Physical Properties of Impregnated Ganitri Wood by Furfuryl Alcohol and Nano-SiO$_2$

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Abstract. Ganitri wood (Elaeocarpus sphaericus) is a fast-growing wood that has low dimensional stability and density. This study aims were to analyze the effect of Furfuryl Alcohol (FA) and nano-SiO$_2$ impregnation on the dimensional stability and density of ganitri wood and also examine the characteristics of impregnated ganitri wood. Impregnation used three treatments, including untreated (water), FA, and 0.5% FA-nano-SiO$_2$. The impregnation process was initiated by giving a 0.5 bar vacuum for 60 minutes, followed by applying a pressure of 2.5 bar for 120 minutes. Weight percent gain, leachability, anti-swelling efficiency, water uptake, bulking effect, and density were affected by the treatment. It was due to the coverage of FA and nano-SiO$_2$ on vessels of ganitri wood (SEM analysis). Also, the presence of nano-SiO$_2$ in wood treated (SEM-EDX analysis). FT-IR showed there were no FA bonds with ganitri wood cell wall components or between Nano-SiO$_2$ and ganitri wood. The crystallinity of ganitri wood decreases because FA is amorphous and nano-SiO$_2$ is semi-crystalline. The optimum dimensional stability and density were obtained at FA treatment.

1. Introduction

Nowadays, there are many methods for quality improvements of fast-growing wood as a substitute for high-quality wood uses. Ganitri wood (Elaeocarpus sphaericus) is planted in community forests in West and Central Java [1]. Ganitri wood is classified in the durability class V and strength class III-IV categories. Although it is not considered as commercial timber and not yet widely known, ganitri wood has many benefits. Ganitri wood is commonly used for light construction materials, tools, furniture, plywood, connecting boards, and is also used as raw material for the guitar and piano industry in Bandung, Indonesia [2,3].

Ganitri wood has a high proportion of juvenile wood which causes low physical and mechanical properties [4]. Therefore, wood modification is needed to improve the quality of ganitri wood. One of wood modification is impregnation by using Furfuryl Alcohol (FA) and nano-SiO$_2$. FA is more environmentally friendly because made from organic materials such as agricultural waste, which is renewable and does not cause environmental pollution. Besides, FA is suitable to be applied to wood that has low density so that it can fill in the pits and make the wood denser [5].

In this study, nano particles were added to FA solutions. The nanoparticle-based treatment has several advantages, such as being more effective in coating wood surfaces and high dispersion
stability [5]. Therefore, nano-SiO$_2$ was used in this study, because nano-SiO$_2$ in the amorphous form is not harmful to health and its surface can interact with the biological environment [6].

The impregnation treatment using nano-SiO$_2$ can increase the wood resistance to scratches, UV radiation, fire and moisture. Nano-SiO$_2$ which has a low viscosity can be easier to distribute in the wood so that it can increase the strength and quality of the wood [7]. This research focus on impregnation using FA and nano-SiO$_2$ to increase the dimensional stability and density of ganitri wood. In addition, the characteristics of impregnated ganitri wood will be evaluated using Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy (SEM-EDX), Fourier Transform Infrared Spectroscopy (FT-IR), and X-ray Diffraction Analysis (XRD).

2. Methods

2.1 Materials

The sample used in this research was 6 years old ganitri wood (Elaeocarpus sphaericus) originated from community forests in Sukabumi, West Java. The tree has a 7-meters free branch height and diameters of 28 cm. The chemicals used are furfuryl alcohol (FA), nano-SiO$_2$ (particle diameter 15 ± 5 nm; Anhui Elite Industrial Co., Ltd, China), maleic anhydride, disodium tetraborate, and distilled water. The tools used are chainsaw, table circular saw, analytical balance, calipers, ovens, fans, sonicators, impregnation devices, moisture meter, and aluminum foil. The characterization of the impregnated ganitri wood was carried out with Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX) Hitachi S-3400N Japan, X-Ray Diffraction Analysis (XRD) XRD-7000 Shimadzu Japan, and FT-IR Fourier Transform Infrared Spectroscopy (FT-IR) Perkin Elmer One Pectrum Type.

