

Alkali and Silane Treated Ramie Yarn Fiber for 3D-Printed Filament Composite Material Reinforcement [†]

Lilis Safitri * , Sutikno Sutikno and Putu Suwarta

Department of Mechanical Engineering, Institut Teknologi Sepuluh Nopember, Kampus ITS Sukolilo, Surabaya 60111, Indonesia; sutikno@me.its.ac.id (S.S.); putu_suwarta@me.its.ac.id (P.S.)

* Correspondence: 6007222024@student.its.ac.id

[†] Presented at the 8th Mechanical Engineering, Science and Technology International Conference, Padang Besar, Perlis, Malaysia, 11–12 December 2024.

Abstract: Natural fiber such as ramie is a type of reinforcement material derived from natural sources. These reinforcement materials offer an environmentally sustainable solution contributing to eco-friendly practices. However, natural fibers face challenges as reinforcement materials due to the presence of non-cellulosic impurities and structural irregularities, which reduce crystallinity. This study explores the impact of alkali using sodium hydroxide (NaOH 5%) and silane using 3-(Aminopropyl) trimethoxy silane (APTES 1% and 3%) treatments on the chemical structure and crystallinity index of ramie yarn fiber (*Boehmeria nivea*). Alkali treatment effectively removes non-cellulosic impurities, resulting in an improved crystalline structure, while silane treatment modifies the fiber surface, introducing functional groups that alter its chemical structure. The chemical modifications were analyzed by using Fourier transform infrared spectroscopy (FTIR), and the crystallinity index was measured through X-ray diffraction (XRD). The findings revealed that alkali treatment significantly increased the crystallinity index (CrI) of ramie fibers to the highest value of 82.63%, and silane treatment primarily enhanced surface reactivity, facilitating better adhesion and chemical bonding with the matrix. This research highlights the potential of alkali and silane treatments for optimizing ramie fiber for use in advanced polymer composite applications.



Academic Editors: Noor Hanita Abdul Majid, Agus Dwi Anggono, Waluyo Adi Siswanto, Tri Widodo Besar Riyadi, Mohammad Sukri Mustapa, Nur Rahmawati Syamsiyah and Afif Faishal

Published: 13 February 2025

Citation: Safitri, L.; Sutikno, S.; Suwarta, P. Alkali and Silane Treated Ramie Yarn Fiber for 3D-Printed Filament Composite Material Reinforcement. *Eng. Proc.* **2025**, *84*, 57. <https://doi.org/10.3390/engproc2025084057>

Copyright: © 2025 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: alkali; silane; ramie yarn fiber

1. Introduction

The growing interest in sustainable materials has led to significant advancements in the development and application of composite materials across various industries. In recent years, many sectors have shifted from synthetic to eco-friendly materials, including in structural applications. Composite materials, known for their versatile properties, consist of two primary components: the reinforcement and the matrix. The reinforcement, which provides strength and stiffness, can be classified into synthetic or natural fibers, available in various forms such as long or short, and randomly or directionally aligned [1]. The matrix, often a polymer that is either thermoplastic or thermosetting, binds the fibers together and transfer the applied loads within the composite structure.

Natural fibers, such as those derived from plants, have gained increasing attention as alternatives to traditional synthetic fibers like carbon, aramid, and E-glass. Their benefits include low cost, ease of processing, high availability, and biodegradability [2,3]. Plant-based fibers, such as ramie (*Boehmeria nivea*), also offer advantageous mechanical properties, including higher stiffness and superior strength-to-weight ratios. When their fibrils are

oriented uniaxially, these fibers exhibit enhanced mechanical performance [4]. Furthermore, the use of biodegradable matrices in combination with natural fibers enhances the sustainability of composites and reduces production costs [5].

Ramie is one potential natural fiber that grows in tropical climate regions like Indonesia. These natural fibers are produced from harvest to degumming [6]. Ramie, a bast fiber known for its high cellulose content and tensile strength, offers a high elastic modulus of 44–128 GPa, comparable to glass fiber's 70 GPa, making it a strong and sustainable candidate for polymer composite reinforcement [7–9]. However, untreated natural fibers often suffer from poor interfacial bonding with polymer matrices due to their hydrophilic nature, limiting their application in high-performance composites [10]. Surface modifications, such as alkali and silane treatments, are widely employed to improve fiber–matrix compatibility by altering the fiber's chemical structure and enhancing its mechanical and interfacial properties. Alkali treatment removes non-cellulosic substances, including hemicellulose and lignin, thereby increasing fiber crystallinity and exposing hydroxyl groups for better bonding [11–13]. Silane treatment, on the other hand, introduces silanol groups, which form covalent bonds with both the fiber surface and the polymer matrix, further improving adhesion [14,15].

