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https://doi.org/10.5109/2321001

出版情報：Evergreen. 6 (1), pp.29-38, 2019-03. 九州大学グリーンアジア国際リーダー教育センター
バージョン：

EVERGREEN Joint Journal of Novel Carbon Resource Sciences & Green Asia Strategy, Vol. 06, Issue 01, pp.29-38, March 2019

Characterization of Sodium-Bicarbonate-Treated Zalacca Fibers as Composite Reinforcements

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(Received January 28, 2019; accepted March 22, 2019).

This research is to study the improvement of chemical, physical and mechanical properties of zalacca fibers after $NaHCO_3$ treatment. It was carried out by immersion in 10% $NaHCO_3$ solution for 24, 120 and 240 h. Fiber content analysis and FTIR showed an increase of cellulose and a decrease of hemicellulose and lignin content. XRD indicated an increase of crystallinity. SEM revealed cleaning and roughening effects on the fiber surface. TGA-DTA revealed a slight decrease in thermal stability. The tensile testing showed that the highest tensile strength and elastic modulus were obtained by the treatment for 120 h.

Keywords: zalacca fibers, sodium bicarbonate, chemical treatment, crystallinity.

1. Introduction

The ever-increasing scarcity of conventional materials and energy resources, which happens in most countries including Asian countries like Japan[1)] and Indonesia[2), 3)], encourages the utilization of high-specific-strength materials in engineering sector such as composites. Several materials are considered not environmentally-friendly as they cannot be directly discarded or recycled at the end of their useful life. Therefore, biocomposites consisting of at least one natural component such as matrices and/or fibers are introduced[4)]. The mechanical properties of matrices, such as polymers or biopolymers, can be enhanced by adding natural fibers. The reinforcement using natural fibers has been widely implemented due to their excellent acoustic performance and high processability[5)], weight reduction, low cost and recyclability[6)]. The natural fibers are often used as additive reinforcement for hybrid composites, like kenaf/E-glass reinforced hybrid polypropylene (PP) composites, which increases their tensile modulus[7)].

Among natural fibers, plant fibers are the most highly utilized due to their high availability, varieties and much lower costs[8)]. Their sources are categorized as primary and secondary plants[4)]. Unlike primary plants such as flax, hemp, jute, kenaf and sisal, the fibers of secondary plants are by-products such as coirs and sugarcane bagasse. Plant fibers are often considered as natural composites, comprising cellulose microfibrils embedded in the matrices of hemicellulose and lignin[9)]. Cellulose, having the highest tensile strength and elastic modulus of the fiber components[10)], is recognized as straight polymer having both amorphous and crystalline structures, while hemicellulose is hydrophilic, amorphous, dissolved in alkaline, and easily hydrolyzed in acid. Furthermore, lignin is hydrophobic, amorphous and soluble in acetic acid and alkaline[11)]. Also it gives rigidity to plants.

The low-bonding ability with synthetic polymer matrices, due to the hydrophilicity of natural fibers and hydrophobicity of synthetic polymers, limits the use of natural fibers in industries[12)]. To improve their mechanical properties and compatibility with polymer matrix, alkaline treatment is the most widely used method[13)]. However, it is unsafe due to its irritation effect on tissues and corrosion on metals. One of the eco-friendly chemical treatment is carried out using sodium bicarbonate ($NaHCO_3$), often known as baking soda.

The mixture of $CrSO_4$ and $NaHCO_3$ is used for coir fibers treatment[14)] which improves the reduction of hydroxyl groups in the fibers allowing their tensile properties to increase. Furthermore, the treatment enhances the interfacial shear strength (IFSS) between the fibers and PP matrix, so that the composite mechanical characteristics, including tensile strength and modulus, flexural modulus, impact strength and hardness, are enhanced. The mixture also enhances the structural, mechanical and thermal properties of lady's finger fibers[15)]. The use of $NaHCO_3$ for sisal fiber treatment up to 120 h significantly enhances its tensile strength, elastic modulus and IFSS between sisal fibers and epoxy matrix[16)]. This is caused by the release of Na^+ ions and the formation of carbonic acid and hydroxide ions. The interaction between fibers and Na^+ ions is similar to that which occurs in alkaline treatment[9)]. The subsequent study of the treatment of flax-reinforced epoxy composites reveals that 10% solution for 120 h improves the tensile strength and modulus up to 20 and 45 %, respectively[17)]. The study of the effect of sodium bicarbonate on the mechanical properties of the sisal fiber-reinforced poly-lactic acid (PLA) composites indicates that the treatment for 72 h exhibits the maximum tensile strength of sisal fibers and contributes to the optimum tensile, flexural and compressive strength of the 30 wt. % sisal fiber-reinforced composites[18)]. For impact strength, the 24 h treatment gives the maximum values. Compared to Na_2CO_3 as a stronger alkali[19)], $NaHCO_3$ has mild alkaline properties so that it is considered to be harmless to natural fibers.

Zalacca (*Zalacca edulis*), a tropical plant originating from Southeast Asia, is cultivated for its fruits. Midribs cutting to increase fruit harvest is done bi-yearly after the harvest with 4-6 midribs. The cellulose content of zalacca midrib fiber (ZF) reaches 42.54 %, higher than wheat straw, coir, alpha grass and bagasse. Furthermore, its average tensile strength reaches up to 182.12 MPa, stronger than coir and nearly similar to bagasse. Its mechanical properties can be improved by alkaline treatment[20)]. To enhance the properties of ZF and its compatibility with polymer matrix using the eco-friendly treatment, the sodium bicarbonate is an alternative. However, the study of the effect of $NaHCO_3$ treatment on chemical, physical and mechanical properties of ZFs has not been done yet. The aim of this research is to characterize the raw and $NaHCO_3$-treated ZFs by examining their chemical, physical and mechanical properties.