2.2 Sample Preparation

Ganitri wood is sawn without distinguishing sapwood and heartwood. The sample size was 2 cm x 2 cm x 2 cm [8], which was used to measure the weight percent gain (WPG), leachability (L), anti-swelling efficiency (ASE), water uptake (WU), bulking effect (BE), and density.

2.3 Preparation of Impregnation Solutions

Two types of impregnation solutions were 50 wt% FA-distilled water solution and 50% FA-distilled water solution containing 0.5 wt% nano-SiO$_2$ (mixed by sonication Cole Parmer, the amplitude of 40% for 30 minutes).

2.4 Impregnation Process

The samples were immersed by the impregnation solution in the impregnation devices. The impregnation process was initiated with vacuumed of 0.5 bar for 60 minutes, followed by a pressure of 2.5 bar for 120 minutes. For the polymerization, the samples were wrapped in aluminum foil and kept at room temperature for 12 hours, then put in an oven at 100 °C for another 12 hours. The samples were dried in an oven at 103 ± 2 °C. Samples were measured and weighed to determine WPG, leachability, WU, ASE, BE, and density [9,10].

2.5 Characterization of Impregnated Ganitri Wood

The samples were characterized to determine the presence of a mixture of FA and nano-SiO$_2$ particles in ganitri wood using SEM-EDX (Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy), XRD (X-Ray Diffraction Analysis), and FT-IR (Fourier Transform Infrared Spectroscopy).

2.6 Data Analysis

Data analysis used a completely randomized design with one factor that is the factor of treatment variation (2 levels). The analysis was carried out by using the IBM SPSS Statistics (Statistical Package for Service Solutions) program version 23.0, followed by Duncan's test at $\alpha = 1\%$ [11].
3. Result and Discussion

3.1 Dimensional Stability and Density of Impregnated Ganitri Wood

3.1.1 Weight Percent Gain. FA and nano-SiO$_2$ impregnation treatment significantly affected the WPG, leachability, ASE, WU, BE, and density of ganitri wood as shown in Table 1. The WPG was more than 100% because FA and nano-SiO$_2$ had entered and penetrated all dots. This is evidenced by the increased WPG of ganitri wood after being given FA and nano-SiO$_2$ impregnation treatment, so that the dots to be covered so that water is unable to penetrate the cell walls [9,12]. The WPG for wood can reach 50-200% because it uses conventional methods [13,14].

| Treatmen   | WPG, % | Leaching, % | ASE, % | WU, %   | BE, % | Density, g/cm$^3$ |
|-----------|--------|-------------|--------|---------|-------|------------------|
| Untreated | 0$^a$  | 0$^a$       | 0$^a$  | 90.85 (± 5.25)$^b$ | 4.81 (± 0.69)$^a$ | 0.38 (± 0.02)$^a$ |
| FA        | 146.55 (± 38.93)$^b$ | 69.52 (± 11.03)$^b$ | 123.47 (± 52.03)$^b$ | 38.84 (± 10.65)$^a$ | 6.52 (± 1.85)$^a$ | 0.81 (± 0.07)$^b$ |
| 0.5% FA-  | 150.38 (± 28.16)$^b$ | 89.49 (± 1.20)$^c$ | 228.70 (± 32.50)$^c$ | 24.75 (± 8.59)$^c$ | 13.26 (± 1.03)$^c$ | 0.86 (± 0.11)$^c$ |
| SiO$_2$   |                         |                         |        |         |       |                  |

WPG, weight percent gain; ASE, anti-swelling efficiency; WU, water uptake; BE, bulking effect.

$^a-c$ values followed by the same letters show no real difference based on the Duncan test.