This study investigates the effects of alkali and silane treatments on the chemical structure and crystallinity properties of ramie yarn fiber. Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD) analyses are employed to evaluate the structural changes and crystallinity index. The findings aim to provide insights into the potential of treated ramie fibers as sustainable reinforcement in 3D printing filament composite materials, contributing to the development of eco-friendly and high-performance materials.

2. Experimental

2.1. Material

Ramie yarn fiber was purchased from local corporate CV. Ramindo Berkah Persada Sejahtera, Central Java, Indonesia. Reagent-grade sodium hydroxide (NaOH) pellets and 3-aminopropylethoxysilane (APTES) were acquired from Sigma Al-adrich.

2.2. Ramie Fiber Extrusion

Figure 1 illustrates the extraction process of ramie yarn fiber. The process begins with the harvesting of ramie stems and continues with steaming to soften the fibers, making decortication more efficient. The stems are manually decorticated to separate the fibers from the stalks. The extracted fibers undergo a degumming process to remove impurities, such as gum and pectin, resulting in cleaner and more refined fibers. Following degumming, the fibers are straightened, cut, and rolled into manageable sizes.

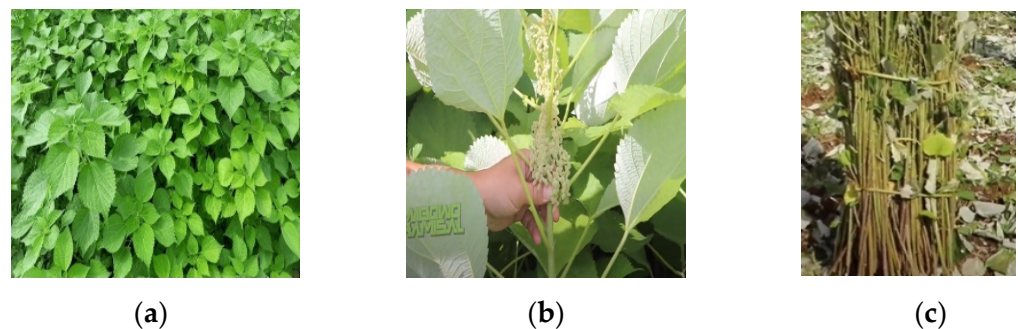


Figure 1. Cont.



Figure 1. Process of ramie fiber yarn extraction: (a) Ramie. (b) Harvesting. (c) Steaming of ramie. (d) Ramie yarn fiber decorticated. (e) Extracted ramie yarn fiber.

2.3. Surface Treatment on Ramie Yarn Fiber

2.3.1. Alkali Treatment

The alkali treatment process began with the preparation of a 5% sodium hydroxide (NaOH) solution. A calculated amount of NaOH pellets was dissolved in distilled water under constant stirring to ensure a homogenous solution. The ramie fibers were then fully immersed for a duration of 2 h in the 5% NaOH solution following the procedure outlined in Figure 2. The fibers were immersed in the solution of NaOH and aquades (distilled water) for two hours at a controlled temperature of 50 °C, allowing for sufficient time for the alkali to react with non-cellulosic substances, including hemicellulose, lignin, and pectin. After the soaking process, the fibers were thoroughly rinsed multiple times with distilled water to remove residual NaOH. The rinsing continued until the fibers reached a neutral pH, which was confirmed by using litmus paper to ensure the complete removal of alkali remnants. Following rinsing, the fibers were carefully spread out and placed in a laboratory dryer. They were dried at 100 °C for 50 min to achieve consistent moisture removal and prepare them for subsequent treatments. This controlled drying process ensured that the fibers retained their structural integrity while being fully dehydrated.