2. Experimental Method

2.1 Materials

Fibers were collected from the midribs of zalacca plants located in The Province of Yogyakarta, Indonesia, Fig. 1 (a). Initially, the midribs were cut ±30 cm from the roots of ±3 years-old-plants, Fig. 1 (b). Next, they were immersed in distilled water for 2 weeks to separate the fibers and husk. Then the fibers were immersed in distilled water for 1 h and spread out in the open air for 2 days. They were then cut into 40 mm ± 5 mm length and dried in a ventilated oven at 103°C ± 2°C for a day, followed by placed them in a desiccator for 24 h. Finally, they were stored in sealed plastic containers, as shown in Fig. 1 (c). Analytical grade chemical $NaHCO_3$, purchased from Merck®, was used.

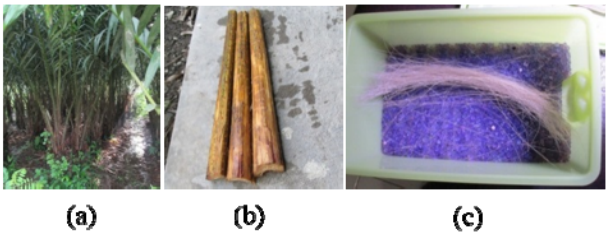


Fig. 1: Zalacca edulis: (a) plants; (b) midribs; and (c) fibers

2.2 Chemical Treatment

The concentration of 10 % $NaHCO_3$ solution was prepared by dissolving 100 g of $NaHCO_3$ into 900 g of water. Initially, five grams of ZFs were immersed in 100 ml $NaHCO_3$ for 24, 120 and 240 h, followed by washing in distilled water and then dried in the open air and 105°C-temperatured oven for 24 h and 45 minutes, respectively. The fibers and chemical were weighed using Ohaus PA224 analytical balance with capacity and accuracy of 220 g and 0.1 mg, respectively.

2.3 Fiber content analysis

Cellulose and lignin content of ZF was determined by applying Kurchner-and-Hoffer and Klason methods, respectively. The hemicellulose content was measured according to NFT 12-008 standard. The untreated and chemically treated ZFs were milled to a powder size and then extracted using CH_2Cl_2 and hydrolyzed in 72 % H_2SO_4 solution. Lignin, which is insoluble, was separated and quantified. The cellulose was attained by extracting the samples with CH_2Cl_2 and then adding them into a mixture of ethanol and 95 % HNO_3. The insoluble cellulose was then weighed. The hemicellulose was obtained by heating the samples in HBr, thereby transforming them into furfural and then extracted via distillation and measured using spectrophotometry.

2.4 XRD

The determination of ZF's X-ray diffraction (XRD) both before and after the treatment was performed using Philips X-ray diffractometer Model PW 1800 under CuKα radiation of 30 kV and 17.5 mA. The step size and step scan used for the 2θ's reading range of 10-60° were 0.075° and 2.5s, respectively. The degree of crystallinity was represented by crystallinity index (CI) using Eq. (1), in which I_{am} and I_{002} were the peak intensity representing the amorphous and crystalline part, respectively.

$$CI = (I_{002} - I_{am})/I_{002}.100\% \quad (1)$$

Meanwhile the crystalline size (L) was calculated using the Scherrer's formula[21)]:

$$L = K.\lambda/(B.\cos\theta) \quad (2)$$

in which K, λ, B and θ are the Scherrer's constant (0.89), X-ray wavelength used in the measurement (0.154 nm), peak's full-width at half-maximum (FWHM) and Bragg angle, respectively.

The I_{am}, I_{002}, B and θ values were estimated precisely using MDI Jade 6.5 software.

2.5 FTIR

Fourier transform infrared (FTIR) spectrometry analysis was conducted to observe each change in the functional groups on the fiber surface before and after the chemical treatment, using Shimadzu IR Prestige-21 Spectrometer. Five percent of the powdered fibers mixed with 95 % KBr were passed through a disk. The spectrum of each fiber was recorded in the range of 400-4000 cm^{-1} by 32 scans at a resolution of 4 cm^{-1}.

2.6 TGA-DTA

The examination of thermal stability of the fibers by thermogravimetry and differential thermal analysis (TGA-DTA) was carried out both before and after the treatment. The tests were conducted using Linseis Type STA PT 1600 DTA-TGA analyzer equipped with nitrogen purge gas. The thermogravimetry and differential thermal analyzer have resolution of 10 µg and 0.01 mW, respectively. The powdered sample fibers of 15-20 mg were placed in a sample pan and heated from room temperature to 600°C at a rate of 10°C/min and weighed simultaneously.

2.7 SEM

The surface morphology of ZF was examined using FEI type Inspect S50 scanning electron microscope (SEM) instrument with 10 kV voltage. The gold-coated samples were placed on a silver-painted holder.

2.8 Density of the fibers

The apparent density of ZF was determined using Archimedes principle based on ASTM D276 standard. Five samples consisted of a bunch of ZFs were immersed in pure methanol ($\rho_{methanol} = 0.791$ g/cm^3). The weighing process was performed using Ohaus PA224 analytical balance with capacity and accuracy of 220 g and 0.1 mg, respectively.

