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Effect of chemical treatment on wettability of Zalacca fibres as composites reinforcements

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Abstract. The aim of this research is to study the influence of sodium hydroxide, sodium bicarbonate and calcium hydroxide treatment on the wettability characteristics of zalacca fibres. The wettability test was carried out by measuring the contact angle between the fluid and fibre surface. The distilled water and ethylene glycol represent the polar and dispersive fluid, respectively. By entering the contact angle and liquid surface energy of distilled water and ethylene glycol simultaneously into the substitution of Young-Dupres and Owen-Wendt equation, the surface energy of fibres was determined. The treatment caused the decrease in contact angle inducing the enhancement in surface energy. The increase of surface energy of the zalacca fibres by NaOH treatment was the highest, followed by $\text{Ca}(\text{OH})_2$ and NaHCO_3 treatment. Based on the fibre content analysis and SEM examination, this is due to the basicity of the solution causing the cleaning effect, in which the sodium hydroxide is the strongest, followed by calcium hydroxide and sodium bicarbonate solution. The wettability of zalacca fibres as composite reinforcement is raised by NaOH, $\text{Ca}(\text{OH})_2$ and NaHCO_3 treatment.

Keywords: zalacca fibres; wettability; surface energy; contact angle; chemical treatment

1. Introduction

In this present materials with high specific strength and stiffness are required due to the inadequacy of the conventional material and energy resources. The emerging environmental issue encourages the utilization of green composite, material consisted of minimal two components which at least one is renewable [1]. Composite is arranged from matrix and reinforcements, usually in the form of fibres [2]. There are a lot of natural especially plant fibres, like banana fibres, coir, jute, kenaf, sisal, sugarcane bagasse and wood fibres. Nevertheless the plant fibres have not been applied broadly in industries due to their low compatibility with synthetic polymer matrix [3]. To obtain the optimum mechanical properties of composites, there are essential factors: mechanical properties of matrix and fibres, adhesivity of matrix-fibres [4], length and orientation, volume fraction and thermal stability of the fibres [5]. The adhesivity correlated to interfacial compatibility of the fibre surface is influenced by its wettability [6].

The adhesion between two contacted solids are directly correlated with surface energy of each solids [7]. The surface energy of fibres and matrix can be used to measure the strength of material interface. The surface energy (γ) is divided as polar (γ^p) and dispersive (γ^d) components [8] :



$$\gamma = \gamma^p + \gamma^d \quad (1)$$

in which γ^p and γ^d represent the polar and dispersive surface energy (mJ/m^2), respectively. The polar component is arose caused by dipolar interaction meanwhile dispersive one is occur due to Van der Waals force between the molecule of the materials [9].

The relationship between contact angle (θ) of a liquid drop on the substrate and the surface energy of the liquid (γ_L), surface energy of the solid (γ_S) and interfacial energy between the solid and liquid (γ_{SL}) is expressed by the Young-Duprex equation [7].

$$\gamma_S = \gamma_{SL} + \gamma_L \cdot \cos \theta \quad (2)$$

The surface energy of the solid can be calculated by measuring the contact angle of polar and nonpolar liquid on the material surface using Owen and Wendt equation. Usually the distilled (deionized) water and ethylene glycol are polar and nonpolar (dispersive) liquid used, respectively.

$$\gamma_{SL} = \gamma_S + \gamma_L + 2 \left[(\gamma_L^d \cdot \gamma_S^d)^{1/2} + (\gamma_L^p \cdot \gamma_S^p)^{1/2} \right] \quad (3)$$

By substituting the eq. (3) to eq. (2), the relationship is obtained.

$$\frac{-(1 + \cos \theta) \cdot \gamma_L}{2 \sqrt{\gamma_L^d}} = \sqrt{\gamma_S^p} \cdot \sqrt{\frac{\gamma_L^p}{\gamma_L^d}} + \sqrt{\gamma_S^d} \quad (4)$$

Zalacca (*Zalacca edulis*) is a native plant from Southeast Asia, especially Indonesia. It is farmed for its fruits. The fruit has white flesh enclosed with snake-like peel which is sourly sweet. After harvesting the fruits, the old midribs are cut for increasing the next crop. The cut midribs then are discarded as wastes. There are efforts to utilize the midrib wastes as fibre for composite reinforcements due to its cellulose content [10]. However, the study of the wettability of zalacca fibres (ZF) and the influence of chemical treatments on their wettability has not been done yet.