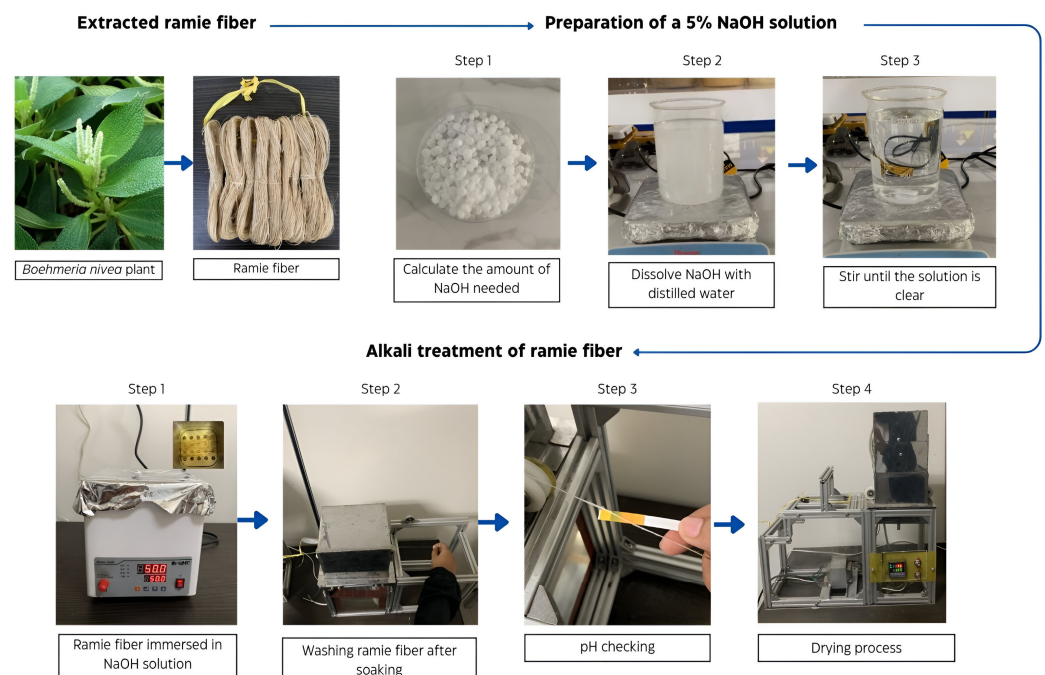


Figure 2. Process of alkali treatment.

2.3.2. Silane Treatment

A solution of ethanol and distilled water in a 70:30 ratio was prepared by stirring it until it became homogeneous outlined in Figure 3 [12]. Next, 3-(Aminopropyl) trimethoxysilane (APTES) was added to the solution, which was stirred for 15 min to ensure proper mixing. The pH of the mixture was adjusted to a range of 4–5 by using acetic acid. The ramie fibers were then submerged in the solution and left to soak for 1 h at room temperature. After the immersion, the fibers were thoroughly rinsed multiple times to eliminate any residual silane from their surface. The treated fibers were dried in a dryer at 100 °C for 50 min to remove all moisture and prepare them for further analysis.

