The Effect of Alkali Treatment on the Surface and Mechanical Properties of Fibrovascular Bundles of *Salacca sumatrana* Becc. Fronds

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Fibrovascular bundles (FVB) are a cell tissue in monocot plants composed of fibers, xylem, phloem, and axial parenchyma, binding to form bundles. FVB has the potential to be used as a raw material for composite boards. However, it has several weaknesses, including low strength and surface properties that do not support gluing. This study therefore aimed to investigate the effect of a combined NaOH + Na_2SO_3 treatment on the physical, chemical, and mechanical properties changes in *S. sumatrana* Becc. fronds. After separation from the fronds, the fibrovascular bundles were separately immersed in several conditions of NaOH + Na_2SO_3, for 30 min and 60 min, then washed and dried. Subsequently, the tissues were evaluated using scanning electron microscopy, X-ray diffraction, Fourier-transform infrared spectroscopy, and tensile strength tests. The pits and deposits of the fibrovascular bundles completely collapsed, degraded, and swelled after treatment with 1 M NaOH + 2% Na_2SO_3. The treatment resulted in the eventual elimination of hemicelluloses and lignins. Separation of the elementary fiber on the fibrovascular bundles occurred at higher concentration treatments. In addition, the strength of the tissue improved after 60 min of immersion in a mixture of 1% NaOH and 0.2% Na_2SO_3. Based on these results, treatment with a combination of 1% NaOH + 0.2% Na_2SO_3 was concluded to change the chemical and physical properties as well as improve the mechanical properties of the fibrovascular bundles.

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INTRODUCTION

Due to the economic benefits and increasing awareness of environmentally and ecofriendly products, natural fibers, including fibrovascular bundles and non wood based fiber, are known to serve as alternative a substitute for wood as a raw material for composite board, which has been manufactured using particles or fibers from wood. Natural fibers have numerous benefits in industrial applications, including having a low weight, low cost, being nontoxic, a renewable natural resource, and biodegradable, as well

as having a high specific tensile strength and stiffness (Pickering *et al.* 2016).

Fibrovascular bundles are one of the natural fibers produced in the stem or trunk, frond, and leaf sheath of palm trees (Zhai *et al.* 2013; Elanchezhian *et al.* 2018). Anatomically, the fibrovascular bundles of Salacca fronds not only contain a sclerenchyma fiber tissue that functions as mechanical reinforcement, but they also contain vascular tissue that reduces the strength of fibrovascular bundles (Hakim *et al.* 2019). The Salak Sidempuan (*Salacca sumatrana* Becc.) is a palm originating from Sumatra Island, Indonesia. This plant produces not only edible fruit, but also the sparsely studied fibrovascular bundles (FVB) (Hakim *et al.* 2021a,b). However, natural fibers have numerous disadvantages as a composite board raw material, including a lower dimension stability due to greater water absorption, instability at high temperatures, being easily degraded by chemicals, flammability, and poor cohesion between fibers and the matrices/adhesives (Mukesh and Godara 2019; Sood and Dwivedi 2018).

These weaknesses have been studied by several previous researchers with the aim to chemically modify natural fibers. A study by Ganapaty *et al.* (2019) showed that chemical modification is an alternative that is worthy of being considered due to the capacity to improve the interface bond in the fibers and activate the hydroxyl groups to cause stronger interlock bonds between the fibers. The alkaline chemical modification of natural fibers has been extensively used by previous researchers (Shanmugasundaram *et al.* 2018; Vijay *et al.* 2019).

The fibrovascular bundles of salacca have been investigated by several researchers, including studies using alkaline chemical modification. Darmanto *et al.* (2017) used alkaline modification and steaming to increase the tensile strength by 275 MPa in a single FVB frond of *Salacca zalacca*. Meanwhile, Kurniawan *et al.* (2017) successfully increased the tensile strength of FVB fronds (*S. zalacca*) to 554.8 MPa, using a 6 h immersion treatment, at a pressure of 2 bar and a varying degree of steaming. Darmanto *et al.* (2017) also continued the experiment with the steaming and steam explosion treatments of FVB and obtained a 225.7 MPa increase in tensile strength. However, these studies utilized a lot of energy, *i.e.*, pressure, steaming, explosion, and high concentration, and were therefore considered expensive and ineffective in increasing the strength of FVB fronds. This research can solve previous research problems based on a more effective use of energy, namely by using alkaline modification at low concentrations, without pressure, and using room temperature. Modified conditions without using pressure with low concentrations and at room temperature will save energy and are more eco-friendly. Alkali treatment including the use of NaOH+Na_2SO_3 at low concentrations, room temperature and without pressure will only be able to swell the cellulose and dissolve some of the wax and dirt on the surface of the lignocellulosic material (Oudaini *et al.* 2011). It is hoped that this treatment will not reach the dissolution, mercerization, and degradation modification stages which can damage the FVB of salacca frond.

Based on this background, there is currently very limited research on the chemical modification of FVB from *S. sumatrana* fronds, using alkaline treatments with low concentration, without pressure and using room temperature. The focus of the chemical modification of FVB is to enhance the quality of the raw material, alter the surface, and improve the mechanical properties. This study therefore aimed to investigate the effect of a treatment of a combination of NaOH + Na_2SO_3 on the change in physical, chemical, and mechanical properties of *S. sumatrana* Becc. FVB fronds.

EXPERIMENTAL

Materials

The fibrovascular bundles from *S. sumatrana* fronds were supplied from an agroforestry system cultivated in the District of Tapanuli Selatan, Province of Sumatera Utara, Indonesia. The fronds were harvested at approximately 15 to 20 years old. The sodium hydroxide anhydrate (96%) and sodium sulfite anhydrate (98%) used for the alkali treatment of the FVB were obtained from Merck (Darmstadt, Germany). The ALF medium-viscosity epoxy adhesives (ALF Epoxy adhesive, P.T Alfaglos, Semarang, Indonesia) were used during the mounting of the FVB on the paper, for analysis of the mechanical properties.