3.1.2 Leachability. The lower leachability means the impregnant solutions in treated wood difficult to leach by water. The results showed that the 0.5% FA-SiO$_2$ impregnated wood obtained the highest leachability. It is presumably because nano-SiO$_2$ was not bound to the cell wall components of the ganitri wood. Nano-SiO$_2$ as a bulking agent only coats the outside of the wood pits so that when the leaching test is carried out, nano-SiO$_2$ will dissolve in water. Not many nano-SiO$_2$ entered the lumens are thought to be due to agglomeration and did not bind to FA that entered the cell cavity and wood pits. The FA treated wood has lower leachability than 0.5% FA-SiO$_2$ impregnated wood allegedly because the FA binds to components of wooden cell walls so that it does not leaching in the water.

3.1.3 Anti-swelling Efficiency. The ASE is directly proportional to the WPG. When the cell wall is penetrated by a polymer, the polymer will fill the entire cell cavity which is usually filled by water. It also causes weight gain due to the polymer that enters the wood. The addition of nano-SiO$_2$ to the wood also causes the ASE to increase because the wood is denser, thereby reducing the hygroscopic nature of the wood. The higher ASE means the lower wood's ability to absorb water and increase the dimensional stability of the wood [15,16].

3.1.4 Water Uptake. The higher the WU, the higher the wood's ability to absorb water. More polymer will enter the cell cavity, making it more difficult for the wood to absorb water [10]. The WU of the untreated wood was very high because it was not treated with chemicals, meaning that no polymer entered the wood so that water could still enter the wood cell walls. In contrast to FA and nano-SiO$_2$ impregnated wood which have a lower WU than untreated wood. This is because the cell cavities and lumens in the FA and nano-SiO$_2$ impregnated wood have been covered by the polymer so that water cannot enter the cell walls.

3.1.5 Bulking Agent. Ganitri wood has a low density, after wood impregnation with FA and nano-SiO$_2$ it can increase in weight, as evidenced by the increased WPG. This indicates that FA and nano-SiO$_2$ can function as bulking agents, causing the BE to increase. The higher the content of the bulking agent that binds to the inner cell walls of the wood, the higher the dimensional stability of the wood, thereby minimizing water absorption [16].

3.1.6 Density. The wood density after impregnation treatment increased significantly. It is caused by FA and nano-SiO$_2$ solutions that can penetrate the cell cavity and lumens of ganitri wood as a whole
so that there is a compaction of the wood structure. The WPG increases so that the density of impregnated wood also increases [17]. The addition of 0.5% nano-SiO$_2$ did not have a significant effect on increasing the density of the 0.5% FA-SiO$_2$ impregnated wood when compared to the FA impregnated wood.

3.2 Characterization of Impregnated Ganitri Wood

3.2.1 SEM-EDX. The morphology of impregnated ganitri wood can be seen using SEM (Figure 1). The pits that initially looked empty (Figure 1a) after being impregnated using FA were filled with FA (shown by a circle in Figure 1b). FA that enters and fills the vessel gives a bulking effect to ganitri wood. FA forms a layer like glass on the surface of the pits indicating the result of polymerization. This is what causes the weight of ganitri wood to increase so that the WPG increases. The presence of FA covering the pits is also able to prevent the entry of water into the pits on the cell wall, causing the WU of FA impregnated ganitri wood to decrease. However, not all pits are covered by FA (shown by arrows in Figure 1b) so that the water still can penetrate to the cell walls, as evidenced by the WU in FA impregnated wood which was still relatively high.

The addition of FA and nano SiO$_2$ causes weight gain of ganitri wood which is also indicated by the increased WPG. This is evidenced by the existence of nano-SiO$_2$ that fills the cell walls of the ganitri wood (Figure 1d). Figure 1d shows that the open pits of the Ganitri wood vessel are filled by 0.5% FA-SiO$_2$. Nano-SiO$_2$ appears to clump in the cell cavity indicating that some nano-SiO$_2$ is not polymerized to form bonds among the nano-SiO$_2$, as shown in the circle in Figure 1d. Nano-SiO$_2$ fills the vessel cavity and covers the lumens so that the water cannot pass through the wood cavity and enter it. This proves that nano-SiO$_2$ causes a bulking effect on 0.5% FA-SiO$_2$ impregnated ganitri wood so that the BE increases. Untreated and FA treated ganitri wood was proven that there was no nano-SiO$_2$ content in the wood sample, meanwhile 0.5% FA-SiO$_2$ contains 0.13 wt.% of silicon. This is evidenced by the presence of nano-SiO$_2$ in 0.5% FA-SiO$_2$ wood samples that can enter the ganitri wood through FA as a solvent. The nano-SiO$_2$ has shown in Figures 1c and 1d causes an increase in WPG, leachability, ASE, BE, density, and a decrease in WU.