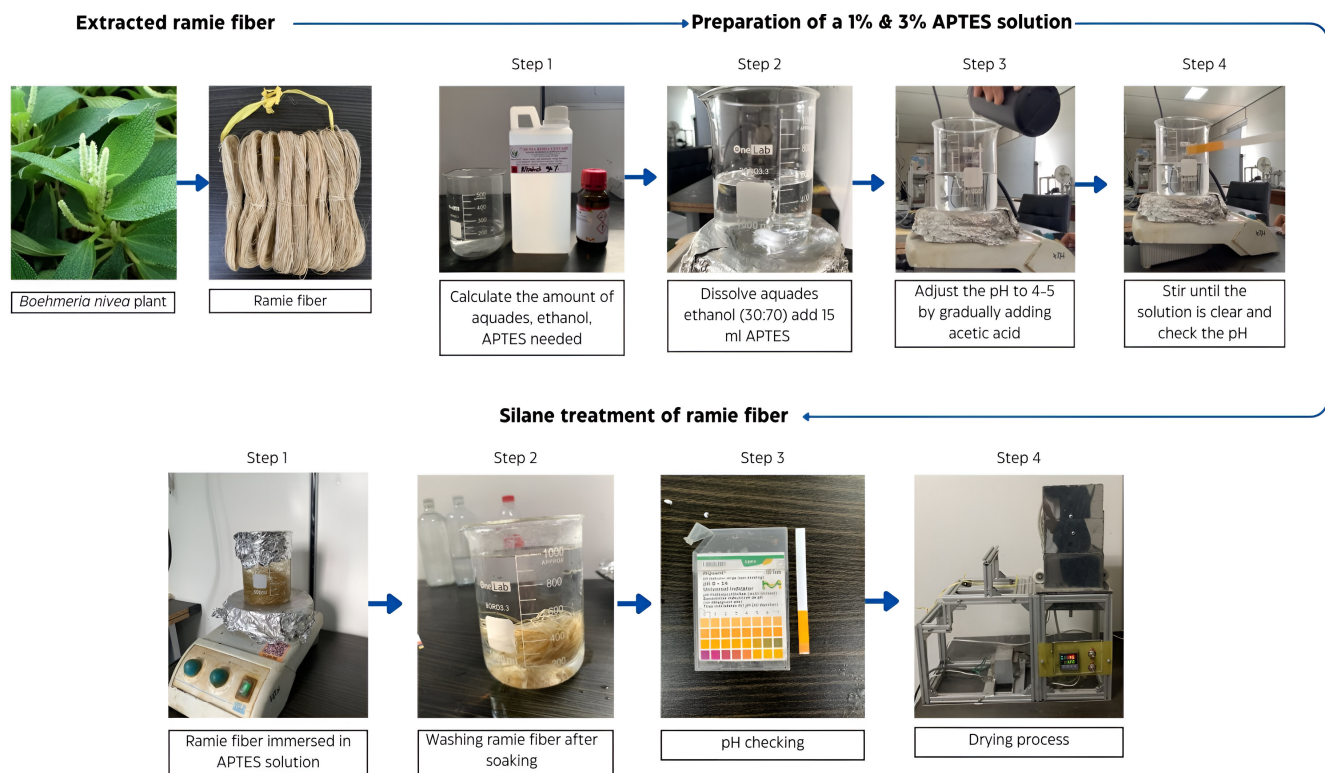


Figure 3. Process of silane treatment.

2.4. Characterization

2.4.1. Fourier Transmission Infrared Analysis (FTIR)

The Nicolet iS10 FTIR spectrometer (Thermo Scientific, Massachusetts, USA) was used to analyze the chemical compositions and functional groups of the treated and untreated ramie fibers. After being positioned on a KBr plate, dried fiber specimens were put into the infrared chamber. To find the distinctive functional groups, the fiber samples' infrared spectra were captured over a wavelength range of 450 to 4000 cm^{-1} .

2.4.2. X-Ray Diffraction Analysis (XRD)

The crystal structure and crystallinity index (CrI) of untreated and treated ramie fibers were analyzed by using an X-Ray diffractometer (model Panalytical X'Pert ProMPD diffractometer) with a Cu-K α radiation source ($\lambda = 0.154056 \text{ nm}$). The measurements were performed over a 2θ range of 5° to 60° at a scan speed of $10^\circ/\text{min}$. The relative crystallinity index (CrI) was calculated by using Segal's Formula (1):

$$\% \text{ Crystallinity} = \frac{I_{cc}}{I_{cc} + I_{ca}} \times 100 \quad (1)$$

The crystallinity index (CrI) is determined by the crystalline intensity lattice diffraction (I_{cc}) and the diffraction intensity of the amorphous region (I_{am}).

3. Result

3.1. Chemical Component Analysis

The FTIR result shown in Figure 4. As seen in the Figure 4, spectra reveal a peak at 3326 cm^{-1} , corresponding to the stretching of primary hydroxyl (O–H) groups in cellulose and hydrogen bonding due to absorbed moisture. The intensity of this peak decreases after the NaOH and APTES treatments, indicating the reduction in hydroxyl groups due to the removal of hemicellulose and lignin or substitution with organo-siloxy groups (–OSiR) during APTES treatment. The peak at 2900 cm^{-1} represents the stretching of aliphatic C–H groups, associated with the aliphatic moieties of hemicellulose and cellulose. For untreated fibers, the peak at 1745 cm^{-1} is attributed to the C=O stretching of acetyl groups in hemicellulose or ester linkages in lignin and hemicellulose. This peak disappears entirely after NaOH treatment, confirming the removal of lignin and most of the hemicellulose. Similarly, the peak at 1242 cm^{-1} , representing the C–O stretching of the aryl group in lignin, is reduced or disappears after treatment, indicating lignin removal during alkali treatment.