In this study, the surface energy of untreated fibres, sodium hydroxide, sodium bicarbonate and calcium hydroxide treated fibres were examined by measuring the contact angle between the fluids and fibre. The fluids were distilled water and ethylene glycol representing polar and dispersive liquids. The chemical treatments for ZF in this study used NaOH 1% and 5% for 2 h, sodium bicarbonate (NaHCO_3) in its solubility limit, 10% in room temperature [11] and lime-water (Ca(OH)_2) in its solubility limit, room temperature. The duration of treatment was determined by the basicity of the solution, indicated by the pH values. 0.15% in

Before the determination of contact angle, the analysis of fibre content and fibre surface examination by scanning electron microscopy (SEM) was carried out to investigate the effect of the chemical treatment on the cellulose, hemicellulose and lignin, and the surface morphology of the fibres, respectively.

2. Materials and Methods

2.1 Materials

The fibres were from the midribs of zalacca plant from the region of Yogyakarta, Indonesia. The midribs were cut from the 3-years-old plant from one plantation and extracted by immersing them in distilled water for two weeks then the fibres were separated from their husk. The fibres were then washed, open-air dried and finally dried in ventilated oven at 105°C for 2 h. They were cut for ± 40 mm length and saved in the plastic container with silica gel for humidity prevention. The chemicals used are analytical distilled water, ethylene glycol, NaOH, CaO and NaHCO_3 .

2.2 Methods

1) Fibre treatment

The pH measured from 1% NaOH, 5% NaOH, saturated $\text{Ca}(\text{OH})_2$ and saturated NaHCO_3 solution were 13.40, 14.00, 12.61 and 8.46, respectively.

For sodium hydroxide treatment, five grams of fibres were soaked in 100 ml 1% and 5% NaOH for 2 hours, respectively. The fibres then were rinsed by distilled water and dried in the ventilated oven at 80°C for 24 hours. The sodium bicarbonate treatment were done by immersing 5 g of fibres in 100 ml 10% NaHCO_3 for 24, 120 and 240 h, respectively. In the calcium hydroxide treatment, five grams of fibres in were submerged in 100 ml 0.15% $\text{Ca}(\text{OH})_2$ for 24, 48 and 72 h, respectively. The rinsing and drying procedure were the same as those of NaOH treatment.

2) Fibre content analysis

The zalcacca fibre content of cellulose, hemicellulose and lignin was established based on Kurchner-and-Hoffer, NFT 12-008 standard and Klason methods, respectively [12]. The untreated and treated fibres were powdered using high-power blender. The lignin was obtained as the insoluble component after the extraction and hydrolisis of samples with CH_2Cl_2 and 72% H_2SO_4 , respectively. The cellulose was gained as the insoluble fraction of the samples after extracted with CH_2Cl_2 and added with the mixture of ethanol and 95% HNO_3 . The hemicellulose was extracted by distillation after mixed in HBr , heated and transformed into $\text{C}_5\text{H}_4\text{O}_2$.

3) SEM examination

The morphology of fibre surface before and after the chemical treatment were examined using scanning electron microscopy (SEM) FEI Type Inspect S-50. The samples were gold coated using low-vacuum sputtering machine before positioned on a silver-painted holder and entered into the chamber of the SEM equipment.

4) Wettability test

The two ends of untreated and treated fibres then were tied in a frame. The distilled water and ethylene glycol (1 μl each) then were dropped by a micropipette to the fibre. The contact angle formed between the liquid and the surface of the fibers were observed and measured by the optical microscope equipped by Optiflex[®] software. The measured contact angle for distilled water and ethylene glycol then was put into eq. (4) simultaneously so that the surface energy of the fibres was gained.