![Figure 1. Morphology of impregnated ganitri wood in the tangential section (a) Untreated wood, (b) FA treated wood, (c) 0.5% FA-SiO$_2$ treated wood 100x, and (d) 0.5% FA-SiO$_2$ treated wood 550x)](image-url)
3.2.2 FT-IR. Figure 2 shows the FT-IR spectrum of untreated and treated ganitri wood. The absorption band at 3386.03 cm\(^{-1}\) (-OH stretching) from the hydroxyl group of wood cellulose ganitri. The -OH group of nano-SiO\(_2\) is shown at 3410.67 cm\(^{-1}\). The -OH group was detected in 3000-3750 cm\(^{-1}\) that indicates the presence of water molecules in the wood sample. The C-H functional group of ganitri wood cellulose appears at a frequency of 2915.28 cm\(^{-1}\) [18,19,20]. The C-H group appears in 2800-3000 cm\(^{-1}\). The wave frequency was 1735.34 cm\(^{-1}\), indicating the presence of C=O hemicellulose. The peak of the C=O wave experienced a shift to 1723.48 cm\(^{-1}\) after impregnating FA and 1734.85 cm\(^{-1}\) after impregnating FA-SiO\(_2\). The C=O groups appear at 1742.53 cm\(^{-1}\), 1723.48 cm\(^{-1}\), and 1734, 85 cm\(^{-1}\). The shift in the peak of the C=O wave is formed due to the surface of the FA furan polymer hydrolytic ring and the vibration of the furan ring frame that binds to the component of the wood cell wall [9,21,22].

![Figure 2. FT-IR spectrum for nano-SiO\(_2\) and ganitri wood with various treatments](image)

Asymmetric Si-O-Si groups appeared at 1107.48 cm\(^{-1}\). At a wave frequency of 811.95 cm\(^{-1}\), a Si-O-(H-H\(_2\)O) group was detected. Vibration stretching and asymmetric Si-O-Si bending occurred at 467.07 cm\(^{-1}\). In 1035.06 cm\(^{-1}\), a C-O group originating from FA appears. The addition of FA causes the emergence of new functional groups such as the furan ring at 1027.67 cm\(^{-1}\) and 778.62 cm\(^{-1}\) [13,22,23]. The discovery of the Si-O-Si group indicated the presence of silica content in FA-SiO\(_2\) impregnated ganitri wood, waves 1050-1115 cm\(^{-1}\) were Si-O-Si vibrations [24].

3.2.3 XRD. Figure 3 shows the XRD spectra of untreated and treated ganitri wood. The three highest peaks at 2\(\theta\) = 22.51°, 22.53°, and 21.83° with the crystal fields I\(_{002}\). The presence of silica was detected at 2\(\theta\) 21.83° which is close to the crystal fields I\(_{002}\). There are characteristics of I\(_{0}\) cellulose shown at the peak angle of 2\(\theta\) = 15.08°. The characteristic amorphous structure is indicated by 2\(\theta\) = 18°. The cellulose peaks are shown at 2\(\theta\) = 22-23°, which is a natural characteristic of cellulose I. The peaks of cellulose I\(_{0}\) and I\(_{0}\) are at 2\(\theta\) = 14-16°. Based on JCPDS data, the peaks shown by the I\(_{002}\) and I\(_{010}\) fields indicate the diffractogram type of cellulose [25,26]. There is also a shift in 2\(\theta\) from 15.08° to 14.67° that indicates a decrease in the intensity of FA impregnated ganitri wood. This is due to the amorphous FA covers the crystalline cellulose area [9]. There is also a peak of 2\(\theta\) 19.82° which is thought to arise as a result of silica activity in the ganitri wood.