The FVBs were obtained through the separation process from the frond. For this process, the primary fronds were separated from the leaf, cut into 100 cm pieces, and soaked in water for 4 weeks, to soften the frond for easier separation of the FVB from the remaining tissue. Subsequently, the fibrovascular bundles were separated from the frond using an iron comb.

Alkali Treatment

The fibrovascular bundles were treated with eight different aqueous alkali solutions at room condition (as shown in Table 1). Subsequently, the fibrovascular bundles were removed from the solution, rinsed with cold water (20 °C ± 3 °C), and air dried. Finally, the fibrovascular bundles were oven-dried for 2 h, at a temperature of 75 °C.

Table 1. Combination Alkali Treatment of Fibrovascular Bundles

Treatment	NaOH Concentration (%)	Na_2SO_3 Concentration (%)	Time (min)
A (untreated)	0	0	30
B (untreated)	0	0	60
C	1	0	30
D	1	0	60
E	1	0.2	30
F	1	0.2	60
G	1	0.4	30
H	1	0.4	60

Evaluation of the Physical, Chemical and Mechanical Properties

The physical characteristics that were analyzed after treatment included the percentage weight loss (% WPL). The % WPL was evaluated according to Eq. 1,

$$\% \text{ WPL} = \frac{W_1 - W_2}{W_1} \times 100\% \quad (1)$$

where W_1 and W_2 represent the weight before and after treatment, respectively. The diameter and density of the FVB were evaluated based on the method described by Munawar *et al.* (2007). In addition, the chemical characteristics analyzed after treatment were as follows: the α-cellulose and hemicellulose contents were determined by ASTM standard D1103 (2013); and the Klason lignin and ash contents were determined by ASTM standard D1106-96 (2013) and ASTM standard D1102 (2001), respectively. In addition, the mechanical properties of modified the FVB were evaluated based on ASTM standard D3379 (1989), using a universal testing machine (Tensilon RTF 1350, Tokyo, Japan) with

a 1 mm/min crosshead speed.

Fourier-transform Infrared (FTIR) Spectroscopy

The FTIR spectroscopy was performed at room temperature (approximately 25 °C), using a FTIR-4200 spectrophotometer (JASCO, Tokyo, Japan), to determine the assignment of absorbance bands to specific functional groups. Each spectrum used the KBr disc method and a resolution of 12 cm^{-1}.

X-Ray Diffraction (XRD)

The preparation sample for XRD analysis was to prepare the modified FVB into the milling disc. The surface pressure was far below that which will cause the crystal to fracture. The sample mass was then placed into a standard holder in the diffractometer stage. The crystallinity index was determined by considering the regions of crystalline and amorphous cellulose. Crystalline cellulose was determined at a 2Θ peak in the reflection plane position (002), with a maximum intensity between 22.5° and 23°, while amorphous cellulose (am) is located between 18°and 19°, at the minimum intensity position (Sghaier *et al.* 2012). The intensity value was used to calculate the modified degree of crystallinity of the FVB. Furthermore, the diffraction spectra were obtained at room temperature (20 to 22 °C) from radiation generated by a Maximax X-ray Diffractometer-7000 (Shimadzu, Kyoto, Japan). The measurements were carried out at 40 kV and 20 mA with a detector placed on the range of 2 theta (2Θ) from 5° to 80°, at a scan speed of 2 °/min. Subsequently, the percentage crystallinity index (%CI) of cellulose was calculated using the formula provided by Segal *et al.* (1959), as shown in Eq. 2,

$$\%\mathrm{CI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \quad (2)$$

where I_{002} is the maximal peak intensity at a 2Θ angle of approximately 22° to 23° and I_{am} is the minimum peak intensity (amorphous region) at a 2Θ angle of approximately 18° to 19°.

Thermogravimetry Analysis (TGA)

The thermogravimetric analysis was conducted using an Ekstar SIII-Type 7300 (Hitachi, Tokyo, Japan), to determine the rate of the change in mass as well as the thermal stability of the modified fibrovascular bundles, with respect to temperature. For this analysis, samples with an approximately 10 mg mass were heated in an alumina crucible from room temperature to 600 °C, at a heating rate of 10 °C/min, while the apparatus was continually flushed with nitrogen, at a 30 mL/min flow rate.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) was used to evaluate the surface morphologies of the modified fibrovascular bundles. Samples were cut into 0.5 cm lengths and dried at ± 80 °C for 1 hour. The samples were coated with Pt–Pd to prevent specimen charging under the electron beam, and then imaged at an accelerating voltage of 1.5 kV. Fibrovascular bundle fibers were examined using a SEM-JEOL-JSM-6390 (JEOL Ltd., Tokyo, Japan).

Statistical Analysis

Factorial completely randomized design was used to analyze the influence of modification treatment on changes in chemical content of fibrovascular bundles. *R-Studio* software version 4.0.0 was performed to statistical analysis.

RESULT AND DISCUSSION

Chemical Properties of the Modified Fibrovascular Bundles (FVB)

Generally, the percentage weight loss increased from treatment A (water immersion for 30 min) to treatment H (1% NaOH + 0.4 % Na_2SO_3 immersion for 60 min), with values of 2.7% and 17.2%, respectively (as shown in Table 2).