3. Results and Discussion

A. Fibre Content analysis

The percentage of cellulose, hemicellulose and lignin content of untreated and sodium hydroxide, sodium bicarbonate and calcium hydroxide treated ZF is shown in Fig. 1. The untreated ZF has the cellulose content of 42.54%, higher than the alfa grass [13], coir fibres [14], wheat straw [15] and sugarcane bagasse [16].

The sodium hydroxide treatment increase the percentage of cellulose content highest (46.34%) compared with the other treatment. It also partially eliminates the hemicellulose and lignin content. The higher concentration of NaOH tends to lower the hemicellulose and cellulose content but raises the percentage of lignin content.

The treatment with sodium bicarbonate rises the percentage of cellulose content but it is not as effective as NaOH treatment. It is due to the lower basicity of the NaHCO_3 solution compared to NaOH. The elimination of hemicellulose content using NaHCO_3 is comparable with the NaOH treatment. The calcium hydroxide treatment evenly reduces the hemicellulose, lignin and cellulose. The longer treatment tends to decrease the percentage of cellulose and hemicellulose content. This is correlated with the study of Le Troedec and co-workers (2008) on the effect of various chemical treatment on the properties of hemp fibres. It shows that the $\text{Ca}(\text{OH})_2$ treatment decrease the degradation temperature

of cellulose but the treatment has only little effect on the crystallinity index. This indicates that the treatment does not increase or decrease the crystalline portion of the fibres.

B. SEM Examination

The morphology of untreated ZF surface is shown in Fig. 2 (a). The surfaces of sodium hydroxide treated fibres are exhibited in Fig 2 (b) and (c) for 1% and 5% NaOH, respectively. It shows that the contours of NaOH treated fibres are clearly visible than the untreated one. The higher concentration of the solution causes the larger surface energy due to the cleaner and rougher surface of the fibres inducing the higher adhesivity between the fluid and fibres. This cleaning effect is caused by the basicity of the NaOH. Due to its pH value, this solution can be classified as caustic [18].

The sodium bicarbonate treatment for 24, 120 and 240 h also causes the surface of ZF become cleaner and rougher, as indicated in Fig. 3 (a), (b) and (c), respectively. However, this effect is not as strong as for sodium hydroxide treatment. This is due to the effect of NaOH which infiltrates the amorphous parts of the lignocellulosic fibre, cleavages the bond between hemicellulose and lignin, and partially dissolves the hemicellulose and lignin.

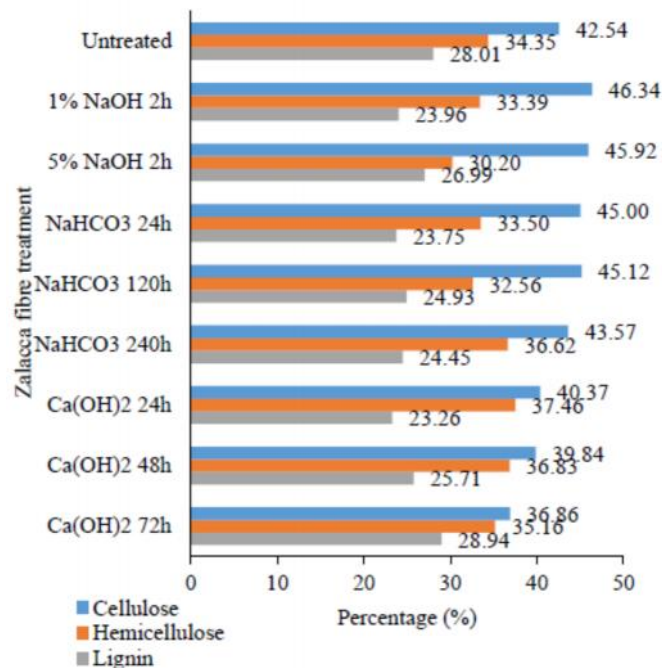


Figure 1. The percentage of cellulose, hemicellulose and lignin content of ZF before and after the chemical treatment