2.9 Diameter measurement of the fibers

The diameter of single fiber was determined using Olympus SZX2-TR30 optical microscope and CellSens® software at room temperature with an accuracy of 10^{-2} µm. It was measured in 4 separate locations along each fiber and the results were then averaged. A total of 80 ZFs were randomly selected, twenty fibers were identified for each of 4 categories: untreated, $NaHCO_3$-treated for 24, 120 and 240 h.

2.10 Single fiber tensile testing

The tensile testing of single fiber was conducted using JTM-UTS210 universal testing machine based on the ASTM C1557-03 standard. The test was performed at a room temperature of 25°C and a relative humidity of approximately 55%. Randomly selected fibers were cut to specific lengths where each end of the fiber was then tied/fastened onto a paper frame maintaining a free 20-mm gauge-length using an epoxy adhesive resin. The load cell capacity was 0.50 kN with a cross-head speed of 5 mm/min. Twenty specimens were selected from each category and tested. Every sample that broke near the clamping area was not analyzed. The test results were then analyzed using analysis of variance (ANOVA) to verify a meaningful difference to the mechanical properties of ZFs following the chemical treatment. The level of significance $\alpha \leq 0.05$ was determined to distinguish the different groups of fibers22).

3. Results and Discussion

3.1 Fiber treatment

The treatment was done by immersing the fibers in 10 % $NaHCO_3$ solution. The reaction of $NaHCO_3$ dissolved in water is shown in the following formulas16):

$NaHCO_3 \rightarrow Na^+ + HCO_3^-$

$HCO_3^- + H_2O = H_2CO_3 + OH^-$

The fiber containing hydroxyl groups and Na^+ ions react as:

$\text{Fiber-OH} + Na^+ + OH^- \rightarrow \text{Fiber-O}^- Na^+ + H_2O +$ impurities

produces fiber that is free of hydrophilic hydroxyl groups. The amount of Na^+ ions depends on the concentration and basicity of the solutions represented by pH values. The calculated pH of the $NaHCO_3$ and the other chemical solutions are shown in Table 1. Based on them, fiber treatment by $NaHCO_3$ is less effective than NaOH solution due to its basicity as the supplier of OH^- which reacts with the hydroxyl groups.

Table 1: Calculated pH of several chemical solutions

Chemical solution	Calculated pH	Reference
10 % $NaHCO_3$	8.46	
1 % NaOH	13.40	
5 % NaOH	14.00	
10 % Na_2CO_3	12.00	19)

3.2 Fiber content

The cellulose, hemicellulose and lignin contents of untreated and $NaHCO_3$-treated ZFs are tabulated in Table 2. The cellulose content is greater than in bamboo and coir fibers, comparable with Tunisian palm fibers, and lower than in sanseviera due to the secondary plant in which ZF is a by-product from fruits.

The $NaHCO_3$ treatment carried out for 24 and 120 h significantly reduced the hemicellulose content from 34.35 % (untreated ZF) to 33.50 and 32.56 %, respectively, and lignin content from 28.01 % to 23.75 and 24.93 %, respectively. The reaction with Na^+ and OH^- ions resulted from the dissolution of $NaHCO_3$ brings about the destruction of the hydroxyl groups presenting in the amorphous region along with amorphous cellulose, hemicellulose and lignin. The treatment that is longer than 120 h slightly reduces the cellulose content due to partial elimination of the amorphous cellulose. $NaHCO_3$ solution is easier to infiltrate in the amorphous than in crystalline region. However, compared to NaOH treatment, the hemicellulose removal and cleaning effects by $NaHCO_3$ are much weaker due to its basicity, as shown in Table 1.

Table 2: Fiber content of untreated**1.**, $NaHCO_3$-treated ZFs and other fibers

Fibers	Fiber content Cellulose (%)	 Hemicellulose (%)	 Lignin (%)	Ref.
Untreated ZFs	42.54	34.35	28.01	
$NaHCO_3$-treated ZFs				
for 24 h	45.00	33.50	23.75	
for 120 h	45.12	32.56	24.93	
for 240 h	43.57	36.62	24.45	
Bamboo	26-43	30	21-31	23)
Coir	32-43	0.15-0.25	40-45	14)
Sanseviera	79.7	10.13	3.8	21)
Tunisian palm fibers	43	8	35	24)

3.3 XRD

The XRD analysis for the untreated and $NaHCO_3$-treated ZFs results in the diffractogram, as shown in Fig. 2. It indicates that the diffraction peak, which corresponds to the (0 0 2) crystallographic planes of cellulose for 2θ, ranges from 22 to 23°. However, the (1 0 1) planes for the amorphous part for 2θ is around 17°. The diffractograms of untreated and $NaHCO_3$-treated ZFs show the same trends although there is a difference in the peak intensity.

The crystallinity index of untreated and $NaHCO_3$-treated ZFs for several periods of treatment are shown in Table 3. There is an increase of CI value of 2.20, 8.82 and 6.24 % after the $NaHCO_3$ treatment for 24, 120 and 240 h, respectively, caused by the increase of the crystalline cellulose content. The amorphous component is partially eliminated. This result is almost similar to the Na_2CO_3 treatment of coir fiber[19]. The significant increase of CI are 6.56, 6.81 and 6.83 % for 24, 96 and 168 h of immersion time, respectively. This is due to the higher basicity of Na_2CO_3 compared to $NaHCO_3$ (see Table 1). There is a slight decrease in the value of CI after treatment for 240 h compared to 120 h. It is caused by the decline of the cellulose content due to the time of treatment (see Table 2). The CI values of ZF are higher than sisal, *Lygeum spartum L.* and *Juncus effusus* fibers, lower than cotton, and comparable with jute (Table 3).