Table 2. Weight Loss and Chemical Content of Modified Fibrovascular Bundles (FVB) from *S. Sumatrana* Fronds

Treatments	% Weight Loss	α-cellulose	Hemicellulose	Lignin	Ash
A	2.7^{a}	44.3^{e}	31.7^{c}	33.2^{a}	0.88^{a}
B	3.0^{a}	44.7^{e}	31.5^{c}	33.1^{a}	0.86^{a}
C	5.2^{b}	46.1^{d}	32.8^{a}	32.1^{b}	0.81^{ab}
D	5.3^{b}	48.5^{c}	32.3^{b}	31.4$_{b}$	0.81^{ab}
E	9.1^{c}	54.4^{a}	28.3^{d}	27.9^{c}	0.78^{bc}
F	11.5^{d}	51.2^{b}	24.7^{e}	24.9^{e}	0.61^{d}
G	13.2^{e}	41.1^{f}	21.9^{f}	25.0^{e}	0.58^{e}
H	17.2^{f}	39.7^{h}	20.5^{f}	20.8^{d}	0.56^{e}

Note: numbers followed by different letters are significantly different (a *p*-value less than or equal to 0.05)

The α-cellulose content of the FVB also increased from 44.3% (treatment A) to 54.4% (treatment E), but then slightly decreased from treatments F, G, and H (51.2%, 41.1%, and 39.7%, respectively). The increase in the α-cellulose percentage from treatments A to E does not mean there was an actual increase in the cellulose content, but rather, implies the content of the other components, *i.e.*, the hemicellulose and lignins, decreased. However, the decrease in the α-cellulose percentage during treatments F, G, and H occurred because the cellulose component actually dissolved. This decrease was due to the NaOH + Na_2SO_3 concentration, which has the ability to degrade amorphous cellulose at high concentrations (Wang *et al.* 2003). According to previous studies, subjecting FVB from *S. zalacca* fronds to a 3% NaOH and steaming treatment, led to an increase in the α-cellulose content of approximately 54.5% (Darmanto *et al.* 2017), while a 5% NaOH treatment led to a 54.5% increase in oil palm empty fruit bunch (Medina *et al.* 2015). In addition, a 15% NaOH treatment led to a 63.4% increase in the α-cellulose content of areca palm (*Dypsis lutescens*) (Shanmugasundaram *et al.* 2018), while a 5% NaOH treatment led to a 45% increase in *Tridax procumbens* (Vijay *et al.* 2019). Furthermore, a 5% NaOH treatment yielded a 46.5% increase in the α-cellulose content of oil palm mesocarp fiber (Birnin-Yauri *et al.* 2016) and a 70.4% increase in banyan root (*Ficus benghalensis*) fiber (Ganapathy *et al.* 2019).

The hemicellulose content of the modified FVB from *S. sumatrana* fronds was found to decrease as the immersion time and Na_2SO_3 concentration increased, from treatment A (31.7%) to H (20.5%). Hemicellulose is one of the easiest lignocellulose materials to degrade *via* alkali treatment, because the structure contains more amorphous

regions compared to crystalline regions (Cai *et al.* 2015). This study was comparable with the report by Darmanto *et al.* (2017), where a 74.9% hemicellulose content was reported after a 3% alkali treatment. Other studies showed a 5% NaOH treatment on Borassus fiber yielded a 3.02% hemicellulose content (Boopathi *et al.* 2012), while a 5% NaOH treatment on banyan roots led to a 10.7% reduction in the hemicellulose content (Ganapathy *et al.* 2019). Furthermore, a 15% NaOH concentration was reported to lead to the removal of hemicellulose in natural fiber, up to 100% (Shanmugasundaram *et al.* 2018).

The lignin content also followed this reduction pattern after alkali treatment, from treatment A (33.2%) to H (18.7%). The combination of the NaOH and Na_2SO_3 treatment on lignocellulose material, including natural fiber, is bound to cause a reduction in the lignin content. This pattern was relatively the same when compared to a previous study on the alkali treatment of natural fiber (Vijay *et al.* 2019).

However, this combination had little effect on the ash content values. Generally, the modification of FVB from *S. sumatrana* fronds led to a decrease in the inorganic compound contents, ranging from treatment A (0.86%) to treatment H (0.56%). Shanmugasundaram *et al.* (2018) reported a drastic reduction in the ash content after a 5% NaOH treatment and its complete removal after a 10% and 15% NaOH treatment.

The effectiveness of the NaOH + Na_2SO_3 treatment in decreasing the chemical contents was compared to previous studies. In this study, the percentage increase in the α-cellulose content after the NaOH + Na_2SO_3 treatment was higher compared to previous studies. Furthermore, the NaOH + Na_2SO_3 treatment was more effective in maintaining the α-cellulose, hemicellulose, and lignin contents, compared to previous studies using *S. zalacca* as a raw material with a higher concentration and high energy steam treatment (Darmanto *et al.* 2017).

Statistically, treatments A and B had no significant effect as treatments C and D for all parameters (% weight loss, alfa-cellulose, hemicellulose, lignin and ash content). Treatments A, B, C, and D only used water and NaOH immersion and did not involve any modification of Na_2SO_3. However, when Na_2SO_3 was added, there was a significant difference between treatments A, B, C, D and treatments E, F, G, and H. In other words, the addition of Na_2SO_3 to NaOH treatment had a positive effect on changes in chemical content.

Fourier-transform Infrared (FTIR) Spectroscopy)

Non-cellulose chemical components, including hemicellulose, lignins, wax, and pectin, are reduced by alkali treatment (Mohan and Kanny 2012). The functional groups formed by the modification process are detectable with Fourier-transform infrared (FTIR) spectroscopy at wavelengths between 4000 and 400 cm^{-1}. Figure 1 shows several functional groups observed in the FTIR spectra of the modified FVB from *S. sumatrana* fronds.

The β-glycosidic links were detected in all the treatment samples at a wavelength of 895.0 cm^{-1}. This indicated there were bonds between the glucose monomers, forming polymers of cellulose, hemicellulose, and lignins, in the modified natural fibers (Mohan and Kanny 2012). Cellulose components were also detected in the stretching of the hydrogen-OH bonds at the peak of the 2380 cm^{-1} wavelength (Ganapathy *et al.* 2019). The acetyl groups present in the lignins and hemicelluloses were detected at a wavelength of approximately 1118.7 to 1249.9 cm^{-1}, with a reducing intensity from treatment A to H. This indicated a reduction in the part of lignin and hemicellulose contents occurred during the modification process (Shanmugasundaram *et al.* 2018). Carboxylate or ester groups on the lignins and hemicelluloses were also detected at wavelengths between 1597.1 and 1689.6

cm^{-1}, with a decreasing intensity from treatment A to H, which indicated a reduction in the part of lignin component during alkali treatment.