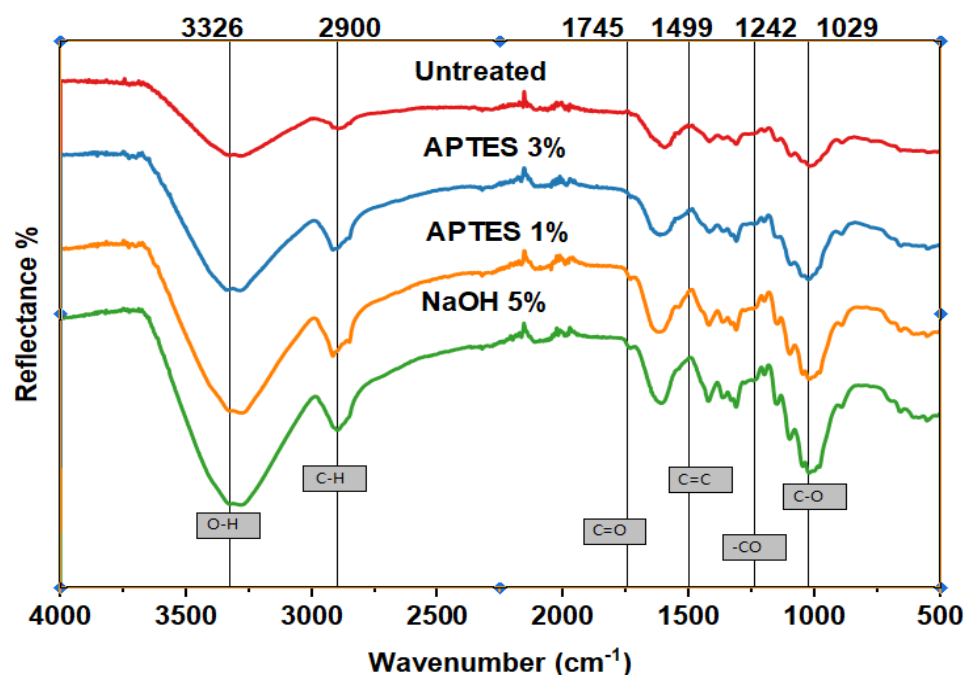


Figure 4. FTIR spectra of ramie yarn fiber.

For fibers treated with APTES, the spectra show new peaks or changes in intensity in the region of $750\text{--}1200\text{ cm}^{-1}$, which indicate the presence of –O–Si–O– and –Si–O–C– stretching vibrations from organo-siloxy groups. The increased intensity of the peak around $1029\text{--}1050\text{ cm}^{-1}$ suggests the overlap between C–O stretching from cellulose and Si–O–Si stretching, supporting the successful grafting of silane onto the fiber surface.

The FTIR spectra of fibers treated with 1% and 3% APTES shown in Figure 5. Characteristic peaks that confirm the successful silane modification of the fiber surfaces. A prominent peak around 1100 cm^{-1} corresponds to the stretching vibrations of Si–O–Si bonds, which result from the condensation of silanol (Si–OH) groups into siloxane linkages during the silane treatment. This peak is more intense for fibers treated with 3% APTES, indicating a higher degree of silane grafting due to the increased concentration of the silane agent. Additionally, a peak at approximately 840 cm^{-1} represents the bending vibrations

of Si-O-Si groups, further confirming the presence of siloxane bonds. The increased intensity of these peaks for 3% APTES-treated fibers suggests enhanced silane interaction and grafting compared with the 1% treatment. This indicates that higher concentrations of APTES improve the extent of fiber modification. These chemical changes are significant for improving the interfacial adhesion between fibers and the polymer matrix in composite materials. By introducing siloxane groups and enhancing surface compatibility, the silane treatment helps to optimize the mechanical and thermal performance of composites. This demonstrates the effectiveness of APTES treatment in modifying natural fibers for advanced material applications.

