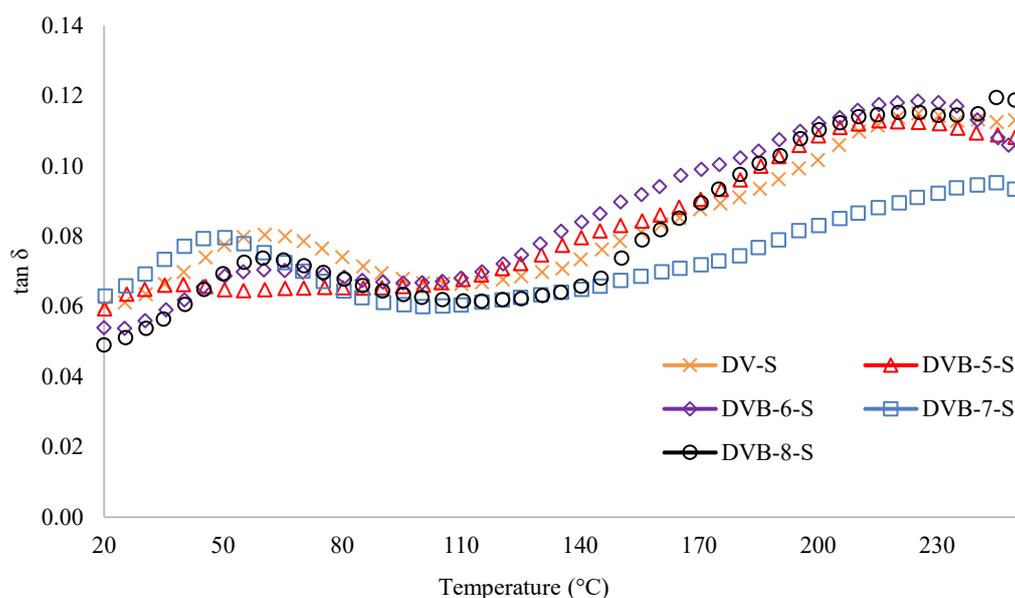


Figure 5 Effect of temperature and tan δ .

Platinum teak veneer is a fast-growing plant species and bacterial cellulose made from nutrients that derived from old coconut water. Both of them are plentiful, inexpensive, and renewable resources. However, further research is required to reduce energy consumption in the delignification and heat compression procedures from an economic perspective. For larger-scale manufacturing, effective and efficient machine design is also essential.

Conclusions

Wood veneer and bacterial cellulose (BC) densified by a heating press produce hybrid veneers with increased mechanical strength. The mechanical strength also increases after the hybrid veneer is stabilized by resin impregnation. This method increases the tensile strength by up to 47.76 % when compared to densified veneer without resin stabilization. However, the modulus of elasticity decreased to -6.68 %. The best results came from seven-day fermentation of assembly BC on media culture, which made the veneer stronger and more stable. Based on DMA result, it can be said that the densified veneer reinforced with BC and stabilized with resin has a good ability to store cyclic energy, and the damping factor increases as the temperature rises.

Acknowledgements

The authors would like to thank the Advanced Characterization Laboratories Cibinong - Integrated Laboratory of Bioproduct, National Research and Innovation Agency through E- Layanan Sains, Badan Riset dan Inovasi Nasional, Indonesia for providing the facilities and scientific and technical support. The authors would like to show their gratitude and appreciation to Firda Aulya Syamani, Sudarmanto, Jayadi and Guntur Wira Yudha, researchers and technicians who helped us with our project. Research funding supported by Kementerian Pendidikan, Kebudayaan, Riset dan Teknologi, Indonesia (NKB 838/UN2.RST/HKP.05.00/2022).

References

- [1] D Klemm, B Heublein, H Fink and A Bohn. Cellulose: Fascinating biopolymer and sustainable raw material. *Angew. Chem. Int. Ed.* 2005; **44**, 3358-93.
- [2] M Poletto, KL Ornaghi Júnior and AJ Zattera. Native cellulose: Structure, characterization and thermal properties. *Materials* 2014; **7**, 6105-19.
- [3] J Shi, J Peng, Q Huang, L Cai and SQ Shi. Fabrication of densified wood via synergy of chemical pretreatment, hot-pressing and post mechanical fixation. *J. Wood Sci.* 2020; **66**, 5.
- [4] J Song, C Chen, S Zhu, M Zhu, J Dai, U Ray, Y Li, Y Kuang, Y Li, N Quispe, Y Yao, A Gong, UH Leiste, HA Bruck, JY Zhu, A Vellore, H Li, ML Minus, Z Jia, A Martini, T Li and L Hu. Processing