The average crystalline size of ZF is higher than cotton but lower than jute and sisal. There were slight increase on crystalline size calculated using Eq. (2) caused by the $NaHCO_3$ treatment. The treatment for 24, 120 and 240 h raises the size 1.03, 6.52 and 7.69 % from the untreated fibers (11.23 nm). The crystalline size raises with the increase of crystallinity. This case is similar to swelling stage preceding the mercerization process using NaOH solution[25]. The swelling occurs when the caustic solution penetrate the amorphous region of cellulose and then modify the native cellulose structure (cellulose 1) becomes Na-cellulose I. It takes place at NaOH concentration of 5-10 %, meanwhile the $NaHCO_3$ solution in this treatment has significantly lower basicity (see Table 1). The larger crystalline size results in the decrease of chemical reactivity and water absorption capacity of the fibers.

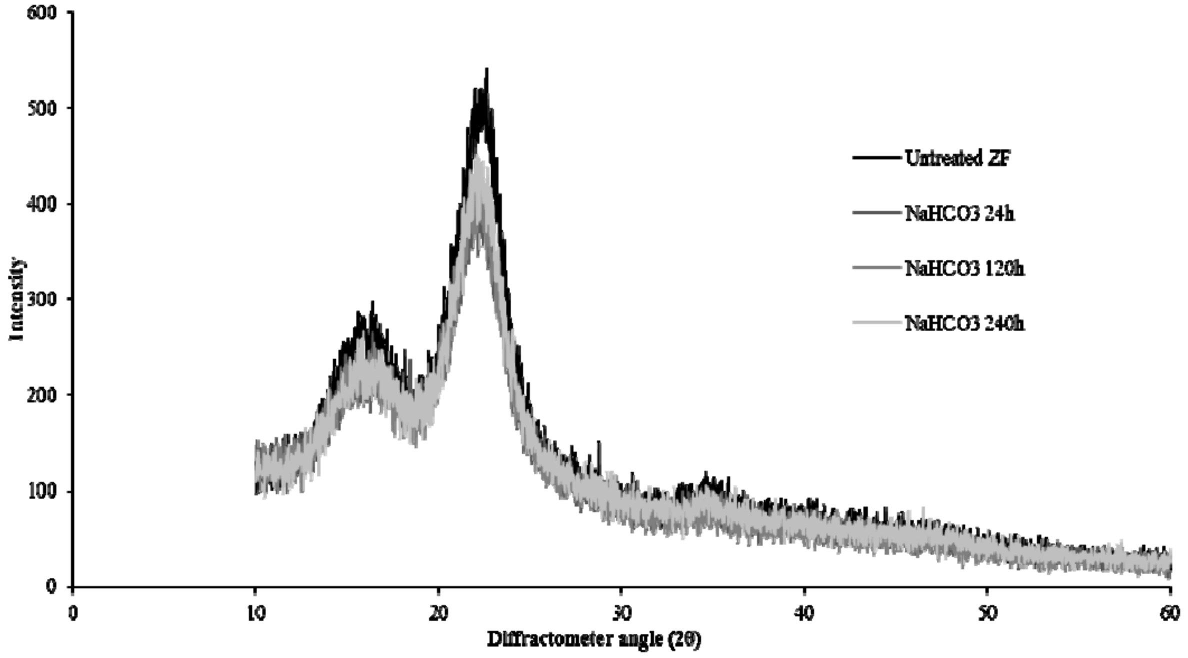


Fig. 2: Diffraction of untreated and NaHCO3-treated ZFs

Table 3: Crystallinity index and crystalline size of untreated and $NaHCO_3$-treated ZFs and other fibers

Fibers	CI (%)	L (nm)	Ref.
Untreated ZF	59.62	11.23	
$NaHCO_3$-treated ZF			
for 24 h	60.93	11.35	
for 120 h	64.88	11.96	
for 240 h	63.34	12.09	
Cotton	68	5-7	26)
Jute	65.8	29.25	27)
Sisal	55	16.99	28)
Lygeum spartum L.	46.19	-	29)
Juncus effusus	33.4	3.6	30)

3.4 FTIR

The infrared spectra of untreated and $NaHCO_3$-treated ZF are revealed in Fig. 3. Like the study of hemp and kenaf fibers by Sgriccia and co-workers31), the FTIR peaks are also baseline corrected but to 3398 cm^{-1}. The pattern is similar to jute27), banana32), bagasse and sponge gourd fibers33). Moreover, it indicates that all spectra of ZF have almost the same banding pattern.