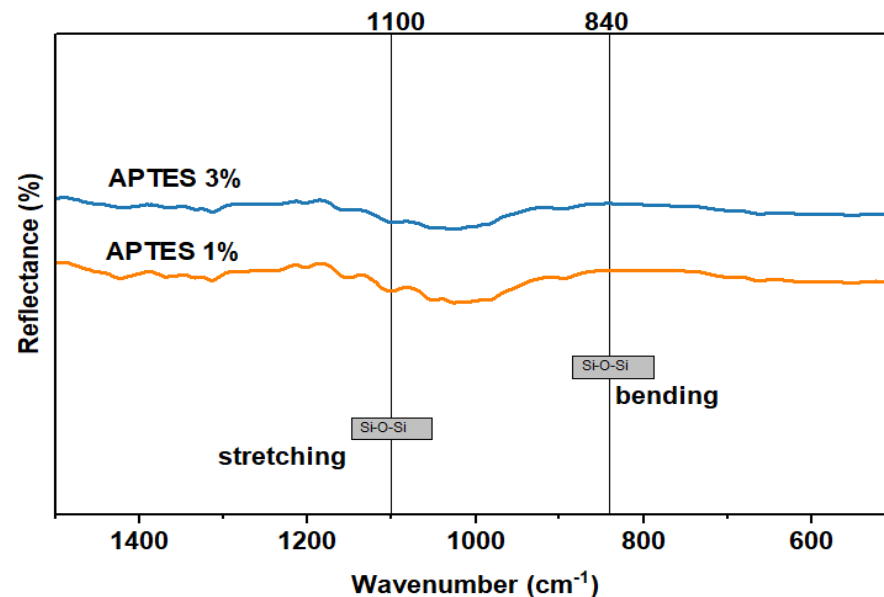


Figure 5. FTIR spectra of ramie yarn fiber treated with silane.

3.2. Crystallinity Index Analysis

The XRD spectrum intensity is shown in Figure 6 with two distinct peaks around $2\theta = 15^\circ$ (101) to $2\theta = 16.4^\circ$ (111) and $2\theta = 22.7^\circ$ (002). The lattice plane for the crystalline structure of type I (I β) cellulose is indicated by these peaks [16]. The majority of cellulose in nature is type I. On the other hand, the crystallinity index (CrI) increases after alkali treatment, which releases hydrogen to create bonds with the hydroxyl (OH) ions in the cellulose fibers. An additional peak at $2\theta = 34.2^\circ$ represents the lattice plane for cellulose type I [17]. There is also a small peak around $2\theta = 20.2^\circ$, which marks the start of structural changes in the cellulose caused by NaOH treatment. This peak suggests that cellulose type I begins to transform into type II, indicating a breakdown in the crystalline region of the cellulose chain.

After treatment with 5% NaOH, CrI increased to 82.63% shown in Table 1, indicating enhanced crystallinity due to the removal of hemicellulose and other amorphous components. The alkali treatment facilitates the reorganization and close packing of cellulose chains, which contributes to a higher degree of crystallinity. This structural improvement is desirable for applications requiring stronger and more thermally stable fiber composites. Conversely, silane treatment resulted in a reduction in CrI. Fibers treated with 1% APTES exhibited a CrI of 79.88%, while those treated with 3% APTES showed a lower CrI of 71.35%. The results indicate that alkali treatment enhances the crystalline nature of the fibers by removing non-cellulosic components, while silane treatment reduces crystallinity due to the incorporation of silane groups. Silane treatment reduces crystallinity by introducing silane groups to the fiber surface, which increases hydrophobicity. This modification makes

the fiber surface more compatible with hydrophobic polymer matrices, enhancing interfacial bonding. By reducing the exposure of hydroxyl (OH) groups and creating a less polar surface, silane-treated fibers achieve better adhesion with hydrophobic polymers, improving the overall performance of the composite material. This dual approach allows for tailored fiber properties depending on the specific application, balancing structural rigidity with improved interfacial bonding in composite materials.