According to these findings, it can be concluded that the NaOH+Na_2SO_3 treatment caused the removal of the binding material such as hemicellulose, lignin, and pectin from the fibrovascular bundle of Salacca frond. The removal of the binding material transformed the surface of the fibrovascular bundle into fibrillated form, with cracks and a rough character.

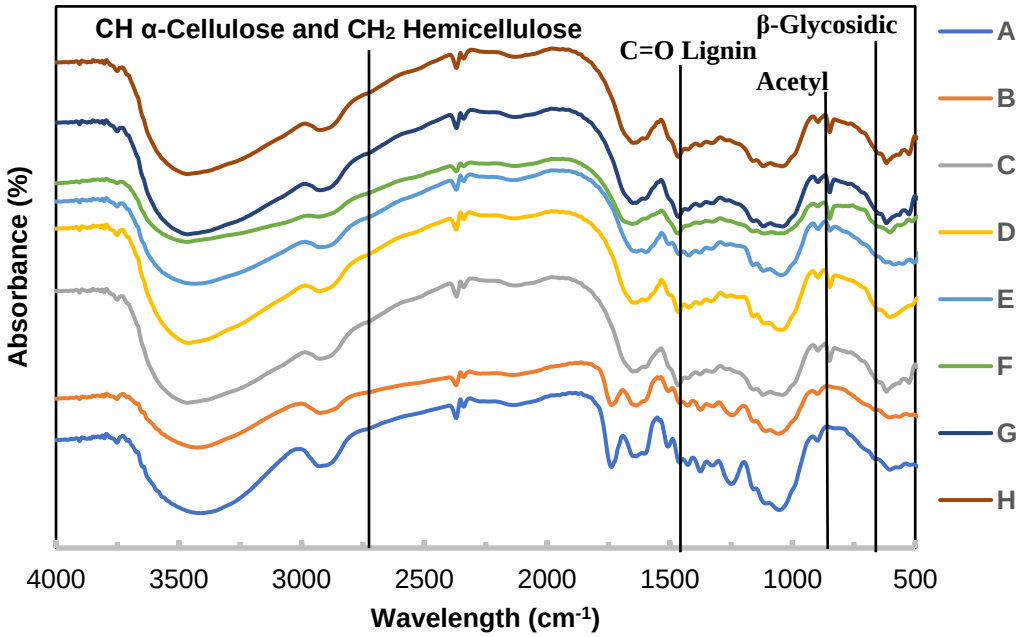

Fig. 1. FTIR spectra of modified FVB (Note: A. Untreated for 30 min; B. untreated for 60 min; C. 1% NaOH for 30 min; D. 1% NaOH for 60 min; E. 1% NaOH + 0.2% Na_2SO_3 for 30 min; F. 1% NaOH + 0.2% Na_2SO_3 for 60 min; G. 1% NaOH + 0.4% Na_2SO_3 for 30 min; and H. 1% NaOH + 0.4% Na_2SO_3 for 60 min)

Physical Properties and Surface Morphologies of the Modified Fibrovascular Bundles (FVB)

The diameter of the FVB after modification was found to decrease as the immersion time and concentration of NaOH or NaOH + Na_2SO_3 combination increased, from treatment A (45.5 µm) to treatment H (20.5 µm) (as shown in Fig. 2).

This reduction caused by NaOH and Na_2SO_3 was attributed to the reduction of several chemistry compounds, *i.e.*, lignin, wax, and oil, on the surface of the FVB. However, the FVB subjected to the water treatment did not show any considerable changes, had a smooth surface, and retained a lot of surface dirt, *i.e.*, wax, and silica. This shows that the hemicellulose, lignins, and wax components covering the surface of the fibrovascular bundles remained intact (Kundu *et al.* 2018). However, after the NaOH + Na_2SO_3 treatment, changes were visible along the surface. The FVB were degraded, and the surface became rougher after the combination treatment.

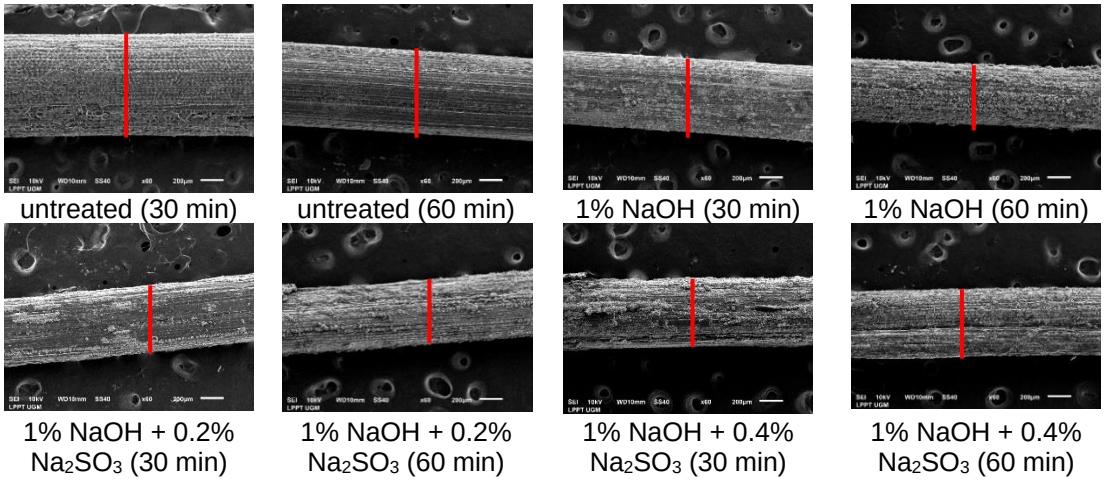

Fig. 2. SEM images of the modified FVB. The diameters are indicated by the red bar.