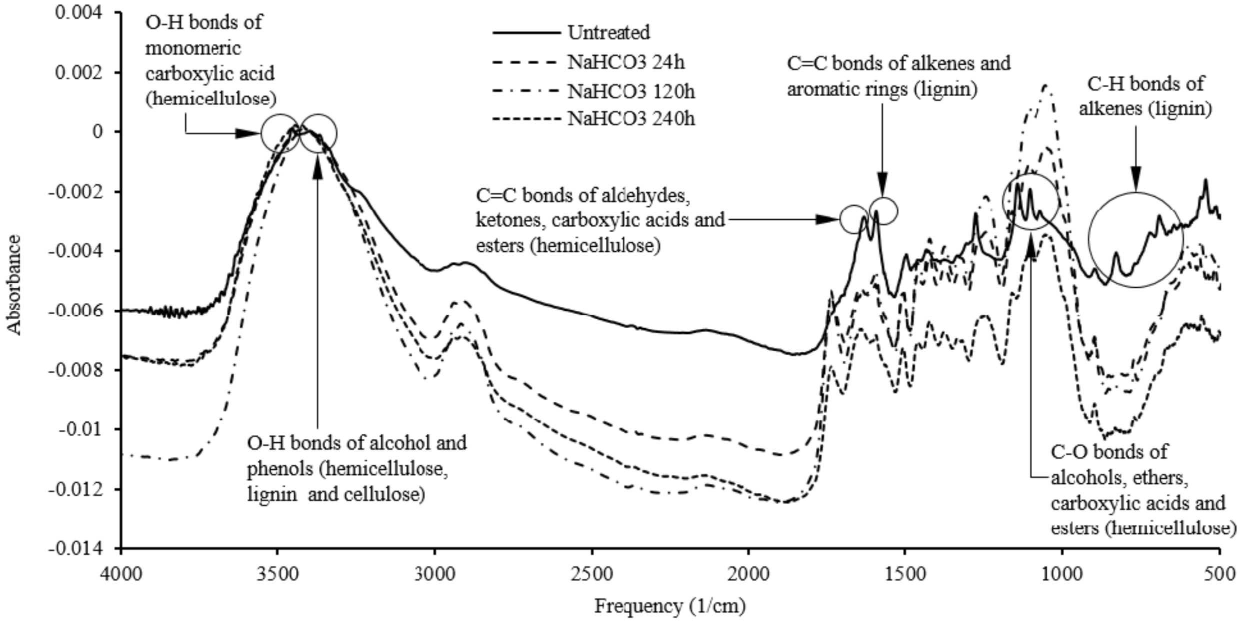


Fig. 3: Spectra of untreated and $NaHCO_3$-treated ZFs

Based on the frequencies for organic functional group34), there are some peaks indicating the existence of the chemical bonds of compounds correlated with cellulose, hemicellulose and lignin.

The broadband observed around 3200-3600 cm^{-1} with some peaks shows that there are O-H bonds from the alcohols and phenols of cellulose, hemicellulose and lignin. There is the elimination of some peaks after $NaHCO_3$ treatment which indicates that the treatment possibly removes hemicellulose, lignin and small amount of cellulose. The destruction of some peaks ranging from 3500 to 3650 cm^{-1} correlated with O-H bonds from the monomeric carbocylic acids of hemicellulose shows that the treatment also partially removes hemicellulose. Meanwhile, the band around 2850-2970 cm^{-1} and its overtone around 1340-1470 cm^{-1} having strong intensity correspond to the C-H bonds from the alkanes of cellulose, hemicellulose and lignin. There is no change in the trends due to the $NaHCO_3$ treatment.

The band around 3010-3095 cm^{-1} and its overtone around 675-995 cm^{-1} are correlated with C-H bonds from alkenes of lignin but the intense peaks happen only between 675-995 cm^{-1}. Meanwhile, the C-H bonds from the aromatic rings of lignin are predicted in the band around 3010-3100 cm^{-1} and its overtone around 690-900 cm^{-1} but the peaks only exist around 690-900 cm^{-1}. The elimination of the peaks in the treated fiber's spectra implies that there is a partly removal of lignin.

The bonds of C-O and C=O from the alcohol, aldehyde and carboxylic acid of hemicellulose are detected in the band around 1050-1300 cm^{-1} and 1690-1760 cm^{-1}, respectively, with the strong intensity. The elimination of the peaks in the treated fibers indicates that there is a partial removal of hemicellulose by $NaHCO_3$ treatment. The bands around 1610-1680 cm^{-1} and 1500-1600 cm^{-1} are associated with C=C bonds from the alkenes and aromatic rings of lignin, respectively. There is an elimination of the peaks in that range which indicates that the treatment possibly removes the lignin. Especially at 1635 cm^{-1}, the peak is present in both untreated and treated fibers. It is correlated with the H-O-H molecules of water, as indicated by the study of Marsyahyo and co-workers referring to the identification of ramie single fiber surface topography[35].

From FTIR analysis, it is established that the sodium bicarbonate treatment partially eliminates the hemicellulose and lignin, as indicated in the fiber content analysis and the increase in degree of crystallinity.

3.5 TGA-DTA

The TGA and DTA graphs are illustrated in Figs. 4 and 5, respectively. Degradation of natural fibers normally occurs in 3 stages[36]: (1) loss of moisture, from room temperature to about 200°C; (2) hemicellulose and some portion of lignin decomposition, in the range of 220 to 350°C; and (3) cellulose and lignin decomposition, in the range of 350 to 450°C. These 3 stages of ZF are shown in the TGA graph as 3 areas of mass change and also proven by 3 peaks in DTA graph.