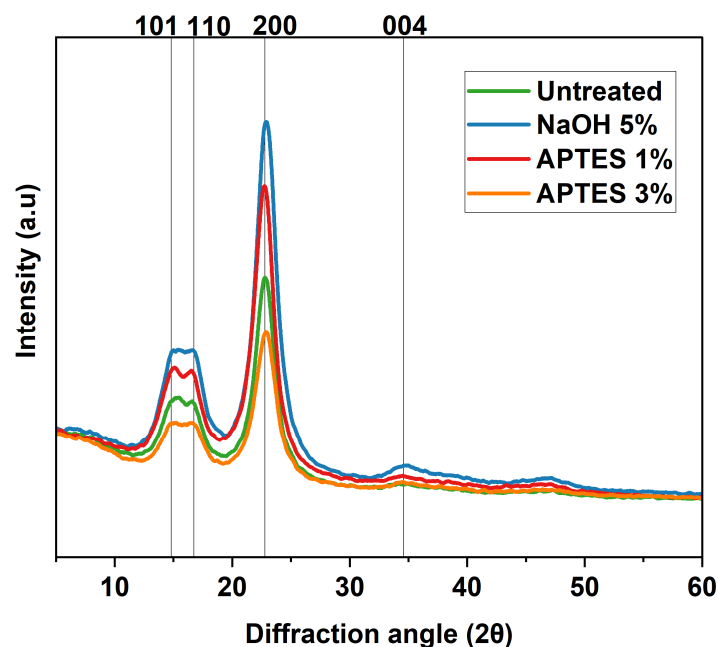


Figure 6. XRD patterns of untreated and treated ramie fiber yarn extraction.

Table 1. The crystallinity indexes of untreated and treated ramie yarn fiber.

No.	Sample	All Crystalline Area	All Crystalline and Amorphous	Crystallinity Index (%)
1	Untreated	6721.10	8826.28	76.05
2	NaOH 5%	1067.26	12,918.18	82.63
3	APTES 1%	9145.15	11,448.10	79.88
4	APTES 3%	5344.14	7490.32	71.35

4. Conclusions

This study demonstrates the effects of alkali and silane (APTES) treatments on the chemical, structural, and morphological properties of ramie fibers, with a focus on their potential use in composite materials.

FTIR analysis confirmed the successful reduction in hemicellulose and lignin during the treatment of alkali and the successful grafting of silane onto the fiber surface during APTES treatment. Alkali-treated fibers exhibited a reduction in hydroxyl groups, enhancing the compatibility of the former with hydrophobic polymer matrices. Silane treatment introduced siloxane bonds, as evidenced by the Si–O–Si stretching and bending peaks, which improved the interfacial adhesion between fibers and polymers.

XRD analysis revealed that alkali treatment increased the crystallinity index (CrI) of the ramie yarn fibers, while it reduced the amorphous components and the closer packing of cellulose chains. However, silane treatment led to a decrease in CrI, particularly at higher APTES concentrations, due to the deposition of silane onto the fiber surface. This indicates

that while alkali treatment enhances the crystalline structure of the fibers, silane treatment primarily modifies the surface chemistry to improve fiber–matrix interactions.

Overall, the dual treatments enable the tailoring of ramie fiber properties for composite applications. The alkali treatment enhances the mechanical of the fibers by increasing crystallinity, while the silane treatment improves interfacial bonding with polymers. These findings underscore the importance of optimizing treatment parameters to balance structural and surface modifications, ultimately enhancing the performance of ramie fiber-reinforced composites.

Author Contributions: Preparation of initial draft includes conceptualization, methodology, investigation, formal analysis, data curation, and writing—original draft preparation: L.S.; Supervision, review, and feedback: S.S. and P.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Ministry of Education and Culture, Republic of Indonesia, under grant number 1855/PKS/ITS/2024.

Institutional Review Board Statement: Not applicable. This study did not involve humans or animals that require ethical review or approval.

Informed Consent Statement: Not applicable. This study did not involve human participants.