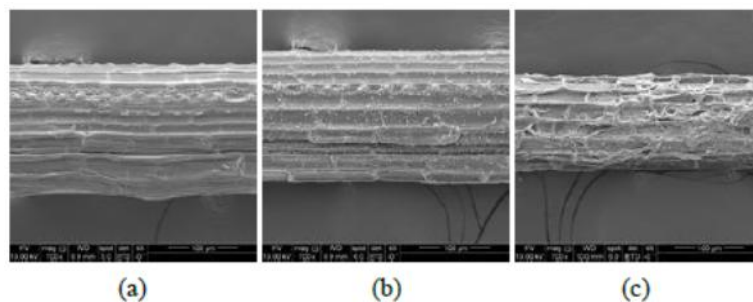


Figure 2. SEM images of ZF surface: (a) without treatment; (b) with 1% NaOH treatment and (c) with 5% NaOH treatment for 2 h

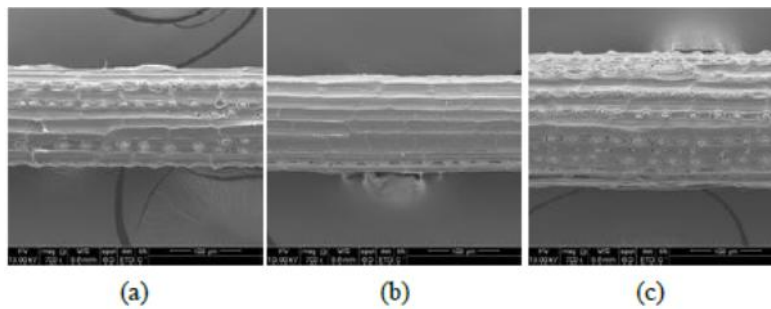


Figure 3. SEM images of ZF surface with NaHCO_3 treatment for: (a) 24 h; (b) 120 h and (c) 240 h

Fig. 4 (a), (b) and (c) show the calcium hydroxide treated ZF for 24, 48 and 72 h, respectively. The fibres surface becomes clean and rough caused by the $\text{Ca}(\text{OH})_2$ as cleaning agent [19].

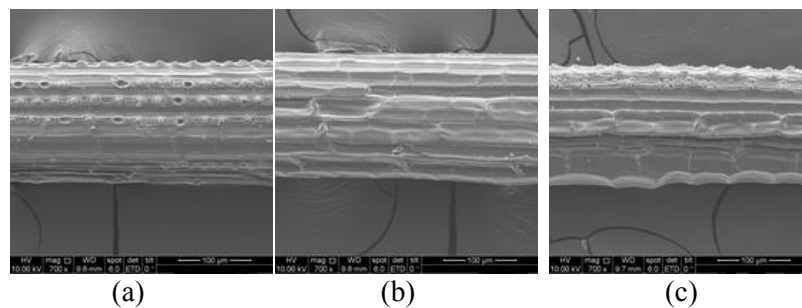


Figure 4. SEM images of ZF surface with $\text{Ca}(\text{OH})_2$ treatment for: (a) 24 h; (b) 48 h and (c) 72 h

C. Contact Angle

The measurement of contact angle between the liquids and fibre surface was shown in Fig. 5 (a) and (b) for distilled water and ethylene glycol, respectively. The contact angles obtained were indicated in Fig. 6 for untreated, alkaline, sodium bicarbonate and lime-water treated ZF, respectively.

The alkaline treatment with 1% and 5% NaOH solution for 2 h decreased the contact angle between the liquid and ZF surface 5.88 and 7.55 % for distilled water and 5.95 and 6.12 % for ethylene glycol, respectively. It indicated that there were a decline in contact angle with the increase of the alkaline concentration.