Additional information regarding XRD test data can be seen in Table 2. There was a decrease in the degree of crystallinity in the FA and 0.5% FA-SiO\(_2\) impregnated ganitri wood samples [9]. In FA impregnated ganitri wood samples, the presence of this amorphous FA was able to cover the crystalline area, causing the crystalline area in the ganitri wood to decrease. Therefore, the crystallinity of FA impregnated wood decreases. Nano-SiO\(_2\) is semi-crystalline, causing the crystallinity degree of FA-SiO\(_2\) impregnated ganitri wood to decrease. The properties of nano-SiO\(_2\) are thought to be caused by the ultrasonication treatment [27].
Figure 3. XRD spectra of ganitri wood with various treatments

| Treatment         | Degree of Crystallinity, % |
|-------------------|-----------------------------|
| Untreated         | 31.31%                      |
| FA                | 24.66%                      |
| 0.5% FA-SiO<sub>2</sub> | 21.09%                    |

The XRD analysis results indicate that there is an effect of the addition of FA and nano-SiO<sub>2</sub> on the WPG, leachability, BE, WU, ASE, and density. This effect is supported by the presence of nano-SiO<sub>2</sub> peaks which correspond to the diffraction field according to the JCPDS data.

4. Conclusion
FA and nano-SiO<sub>2</sub> impregnation have a significant effect on WPG, leachability, ASE, WU, BE, and density of ganitri wood. The increase of WPG, BE, ASE, leachability, and density indicates that FA and nano-SiO<sub>2</sub> can fill all the lumen cells so that causing the WU to decrease. The SEM analysis results of impregnated ganitri wood showed that the pits were covered by FA and nano-SiO<sub>2</sub> and also strengthened by the results of EDX analysis which stated that there was a silica content in the pits. The degree of crystallinity of untreated, FA, and 0.5% FA-SiO<sub>2</sub> ganitri wood was decreased due to FA is amorphous and nano-SiO<sub>2</sub> is semi-crystalline characteristics. FTIR analysis showed that there was no chemical bonding of both FA and nano-SiO<sub>2</sub> on ganitri wood. Ganitri wood with the best dimensional stability and density was obtained in the FA treatment. The addition of FA and nano-SiO<sub>2</sub> with a concentration of 0.5% was not sufficient to significantly increase dimensional stability and density.

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References
[1] Rohandi A and Gunawan 2014 Population distribution and plant potential of Ganitri (Elaeocarpus ganitrus Roxb) in Central Java J. Ilmu Kehutanan 8 (1): 25-33
[2] Heyne K 1987 Tanaman Berguna Indonesia Jilid II (Jakarta: Forestry Research and Development Agency, Ministry of Forestry)
[3] Rachman E 2012 Study of Potency and Utilization of Ganitri (Elaeocarpus spp.) Mitra Hutan Tanaman 7 (2): 39-50

[4] Rahayu IS, Laksono GD, Darmawan W, Maddu A and Prihatini E 2021 Demarcation area between juvenile and mature wood in Elaeocarpus angustifolius Biodiversitas 22 (5): 2583-2590

[5] Teng TJ, Arip MNM, Sudesk K, Nemoikina A, Jalaludin Z, Ng E and Lee H 2018 Conventional technology and nanotechnology in wood preservation: A review BioRes. 13 (4): 9220-9252

[6] Ounoughene G, Chivas JC, Longuet C, Le Bihan O, Cuesta L and Le Coq L 2019 Evaluation of nano-SiO₂ emission in polydimethylsiloxane composite during incineration J. of Hazard. Materials 371: 415-422

[7] Fufa SM and Hovde PJ 2010 Nano-based modification of wood and their environmental impact: review World Conference on Timber Engineering

[8] [BS-373] British Standard 1957 Methods of Testing Small Clear Specimens of Timber