Data Availability Statement: The data that support the findings of this study are available upon request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Zachariah, S.A.; Shenoy, S.; Pai, D. Experimental analysis of the effect of the woven aramid fabric on the strain to failure behavior of plain weaved carbon/aramid hybrid laminates. *FU Mech. Eng.* **2024**, *22*, 013. [\[CrossRef\]](#)
2. Qi, Y.; Huang, Y.-X.; Ma, H.-X.; Yu, W.-J.; Kim, N.-H.; Zhang, Y.-H. Influence of a Novel Mold Inhibitor on Mechanical Properties and Water Repellency of Bamboo Fiber-based Composites. *J. Korean Wood Sci. Technol.* **2019**, *47*, 336–343. [\[CrossRef\]](#)
3. Sanjay, M.R.; Madhu, P.; Jawaidd, M.; Sentharamaikannan, P.; Senthil, S.; Pradeep, S. Characterization and properties of natural fiber polymer composites: A comprehensive review. *J. Clean. Prod.* **2018**, *172*, 566–581. [\[CrossRef\]](#)
4. Djafari Petroudy, S.R. Physical and mechanical properties of natural fibers. In *Advanced High Strength Natural Fibre Composites in Construction*; Elsevier: Amsterdam, The Netherlands, 2017; pp. 59–83, ISBN 978-0-08-100411-1.
5. Jain, B.; Mallya, R.; Nayak, S.Y.; Heckadka, S.S.; Prabhu, S.; Mahesha, G.T.; Sancheti, G. Influence of Alkali and Silane Treatment on the Physico-Mechanical Properties of Grewia serrulata Fibres. *J. Korean Wood Sci. Technol.* **2022**, *50*, 325–337. [\[CrossRef\]](#)
6. Wicaksono, I.A.; Windani, I.; Erny, E. Prioritas Strategi Pengembangan Serat Rami (Boehmeria nivea proper) Jenis Ina Grass di Kabupaten Wonosobo. *Agrolandnasional* **2021**, *28*, 197–203. [\[CrossRef\]](#)
7. Samir, A.; Ashour, F.H.; Hakim, A.A.A.; Bassyouni, M. Recent advances in biodegradable polymers for sustainable applications. *NPJ Mater. Degrad.* **2022**, *6*, 68. [\[CrossRef\]](#)
8. Karimah, A.; Ridho, M.R.; Munawar, S.S.; Adi, D.S.; Ismadi; Damayanti, R.; Subiyanto, B.; Fatriasari, W.; Fudholi, A. A review on natural fibers for development of eco-friendly bio-composite: Characteristics, and utilizations. *J. Mater. Res. Technol.* **2021**, *13*, 2442–2458. [\[CrossRef\]](#)
9. Hosseini-Toudeshky, H.; Navaei, A. Characterization of elastic modulus at glass/fiber interphase using single fiber composite tensile tests and utilizing DIC and FEM. *Mech. Adv. Mater. Struct.* **2024**, *31*, 6126–6138. [\[CrossRef\]](#)
10. Abubakar, M.N.; Bello, T.K.; Isa, M.T.; Lawal, K. Effect of alkaline treatment on the physical and mechanical properties of borassus flabellifer leaf fiber. *Polym. Bull.* **2023**, *80*, 12577–12590. [\[CrossRef\]](#)
11. Lee, S.; Park, C.H. Influence of alkaline treatment on surface roughness and wetting properties of hydrophobized silk fabrics. *Text. Res. J.* **2018**, *88*, 777–789. [\[CrossRef\]](#)
12. Hashim, M.Y.; Amin, A.M.; Marwah, O.M.F.; Othman, M.H.; Yunus, M.R.M.; Chuan Huat, N. The effect of alkali treatment under various conditions on physical properties of kenaf fiber. *J. Phys. Conf. Ser.* **2017**, *914*, 012030. [\[CrossRef\]](#)

13. Orue, A.; Jauregi, A.; Unsuain, U.; Labidi, J.; Eceiza, A.; Arbelaiz, A. The effect of alkaline and silane treatments on mechanical properties and breakage of sisal fibers and poly(lactic acid)/sisal fiber composites. *Compos. Part A Appl. Sci. Manuf.* **2016**, *84*, 186–195. [[CrossRef](#)]
14. Lu, T.; Jiang, M.; Jiang, Z.; Hui, D.; Wang, Z.; Zhou, Z. Effect of surface modification of bamboo cellulose fibers on mechanical properties of cellulose/epoxy composites. *Compos. Part B Eng.* **2013**, *51*, 28–34. [[CrossRef](#)]
15. Alshahrani, H.; Vr, A.P. Mechanical, wear, and fatigue behavior of alkali-silane-treated areca fiber, RHA biochar, and cardanol oil-toughened epoxy biocomposite. *Biomass Conv. Bioref.* **2024**, *14*, 6609–6620. [[CrossRef](#)]
16. Kuo, C.-H.; Lee, C.-K. Enhancement of enzymatic saccharification of cellulose by cellulose dissolution pretreatments. *Carbohydr. Polym.* **2009**, *77*, 41–46. [[CrossRef](#)]
17. Wan Ishak, W.H.; Ahmad, I.; Ramli, S.; Mohd Amin, M.C.I. Gamma Irradiation-Assisted Synthesis of Cellulose Nanocrystal-Reinforced Gelatin Hydrogels. *Nanomaterials* **2018**, *8*, 749. [[CrossRef](#)] [[PubMed](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.