ZF with sodium bicarbonate treatment for 24, 120 and 240 h experienced the reduction of contact angle 0.32, 0.68 and 2.10 % for distilled water and 0.63, 1.00 and 2.85 % for ethylene glycol, respectively. The lime-water treatment with 0.15 % $\text{Ca}(\text{OH})_2$ solution reduced the contact angle 0.44, 2.01 and 2.96 % for distilled water and 0.19, 1.48 and 2.32 % for ethylene glycol, respectively. Therefore the longer time of both NaHCO_3 and $\text{Ca}(\text{OH})_2$ treatment lowered the contact angle.

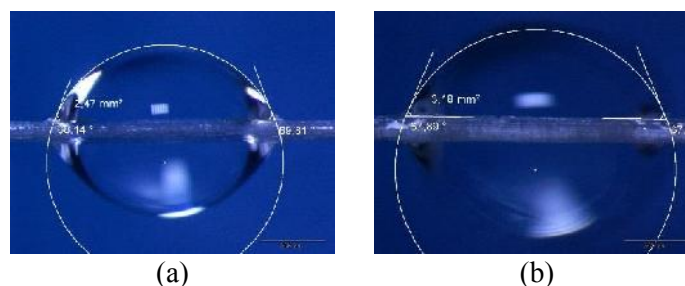


Figure 5. The example of contact angle measurement of ZF surface by: (a) distilled water; (b) ethylene glycol

D. Surface Energy

By putting the values of contact angle obtained and data from the Table 1 into the Eq. (4), the surface energy of the fibres was acquired and shown in Fig. 7. The surface energy of ZF consists of polar and dispersive components. The sodium hydroxide treatment increased both the polar and dispersive surface energy. This is due to the partial elimination of the hemicellulose and lignin binding the cellulose fibrils causes the larger contact are of the fibre surface. The NaOH concentration of 1% and 5 % increases the surface energy for 9.79 and 15.02 %, respectively.

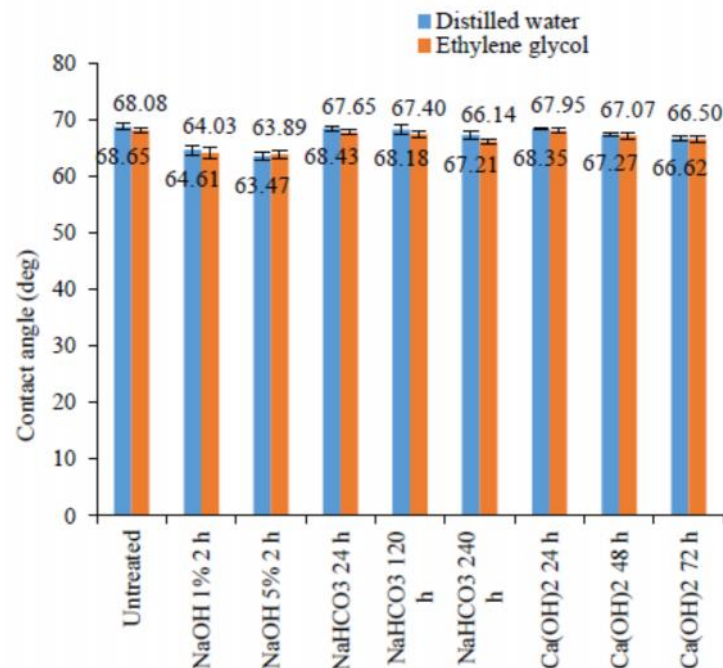


Figure 6. The contact angle measured for untreated, alkaline, sodium bicarbonate and lime-water treated ZF