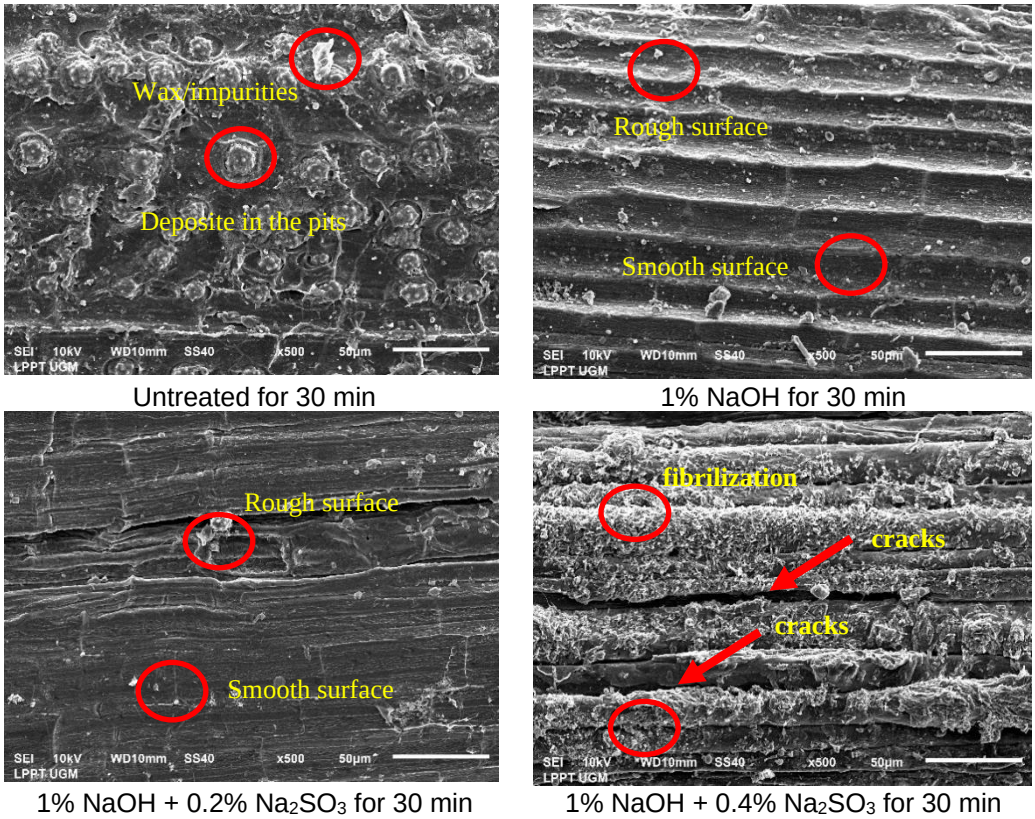

Fig. 3. Surface morphology of the modified FVB from *S. sumatrana* fronds

According to Fig. 3, the deposited materials and impurities (wax/silica) on the pits and surface of the FVB were retained after the water treatment. The NaOH treatment caused the deposited materials to degrade and disappear from the surface. In comparison to the 1% NaOH + 0.2% Na_2SO_3 treatment, the 1% NaOH + 0.4% Na_2SO_3 treatment with a 30 min immersion time produced seemingly interesting results because there were more smooth fibers on the surface of the FVB. These smooth fibers were assumed to be microfibrils transformed into elementary fibers, after undergoing fibrillation and

weakening (Cai *et al.* 2015). The occurrence of fibrillation and damage to the FVB are bound to cause a reduction in the mechanical properties. In addition, cracks were also observed after the alkaline treatments involving the addition of Na_2SO_3. These cracks have an effect of reducing the tensile strength of the FVB. However, in cases where the FVB was used as a raw material for composite board and had a sufficiently clear surface free of deposits and impurities, these cracks were bound to yield a positive effect on the bonding between the fibers and the matrix/adhesive (Rosa *et al.* 2010).

In this study, the density decreased from 0.45 g/cm^3 (treatment A) to 0.37 g/cm^3 (treatment H) (Fig. 4). This reduction was attributed to the degradation of the chemistry compounds during modification, due to the reduction in weight of the FVB. This degradation occurred on the surface, making the non-vascular area narrow; however, the vascular area is predicted to remain intact. Cai *et al.* (2015) reported the alkaline treatment of natural abaca fibers causes the cell wall to shrink, as well as the lumen collapsing.

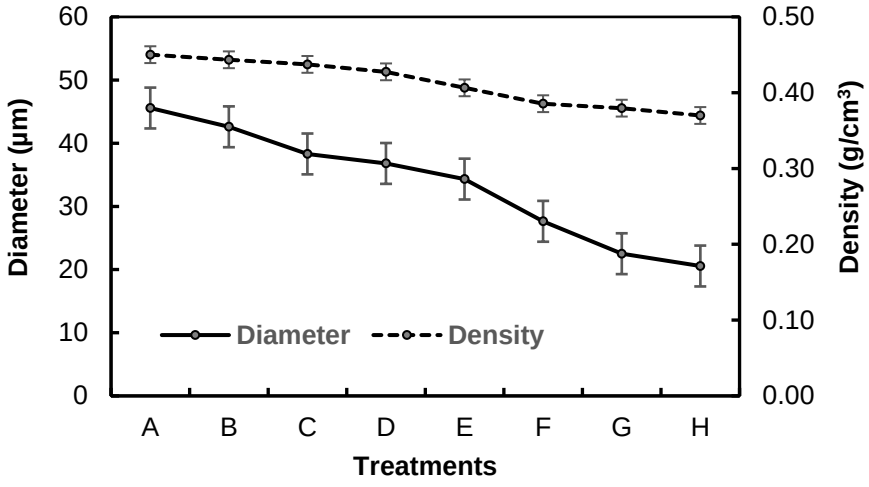

Fig. 4. The diameter and density of the modified fibrovascular bundles (Note: A. Untreated for 30 min; B. untreated for 60 min; C. 1% NaOH for 30 min; D. 1% NaOH for 60 min; E. 1% NaOH + 0.2% Na_2SO_3 for 30 min; F. 1% NaOH + 0.2% Na_2SO_3 for 60 min; G. 1% NaOH + 0.4% Na_2SO_3 for 30 min; and H. 1% NaOH + 0.4% Na_2SO_3 for 60 min; in addition, the vertical bars indicate the standard deviation)