[9] Dong Y, Yan Y, Zhang S and Li J 2014 Wood/polymer nanocomposites prepared by impregnation with furfuryl alcohol and nano-SiO₂ BioRes. 9 (4): 6028-6040

[10] Rahayu IS, Darmawan W, Zaini LH and Prihatini E 2019 Characteristic of fast-growing wood impregnated with nanoparticles J. For. Res. 31 (2): 1-9

[11] Sastrosupardi A 2000 Rancangan Percobaan Praktis Bidang Pertanian (Yogyakarta: Kanisius)

[12] Li W, Wang H, Ren D, Yu YS and Yu Y 2014 Wood modification with furfuryl alcohol catalyzed by a new composite acidic catalyst Wood Sci. Technol. 49 (4): 1-12

[13] Marques PAAP, Trindade T and Neto CP 2005 Titanium dioxide/ cellulose nanocomposites prepared by a controlled hydrolysis method Composites Science and Technology 66 (7): 1038-1044

[14] Croitoru C, Lunguleasa A and Patachia S 2015 New method of wood impregnation with inorganic compounds using ethyl methylimidazolium chloride as carrier Journal of Wood Chemistry and Technology 35 (2): 113-128

[15] Pandey KK, Jayashree V and Nagaveni HC 2009 Study of dimensional stability, decay resistance, and light stability of phenylisothiocyanate modified rubberwood Bioresources 4 (1): 257-267

[16] Hill CAS 2006 Wood Modification: Chemical, Thermal, and Other Processes (West Sussex: John Wiley and Sons Ltd.)

[17] Hadi YS, Rahayu IS and Danu S 2013 Physical and mechanical properties of methyl methacrylate impregnated jabon wood J. Indian Acad. Wood Sci. 10 (2): 77-80

[18] Dachriyanus 2004 Analisis Struktur Senyawa Organik Secara Spektroskopi (Padang: Information and Communication Technology Development Institute Andalas University)

[19] Gian AA, Farid M and Ardhyananta H 2017 Isolasi selulosa dari serat tandan kosong kelapa sawit untuk nano filler komposit absbrosi suara: analisis FTIR Jurnal Teknik ITS 6 (20): 228-231

[20] Ramalla I, Gupta RK and Bansal K 2015 Effect on superhydrophobic surfaces on electrical porcelain insulator, improved technique at polluted areas for longer life and reliability International Journal of Engineering and Technology 4 (4): 509-519

[21] Kinney TJ, Masiello CA, Dugan B, Hickaday WC, Dean MR, Zygourakis K and Barnes RT 2012 Hydrologic properties of biocars produced at different temperatures Biomass and Bioenergy 41: 32-43

[22] Pangau JR, Sangian HF and Lumi BM 2017 Characterization of cellulose material by microwave pretreatment irradiation against cempaka wasian wood powder (Elmerillia ovalis) in North Sulawesi Jurnal MIPA Unstrat Online 6 (1): 53-58

[23] Edwards ER, Oishi SS and Botelho EC 2018 Analysis of chemical polymerization between functionalized MWCNT and poly (furfuryl alcohol) composite Polimeros 28 (1): 15-22

[24] Patil R, Dongre R and Meshrum J 2014 Preparation of silica powder from rice husk IOSR Journal of Applied Chemistry 26-29
[25] Troedec ML, Sedan D, Peyratout C, Bonnet JP and Agnes S 2008 Influence of various chemical treatments on the composition and structure of hemp fibers *Compos. Part A* **39** (3): 514–522

[26] Cheng G, Varanasi P, Li C, Liu H, Melnichenko YB, Simmons BA, Kent MS and Singh S 2011 Transition of cellulose crystalline structure and surface morphology of biomass as a function of ionic liquid pretreatment and its relation to enzymatic hydrolysis *Biomacromolecules* **12** (4): 933–941

[27] Rahayu IS, Zaini LH, Nandika D, Darmawan W and Prihatini E 2020 Physical properties of impregnated sengon wood by mono ethylene glycol and nano-SiO$_2$ from betung bamboo stick *Materials Science and Engineering* **935**: 1-14