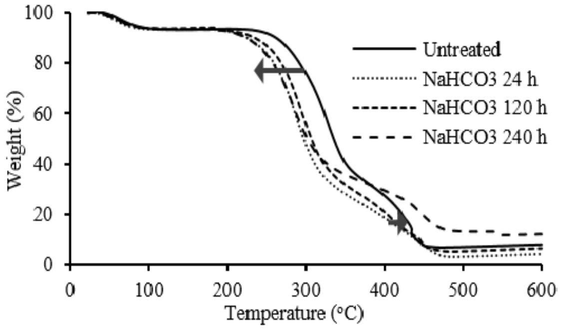


Fig. 4: TGA graph of untreated and NaHCO3-treated ZFs

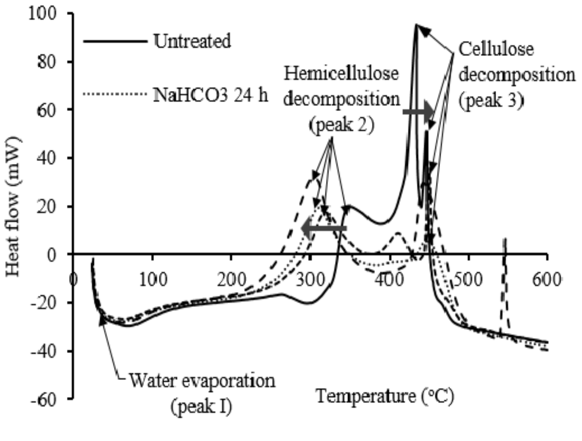


Fig. 5: DTA graph of untreated and NaHCO3-treated ZFs

The initial peak between 40 and 115°C representing stage 1 correlates with the vaporization of water absorbed in the fibers. The $NaHCO_3$ treatment deviates from the beginning and the end of water vaporization from about 50 and 93°C to around 40 and 78°C, respectively. It is confirmed by shifting the peak from 70°C of untreated fiber to 62°C for the treated one in the DTA graph (Fig. 5). It means that the treatment quickens the water evaporation process, caused by the exchange of hydroxyl and Na^+ ions which produces volatile water. However, this treatment is not as effective as NaOH having higher basicity[37].

Stage 2 performed between 220-310°C shows that there is a difference in weight loss between untreated and $NaHCO_3$-treated ZFs. The treated fibers have a slightly larger weight loss due to the elimination of hemicellulose and some lignin, indicated by the first peak shifting from 350°C to the left, 305°C, as shown in Fig. 5. This results is different for NaOH treatment that tends to shift the second peak to the right, although it encourages the elimination of amorphous parts such as hemicellulose, lignin and amorphous cellulose. Thereby the mercerization process using NaOH increases the crystalline region. The dense crystalline cellulose limits the subsequent removal of hemicellulose and lignin.

Stage 3 indicates that the weight loss of untreated fibers is higher than that treated (Fig. 4) due to the high lignin content. This fact in accordance with the DTA graph (Fig. 5) indicating that the third peak of $NaHCO_3$-treated fibers shifts from 445°C to the right, 452°C. It indicates that the $NaHCO_3$ treatment increases the stability of cellulose. However, overall untreated fibers have insignificantly higher thermal stability than those treated which mean that the $NaHCO_3$ treatment slightly lowers the processing temperature of ZFs. Still, both untreated and $NaHCO_3$-treated ZFs tend to be stable up to ±200°C. This fact is similar to the $NaHCO_3$ treatment of sisal fibers[16]. The reduction of thermal stability of the fibers also results in the alkali treatment of jute yarn fibers[38] and the various chemical treatment of okra fibers[39], including scouring, bleaching, acetylation and sulphuric acid with potassium permanganate treatment. It is due to the excessive elimination of hemicellulose and lignin which urges the degradation of other fiber components like cellulose.

3.6 SEM

The examination of the surface morphology using SEM is shown in Figs. 6 (a), (b), (c) and (d) for untreated, $NaHCO_3$-treated ZFs with the immersion time of 24, 120 and 240 h, respectively. Fig. 6 (a) indicates that the surface area of the fiber looks smooth and shows the cell walls as well. There are some protrusions on the fiber surface. The 24 h treatment, as shown in Fig. 6 (b), increases the cleanliness and roughness of the fiber surface. Its texture also looks clearer. The longer treatments, 120 and 240 h, also make the fiber surface cleaner and rougher, as shown in Figs. 6 (c) and (d). Compared to the morphological examination of NaOH treatment[20], the surface of $NaHCO_3$-treated fiber is less rough, due to its elimination effect of hemicellulose and lignin lower than NaOH, (see Table 1). It is caused by the higher ability of strong alkali, like NaOH, to infiltrate the fiber surface and make swelling reaction which change the crystalline structure of the fibers[40].