- bulk natural wood into a high-performance structural material. *Nature* 2018; **554**, 224-8.
- [5] X Han, Y Ye, F Lam, J Pu and F Jiang. Hydrogen-bonding-induced assembly of aligned cellulose nanofibers into ultrastrong and tough bulk materials. *J. Mater. Chem. A* 2019; **7**, 27023-31.
- [6] EA Salca, P Bekhta and Y Seblii. The effect of veneer densification temperature and wood species on the plywood properties made from alternate layers of densified and non-densified veneers. *Forests* 2020; **11**, 700.
- [7] K Qiu and A Netravali. In situ produced bacterial cellulose nanofiber-based hybrids for nanocomposites. *Fibers* 2017; **5**, 11-3.
- [8] H Abrial, A Hartono, F Hafizulhaq, D Handayani, E Sugiarti and O Pradipta. Characterization of PVA/cassava starch biocomposites fabricated with and without sonication using bacterial cellulose fiber loadings. *Carbohydr. Polymer*. 2019; **206**, 593-601.
- [9] MA Naeem, Q Siddiqui, M Mushtaq, A Farooq, Z Pang and Q Wei. Insitu self-assembly of bacterial cellulose on banana fibers extracted from peels. *J. Nat. Fibers* 2019; **17**, 1317-28.
- [10] A Nugroho, I Hidayat, AZ Syahrial and S Sufiandi. The effect of bacterial cellulose on the thermo hydro-mechanical treatment of wood veneer. *Key Eng. Mater.* 2021; **880**, 109-15.
- [11] A Nugroho, Triastuti, S Sufiandi and AZ Syahrial. Wood veneer reinforced with bacterial cellulose: Tensile strength and dynamic mechanical analysis. *Int. J. Adv. Sci. Eng. Inform. Tech.* 2022; **12**, 327-33.
- [12] M Bao, X Huang, M Jiang, W Yu and Y Yu. Effect of thermo-hydro-mechanical densification on microstructure and properties of poplar wood (*Populus tomentosa*). *J. Wood Sci.* 2017; **63**, 591-605.
- [13] M Báder and R Németh. Spring-back of wood after longitudinal compression. *IOP Conf. Ser. Earth Environ. Sci.* 2020; **505**, 012018.
- [14] WD Ellis. Wood-polymer composites: Review of processes and properties. *Mol. Cryst. Liq. Cryst.* 2000; **353**, 75-84.
- [15] A Nugroho, Triastuti, S Sufiandi and AZ Syahrial. Energy absorption of densified veneer-aramid hybrid composites subjected to ballistic impact. *Heliyon* 2022; **8**, e10271.
- [16] M Jawaid and HPSA Khalil. Effect of layering pattern on the dynamic mechanical properties and thermal degradation of oil palm-jute fibers reinforced epoxy hybrid composite. *BioResources* 2011; **6**, 2309-22.
- [17] S Wang, F Jiang, X Xu, Y Kuang, K Fu, E Hitz and L Hu. Super-strong, super-stiff macrofibers with aligned, long bacterial cellulose nanofibers. *Adv. Mater.* 2017; **29**, 1702498.
- [18] ASTM Internationa. *Standard test method for tensile properties of polymer matrix composite materials*. ASTM Internationa, Pennsylvania, 2010, p. 99-109.
- [19] M Nouredine. Study of composite-based natural fibers and renewable polymers, using bacteria to ameliorate the fiber/matrix interface. *J. Compos. Mater.* 2019; **53**, 455-61.
- [20] E Meng, CL Chen, CC Liu, SJ Chang, JH Cherng, HH Wang and ST Wu. Bioapplications of bacterial cellulose polymers conjugated with resveratrol for epithelial defect regeneration. *Polymers* 2019; **11**, 1048.
- [21] M Wu, W Chen, J Hu, D Tian, F Shen, Y Zeng, G Yang, Y Zhang and S Deng. Valorizing kitchen waste through bacterial cellulose production towards a more sustainable biorefinery. *Sci. Total Environ.* 2019; **695**, 133898.
- [22] D Zhao, Y Deng, D Han, L Tan, Y Ding, Z Zhou, H Xu and Y Guo. Exploring structural variations of hydrogen-bonding patterns in cellulose during mechanical pulp refining of tobacco stems. *Carbohydr. Polymer*. 2019; **204**, 247-54.
- [23] MI Shams, H Yano and K Endou. Compressive deformation of wood impregnated with low molecular weight phenol formaldehyde (PF) resin I: Effects of pressing pressure and pressure holding. *J. Wood Sci.* 2004; **50**, 337-42.
- [24] AFS Costa, FCG Almeida, GM Vinhas and LA Sarubbo. Production of bacterial cellulose by *Gluconacetobacter hansenii* using corn steep liquor as nutrient sources. *Front. Microbiol.* 2017; **8**, 2027.
- [25] M Nagamadhu, SV Kumar, SR Kumar, R Suraj and GCM Kumar. Dynamic mechanical analysis and thermal stability of neem wood veneer plastic composites. *Mater. Today Proceed.* 2019; **24**, 2265-73.