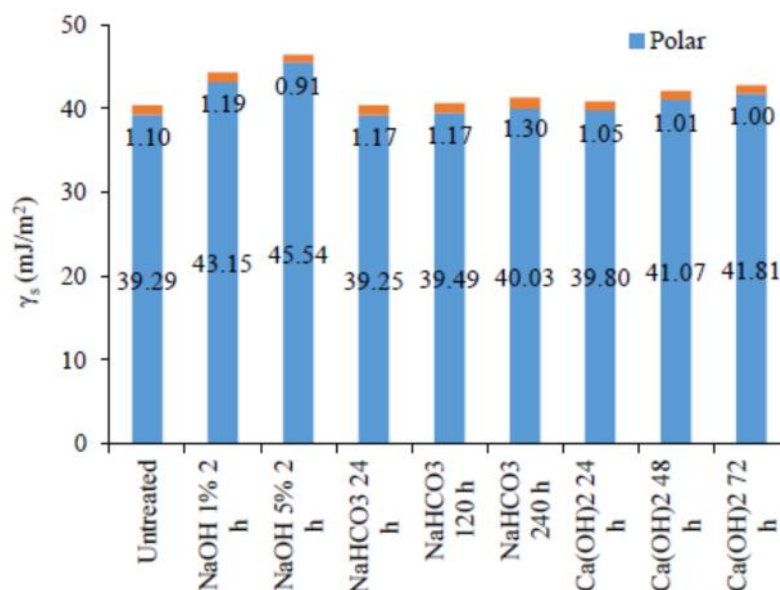


Figure 7. The surface energy of untreated, alkaline, sodium bicarbonate and lime-water treated ZF

Table 1. The surface energy of liquids [9]

Liquid	Surface energy		
	γ_L (mJ/m ²)	γ^d (mJ/m ²)	γ^p (mJ/m ²)
Distilled water	72.8	21.8	51
Ethylene glycol	48	29	19

The sodium bicarbonate treatment of ZF raises both the polar and dispersive surface energy. The longer time of treatment raises the value of surface energy 0.06, 0.67 and 2.31% for 24, 120 and 240 h, respectively. The improvement of surface energy by NaHCO₃ is not as high as for alkaline treatment due to its basicity. The sodium bicarbonate is a moderate alkaline producing carbonic acid and hydroxide ion when dissolved in water.



The OH groups present in the fibre is related mostly with the hydroxyls of alcohol. The interaction with sodium bicarbonate causes the reaction similar to the mercerization treatment [4].

The reaction results in the lower hydrophilicity of the fibre surface. Furthermore, it induces the larger surface energy leading to the higher wettability of the fibre.

The enhancement of ZF surface energy obtained by calcium hydroxide treatment for 24, 48 and 72 h achieves 1.14, 4.20 and 5.98 %, respectively. This is due to the basicity of Ca(OH)₂ which are lower than NaOH and higher than NaHCO₃.

The effect of mercerization-like treatment is influenced by the OH⁻ attracting the H⁺ ion from the hydroxyl groups on the fibre surface. The OH⁻ ions produced by the treating solution depend on its concentration expressed by molarity and especially pH. The higher value of pH indicates the stronger basicity. It was indicated that the increase of surface energy of ZF was proportional to the pH value. Therefore, the effect of the chemical treatment on the wettability is the highest for 5% NaOH, followed by 1% NaOH, Ca(OH)₂ and NaHCO₃. Meanwhile, the longer time of treatment induce the higher wettability of the fibre.

4. Conclusion

The alkaline, lime-water and sodium bicarbonate treatment was done to promote the wettability of zalacca fibres as composite reinforcement. The wettability test was performed by measuring the contact angle between the fluid and the fibre surface. The distilled water and ethylene glycol was used as representation of the polar and dispersive fluids, respectively. The alkaline treatment reduced the contact angle, followed by those of the lime-water and sodium bicarbonate. By putting the value of liquid surface energy of distilled water and ethylene glycol into the Young-Dupres equation, the surface energy of the fibre was determined. The surface energy of the fibre was increased by alkaline treatment, followed by lime-water and sodium bicarbonate treatment. Due to its basicity, the alkaline solution increases the wettability of zalacca fibre, followed by lime-water and sodium bicarbonate ones.