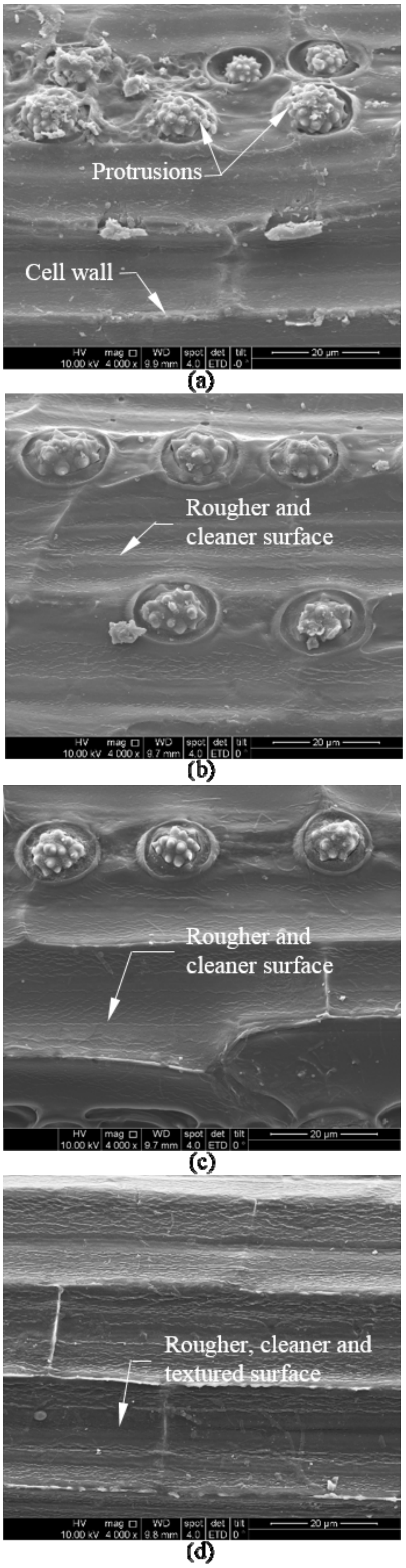


Fig. 6: Surface morphology of: (a) untreated ZF; (b) $NaHCO_3$-treated ZF for 24 h; (c) 120 h; and (d) 240 h

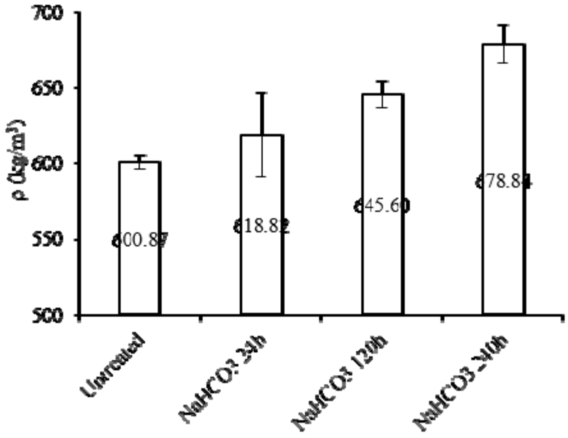


Fig. 7: Density of untreated and $NaHCO_3$-treated ZFs

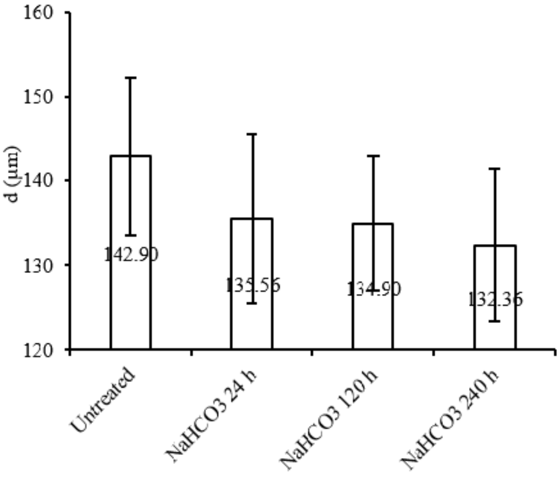


Fig. 8: Diameter of untreated and $NaHCO_3$-treated ZFs

3.8 Diameter measurement

The diameters of untreated and $NaHCO_3$-treated fibers are shown in Fig. 8. The treatment reduces the average diameter through partial elimination of hemicellulose and lignin (see Table 2). The longer immersion time tends to reduce the diameters. The decrease in average diameter obtained from the $NaHCO_3$ treatment for 24, 120 and 240 h reaches 5.14, 5.60 and 7.38 %, respectively. Statistical analysis by ANOVA results in P-value of 4.65×10^{-3}, indicating that the immersion time of treatment have significantly effect in reducing the fiber diameter. However, the observed reduction in diameter is not as high as for NaOH treatment[20)]. It is caused by the higher rate of hemicellulose and lignin removal.

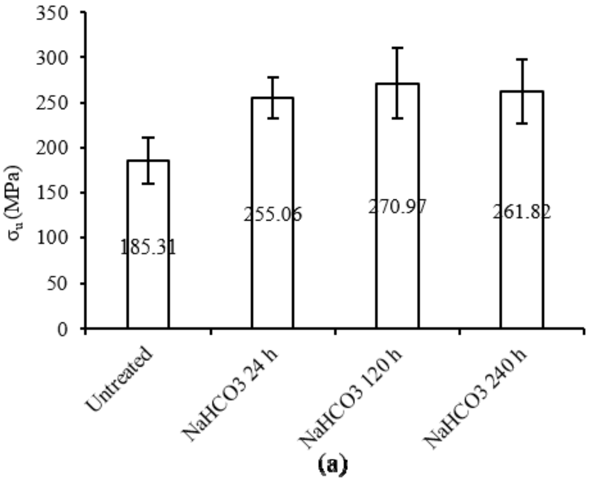
3.9 Single fiber tensile testing

The average tensile strength, elastic modulus and elongation at break of untreated and $NaHCO_3$-treated ZFs are shown in Figs. 9 (a), (b) and (c), respectively. Table 4 shows that the untreated ZF has average tensile strength comparable to bagasse, *Lygeum spartum L.* and Tunisian palm fibers, and higher than coir, FBBPD and

Juncus effusus fibers. $NaHCO_3$ significantly increases the average tensile strength resulting from the increase in the cellulose percentage (see Table 2), proved by the rise in CI (see Table 3), and reduction in the fiber diameter (Fig. 8). Because the cellulose has the highest strength and elastic modulus of lignocellulosic components, the increase in its content causes the stress held by each unit of cross-sectional area to be raised while the decrease in the hemicellulose and lignin content causes the volume of the fiber to shrink. This assumes that there is no change in the fiber length so that the diameters decrease. Smaller cross-sectional area as denominator contributes to the higher tensile stress obtained. This result is similar to the use of $NaHCO_3$ treatment for sisal fibers16), although the tensile strength improvement is not as high as for NaOH-treated specimens20). This fact can be attributed to the high increase in the cellulose content resulting from the NaOH treatment. The different results are met in the study of the chemical treatment on the mechanical behavior of okra fibers39). Their mechanical properties, including tensile strength and elastic modulus, decrease significantly due to the excessive elimination of hemicellulose and lignin content as binders of cellulose microfibrils.