Mechanical Properties of the Modified Fibrovascular Bundles (FVB)

Table 3 shows the mechanical properties and crystallinity index of cellulose. Based on the table, the highest maximum load value of the modified FVB was 127.8 N after a 30 min immersion in water, while the lowest maximum load value was 55.6 N after a 60 min immersion in 1% NaOH + 0.4% Na_2SO_3. The maximum load of the modified FVB did not follow the same trend as the tensile strength. The highest tensile strength of the modified FVB was 46.7 MPa after a 60 min immersion in 1% NaOH+0.2% Na_2SO_3, while the lowest tensile strength was 216.8 MPa after a 60 min immersion in 1% NaOH + 0.4% Na_2SO_3. Interestingly, the tensile strength increased from the water treatment to the 1% NaOH + 0.2% Na_2SO_3 treatment for 60 min, but it decreased after treatment with 1% NaOH + 0.4% Na_2SO_3 treatment for 30 min and 60 min. Conversely, an increase in the tensile strength was not accompanied by an increase in the maximum load. This phenomenon was explainable because the increase in the tensile strength of the modified FVB was due to

reduction in the transversal area of the FVB. Furthermore, this reduction was due to the surface degradation during the modification treatment.

Darmanto *et al.* (2017) previously reported a 1% NaOH modification combined with high temperature at a pressure of 2 bars led to a 355 MPa increase in the tensile strength of FVB from *S. zalacca* fronds. Similarly, Kurniawan *et al.* (2017) reported a 2% NaOH modification combined with steaming at a pressure of 2 bars for 2 h led to a 554.8 MPa increase in the tensile strength of *S. zalacca* frond FVB. These previous studies reported higher tensile strengths; however, this study was more effective and efficient because high temperatures and pressures were not used. Shanmugasundaram *et al.* (2018) reported a 5% NaOH modification for 30 min at room temperature increased the tensile strength of areca palm (*Dypsis lutescens*) FVB by 484.4 MPa, while 10% and 15% NaOH modifications decreased the tensile strength. In addition, Oushabi *et al.* (2017) discovered applying a 5% NaOH solution to FVB from *Phoenix dactylifera* L. led to an increase in the tensile strength of 460 MPa.

Table 3. Mechanical Properties and Cellulose Crystallinity Index (CrI) of the Modified Fibrovascular Bundles (FVB)

Treatments	Crystallinity Index (%)	Maximum Load (N)	Tensile Strength (MPa)	Young's Modulus (GPa)
A	75.0	128 ± 13	224 ± 11	3.1 ± 0.4
B	78.4	127 ± 90	238 ± 16	3.2 ± 0.6
C	82.6	128 ± 13	266 ± 24	3.1 ± 0.5
D	84.8	126 ± 40	273 ± 20	3.0 ± 0.4
E	85.7	120 ± 60	280 ± 30	3.4 ± 0.6
F	86.1	117 ± 60	347 ± 68	3.1 ± 0.5
G	82.9	89 ± 50	322 ± 54	2.7 ± 0.2
H	80.0	56 ± 70	217 ± 31	2.1 ± 0.2

The highest Young's modulus of the modified FVB from *S. sumatrana* fronds was 3.4 GPa after a 60 min immersion in 1% NaOH + 0.2% Na_2SO_3, while the lowest Young's modulus was 2.1 GPa after a 60 min immersion in 1% NaOH + 0.4% Na_2SO_3. A study by Shanmugasundaram *et al.* (2018) reported a 5% NaOH solution treatment of the FVB from areca palm resulted in a Young's modulus of 9.8 GPa, which was higher compared to the results of this study. In addition, Oushabi *et al.* (2017) stated a 5% NaOH treatment on *Phoenix dactylifera* L. palm yielded a Young's modulus similar to this study.

The mechanical properties of the fibers are influenced by the crystallinity index of the material. A higher crystallinity index implies a higher fiber strength. Figure 5 shows the complete XRD diffractogram of the FVB from *S. sumatrana* fronds. The optimal increase in the crystallinity index of the FVB occurred after treatment with 1% NaOH + 0.2% Na_2SO_3 for 60 min. This occurred due to the degradation of amorphous components, including hemicellulose, lignins, and wax. These chemical components are alkaline sensitive and are therefore easily removed *via* a modified alkali treatment (Krishnaiah *et al.* 2017). The crystallinity index decreased as the Na_2SO_3 concentration and immersion time increased. This occurred due to the exposure of the cellulose polymer to sulfite (SO^{3-}), causing some of the cellulose components to dissolve (Moradbak *et al.* 2016).

On the diffractogram, the spectral peaks indicating the presence of the crystalline cellulose I structure are shown in the reflection zones (10$\bar{1}$), (002), and (040) with 2Θ occupying 16.0°, 22.6°, and 34.5°, respectively. In addition, the crystalline cellulose II structure occurs at 2Θ occupying 20.2°, 22.2°, and 34.5°, respectively (Loganathan *et al.*

2020). In lignocellulosic materials treated with alkaline chemicals, the transformation of cellulose I into cellulose II occurs in four consecutive stages, *i.e.*, swelling, dissolution, maceration, and degradation (Sghaier *et al.* 2012). The change from cellulose I to cellulose II occurs at the maceration stage during the alkaline treatment, depending on the concentration and treatment duration. In this study, cellulose I was not transformed into cellulose II, because the alkaline modification was limited to the swelling and dissolving of the amorphous components in the structure of cellulose, *i.e.*, the hemicellulose, pectin, and lignins.