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References

- [1] G. Koronis, A. Silva, and M. Fontul, "Green composites: A review of adequate materials for automotive applications," *Compos. Part B Eng.*, vol. 44, no. 1, pp. 120–127, 2013.
- [2] W. D. Callister and D. G. Rethwisch, *Fundamentals of Materials Science and Engineering an Integrated Approach*, 4th ed. New Jersey: John Wiley and Sons, Ltd., 2012.
- [3] A. Shalwan and B. F. Yousif, "In State of Art: Mechanical and tribological behaviour of polymeric composites based on natural fibres," *Mater. Des.*, vol. 48, pp. 14–24, 2013.
- [4] M. M. Kabir, H. Wang, K. T. Lau, and F. Cardona, "Tensile properties of chemically treated hemp fibres as reinforcement for composites," *Compos. Part B Eng.*, vol. 53, pp. 362–368, 2013.
- [5] S. I. Hossain, M. Hasan, N. Hasan, and A. Hassan, "Effect of Chemical Treatment on Physical , Mechanical and Thermal Properties of Ladies Finger Natural Fiber," *Adv. Mater. Sci. Eng.*, vol. 2013, pp. 1– 6, 2013.
- [6] D. Pasquini, M. N. Belgacem, A. Gandini, and A. A. D. S. Curvelo, "Surface esterification of cellulose fibers: Characterization by DRIFT and contact angle measurements," *J. Colloid Interface Sci.*, vol. 295, no. 1, pp. 79–83, 2006.
- [7] J. N. Israelachvili, *Intermolecular and Surface Forces*, 3rd ed. San Diego: Academic Press Limited, 2011.
- [8] D. K. Owens and R. C. Wendt, "Estimation of the surface free energy of polymers," *J. Appl. Polym. Sci.*, vol. 13, no. 8, pp. 1741–1747, 1969.
- [9] A. Pietak, S. Korte, E. Tan, A. Downard, and M. P. Staiger, "Atomic force microscopy characterization of the surface wettability of natural fibres," *Appl. Surf. Sci.*, vol. 253, no. 7, pp. 3627–3635, 2007.
- [10] W. P. Raharjo, R. Soenoko, A. Purnowidodo, M. A. Choiron, and Triyono, "Mechanical properties of untreated and alkaline treated fibers from zalacca midrib wastes," in *AIP Conference Proceedings*, 2016, vol. 1717, pp. 1–8.
- [11] N. Schlager, J. Weisblatt, and D. E. Newton, *Chemical Compounds*, 1st ed. Detroit: Thomson Gale, 2006.
- [12] V. S. Sreenivasan, S. Somasundaram, D. Ravindran, V. Manikandan, and R. Narayanasamy, "Microstructural, physico-chemical and mechanical characterisation of Sansevieria cylindrica fibres - An exploratory investigation," *Mater. Des.*, vol. 32, no. 1, pp. 453–461, 2011.
- [13] R. M. Rowell, J. S. Han, and J. S. Rowell, "Characterization and Factors Effecting Fiber Properties," *Nat. Polym. an Agrofibers Compos.*, pp. 115–134, 2000.
- [14] A. K. Mohanty, M. Misra, and L. T. Drzal, *Natural Fibers, Biopolymers, and Biocomposites*. 2005.
- [15] S. Panthapulakkal, A. Zereskian, and M. Sain, "Preparation and characterization of wheat straw fibers for reinforcing application in injection molded thermoplastic composites," *Bioresour. Technol.*, vol. 97, no. 2, pp. 265–272, 2006.
- [16] M. Sasaki, "Fractionation of sugarcane bagasse by hydrothermal treatment," vol. 86, pp. 301–304, 2003.
- [17] M. Le Troedec et al., "Influence of various chemical treatments on the composition and structure of hemp fibres," *Compos. Part A Appl. Sci. Manuf.*, vol. 39, no. 3, pp. 514–522, 2008.
- [18] M. Beeks and D. Keller, "Aqueous Cleaning Essentials," in *Handbook for Critical Cleaning Agents and Systems*, 2nd ed., B. Kanegsberg and E. Kanegsberg, Eds. Boca Raton: CRC Press, Taylor & Francis Group, 2011, pp. 35–62.
- [19] R. L. Myers, *100 Most Important Chemical Compounds: A Reference Guide*, 1st ed. Westport Connecticut London: Greenwood Press, 2007.