The untreated fibers also show the lowest results for the modulus of elasticity, where the $NaHCO_3$-treated fibers show a higher modulus, Fig. 9 (b). The increase caused by the 120 h treatment is higher than that caused by 24 and 240 h treatment, due to the higher cellulose content.

Like other lignocellulosic fibers, such as kenaf, ramie, sisal and bagasse, ZF shows brittle behavior under tensile condition, as indicated by low elongation at break, Fig. 9 (c). The $NaHCO_3$ treatment does not indicate a significant change in the elongation at break. This result is validated by ANOVA in which the obtained P-value is larger than the level of significance, 0.05. It reveals that the treatment does not cause the significant effect on the elongation at break. Meanwhile the P-value of tensile strength and modulus are $4.2x10^{-10}$ and $8.2x10^{-6}$, respectively, indicating that they are significantly influenced by the $NaHCO_3$ treatment.



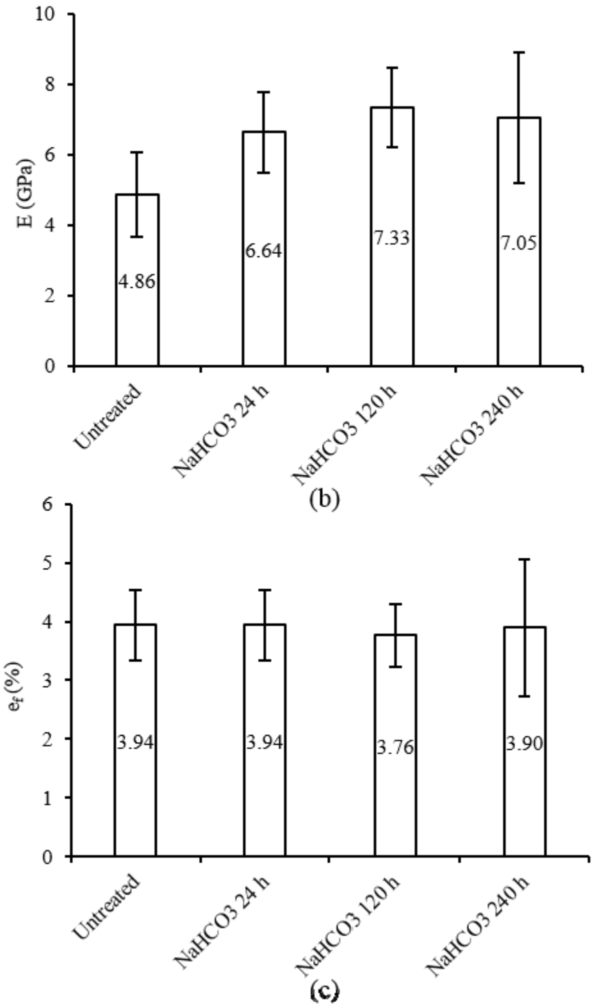


Fig. 9: Tensile testing results of untreated and $NaHCO_3$-treated ZFs: (a) tensile strength; (b) elastic modulus; and (c) elongation at break

Table 4: Mechanical properties of several plant fibers

Fibers	Tensile strength (MPa)	Elastic modulus (GPa)	Elongation at break (%)	Ref.
Untreated ZFs	185.7± 50.7	5.05±1.42	3.8±1.0	
$NaHCO_3$-treated ZFs	318.8± 110.5	9.96±3.16	3.2±0.5	
Bagasse	169-350	5.13-6.24	6.25-7.87	11)
Coirs	37.5-91.6	3.69-8.24	1.19-6.62	14)
Raw fruit bunch branch of palm date (FBBPD)	117	4.3	3.13	41)
Lygeum spartum L.	64.63-280.03	4.47-13.27	1.49-3.74	29)
Raw Tunisian palm fibers	174.2± 42.3	4.01± 1.24	-	24)
Juncus effussus	113±36	4.38±1.37	2.75±0.6	30)

4. Conclusions

Zalacca midrib fibers were immersed in 10% $NaHCO_3$ solution, rinsed and then dried in open air and oven. Their cellulose, hemicellulose and lignin content were quantified. It is found that the sodium bicarbonate treatment increases the cellulose content by the partial elimination of hemicellulose and lignin. The longer treatment time tends to decrease the cellulose. There is an increase of the crystallinity index measured by XRD due to the $NaHCO_3$ treatment. The FTIR analysis shows that the $NaHCO_3$ treatment eliminates several groups correlated to hemicellulose and lignin. The TG-DT analysis shows that the $NaHCO_3$ treatment does not significantly reduces the thermal stability of the fibers. The morphological examination of the fiber surface using SEM shows a cleaner and rougher treated surface. The tensile strength and the elastic modulus of ZFs increase due to higher cellulose content. In general, these results demonstrate that $NaHCO_3$ treatment in ZFs improves chemical, physical and mechanical properties such as strength and elastic modulus. The conclusion, herein is that this treatment assists in demonstrating their potency as composite reinforcements.

Acknowledgements

This research was done with the financial support of the Indonesian Ministry of Research, Technology and Higher Education.

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