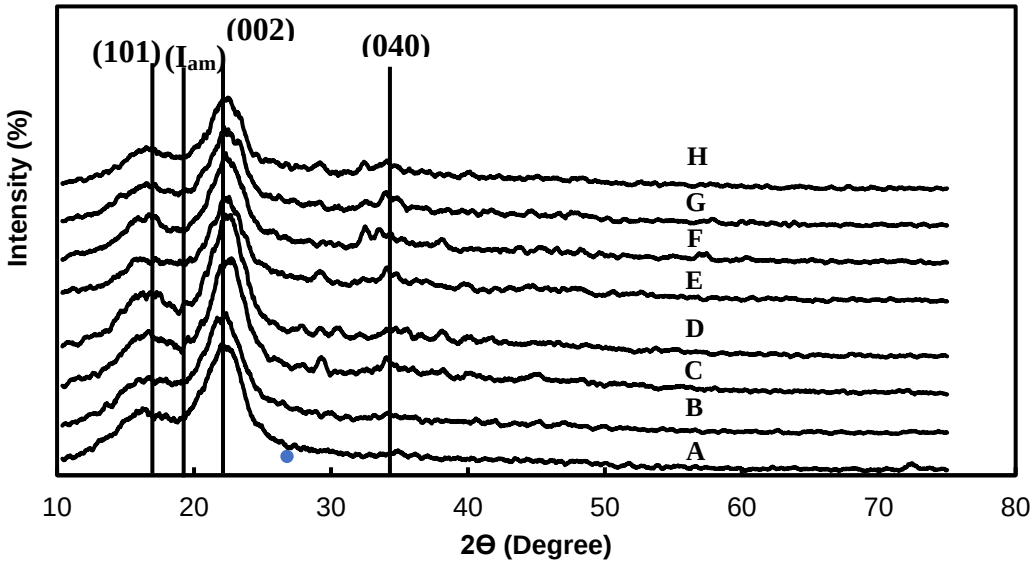

Fig. 5. XRD diffractogram of modified FVB from *S. sumatrana* fronds (Note: A. Untreated for 30 min; B. untreated for 60 min; C. 1% NaOH for 30 min; D. 1% NaOH for 60 min; E. 1% NaOH + 0.2% Na_2SO_3 for 30 min; F. 1% NaOH + 0.2% Na_2SO_3 for 60 min; G. 1% NaOH + 0.4% Na_2SO_3 for 30 min; and H. 1% NaOH + 0.4% Na_2SO_3 for 60 min)

The crystallinity index of the modified FVB subjected to treatment with 1 % NaOH for 30 and 60 min immersions were 82.61% and 84.78%, respectively, while the water treatment counterparts were 75.00% and 78.38%, respectively. In addition, the crystallinity index of the FVB subjected to treatment with 1% NaOH + 0.2% Na_2SO_3 for 30 min and 60 min immersions were 85.71% and 86.11%, respectively, while the counterparts treated with 1% NaOH + 0.4% Na_2SO_3 for 30 min and 60 min immersions were 82.86% and 80.00%, respectively.

The effectiveness of the combination treatment in increasing the tensile strength and Young's modulus of the FVB from *S. sumatrana* fronds amounted to 54.9% and 9.8%, respectively. This value is lower compared to the results reported by Kurniawan *et al.* (2017); however, previous studies used more energy in terms of the alkaline concentration, steaming, and pressure applications. Furthermore, this study was more effective compared to the report by Asim *et al.* (2016), who studied the modification of kenaf natural fiber and pineapple leaves using 6% NaOH.

Thermogravimetric Analysis (TGA)

Figure 6a shows the thermogravimetry (TG) graph illustrating the reduction in weight of the FVB. Generally, thermal stabilization increases with the NaOH and NaOH + Na_2SO_3 treatment. The fibrovascular bundles immersed in water showed a faster degradation rate, compared to the FVB subjected to immersion in NaOH and NaOH + Na_2SO_3. This low thermal resistance occurs because the modification treatment has removed the amorphous regions contained in the hemicellulose, lignins, and wax.

Generally, the thermal degradation process occurs sequentially from the processes of water evaporation, as well as the degradation of hemicellulose, cellulose, and lignins, at temperature ranges of 35 to 160 °C, 220 to 315 °C, 315 to 400 °C, and 400 to 900 °C, respectively (Then *et al.* 2015). Table 4 shows the complete degradation process of the modified FVB. According to the diagram, the modification treatment degraded more rapidly between temperatures of 100 and 300 °C, but stabilized at temperatures greater than 300 °C. However, at 450 °C, the greatest degradation occurred in the water immersion treatment, while the modified treatment counterpart was lower. At the last observed temperature (600 °C), the FVB subjected to the water immersion treatment experienced a weight reduction approximately 83% higher than the modified treatment, where a weight reduction of only 64% (1.3 times lower) occurred. Therefore, the modified FVB was more thermally stable, compared to the unmodified FVB (water immersion).

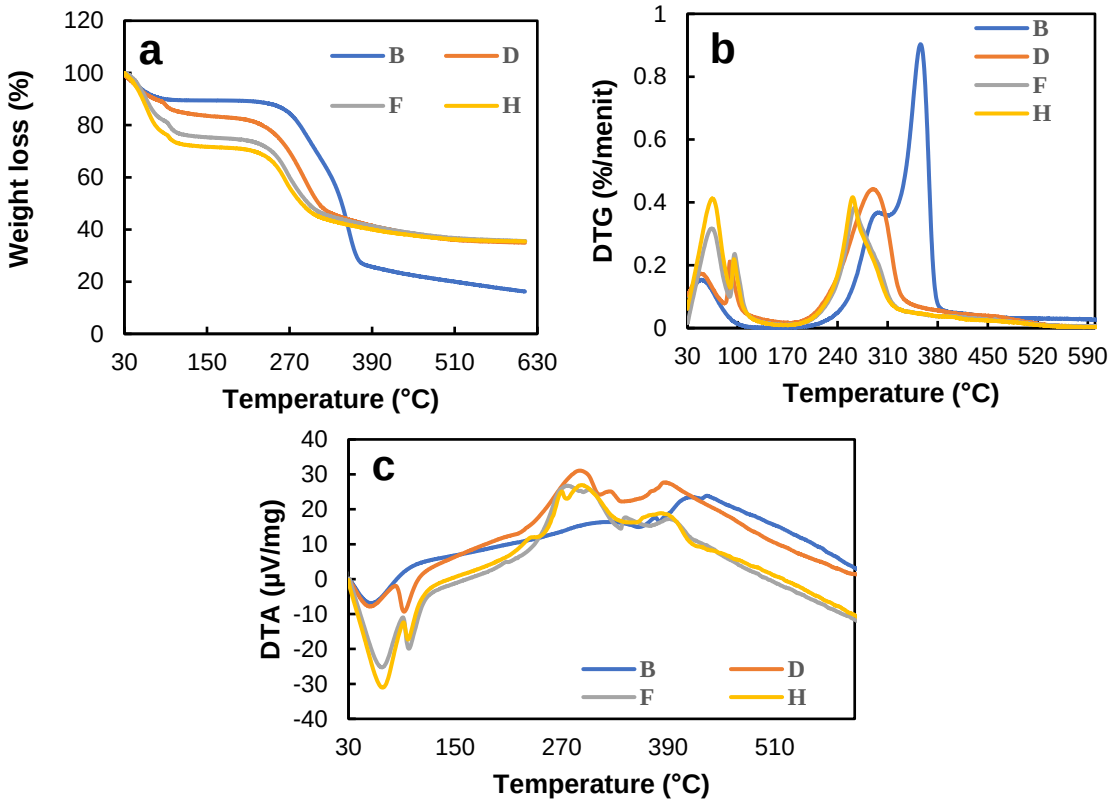

Fig. 6. The thermogram of (**a**) reduction in weight; (**b**) DTG; and (**c**) DTA (Note: B. untreated for 60 min; D. 1% NaOH for 60 min; F. 1% NaOH + 0.2% Na_2SO_3 for 60 min; and H. 1% NaOH + 0.4% Na_2SO_3 for 60 min)

Table 4. Weight Reduction in the Modified Fibrovascular Bundles (FVB)

Treatment	Weight Reduction (%)				
	100 °C	150 °C	300 °C	450 °C	600 °C
B: Untreated (60 min)	10.31	10.53	26.37	77.57	83.36
D: 1% NaOH (60 min)	14.15	16.42	44.72	61.79	64.97
F: 1% NaOH + 0.2% Na_2SO_3 (60 min)	21.72	24.66	50.73	61.49	64.32
H:1% NaOH + 0.4% Na_2SO_3 (60 min)	25.97	28.29	53.18	62.29	64.50

Based on the differential thermogravimetry (DTG) curves (as shown in Fig. 6b), three stages of degradation occurred in the modified FVB from salak fronds. The first stage occurred between 30 and 100 °C, which indicated a process of the evaporation of water and some materials with a low molecular weight (Sair *et al.* 2017). The second stage occurs due to the degradation of hemicellulose, lignins, and wax, within a temperature range of 150 °C to 200 °C (Akhtar *et al.* 2016). Maximum degradation occurred at a temperature of 355 °C for treatment B (water; 60 min), 300 °C for treatment D (1% NaOH; 60 min), and 263 °C for treatments F (1% NaOH + 0.2% Na_2SO_3; 60 min) and H (1% NaOH + 0.4% Na_2SO_3; 60 min). The maximum degradation peaks drastically decreased for the NaOH and NaOH + Na_2SO_3 treated samples, which indicates that alkaline modification using a combination of NaOH + Na_2SO_3 makes FVB less thermally stable. Furthermore, the last stage is cellulose degradation, occurring at 400 to 450 °C, in both the water immersion and modification treatments. Generally, cellulose degradation is initiated at a temperature range of 170 to 500 °C by the decarboxylation, decomposition, and depolymerization of cellulose and hemicellulose fragments (Vijay *et al.* 2019).

Figure 6c shows the differential thermal analysis (DTA) results for the FVB samples subjected to treatments B, D, F, and H. The endothermic reactions in the water immersion and modification treatments occurred between 30 and 150 °C, which indicated the presence of water molecules in the FVB sample. In addition, exothermic reactions occurred within a temperature range of 150 to 400 °C. Exothermic peaks visible beyond 250 °C indicate the degradation of cellulose, hemicellulose, and lignins in the sample (Akhtar *et al.* 2016; Krishnaiah *et al.* 2017). In the FVB modification treatment, the exothermic peak was first reached at a temperature of approximately 270 °C, while the water immersion counterpart was reached at a temperature of approximately 400 °C. This difference in enthalpy indicated that the chemical modification treatment contributes thermal instability to the FVB.

CONCLUSIONS

1. The percentage cellulose content increased due to the reduction in the amorphous components of the hemicellulose and lignins, up to a concentration of 1% NaOH + 0.2% Na_2SO_3 with a 30 min immersion, while the degradation of the cellulose components and amorphous tissues was initiated by a 1% NaOH + 0.2% Na_2SO_3 treatment with a 60 min immersion.
2. The modification of the fibrovascular bundles using NaOH and NaOH + Na_2SO_3 treatments led to a reduction in the diameter as well as the area, due to surface degradation and a decrease in the density of the FVB.

3. The modification of the fibrovascular bundles using NaOH and NaOH + Na_2SO_3 treatments has the capacity to improve the tensile strength and Young's modulus, up to a concentration of 1% NaOH + 0.2% Na_2SO_3 with a 60 min immersion. This improvement was accompanied by a reduction in the surface area, due to the degradation caused by modification, rather than an increase in the maximum load received by the FVB. The crystallinity index of the FVB increased with the degradation of the amorphous components, *i.e.*, hemicellulose, lignins, and wax, after a 1% NaOH + 0.2% Na_2SO_3 treatment with a 60 min immersion.
4. The chemical modifications of NaOH+Na_2SO_3 to fibrovascular bundles led to increased strength and improved surface properties. Furthermore, the fibrovascular bundle can be used as raw material for composite boards by pre-treating the combination of NaOH+ Na_2SO_3 as an alkaline chemical modification.

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