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Effect of Addition Titanium Dioxide Nanoparticle on Properties of Pineapple Leaf Fiber Mediated TEMPO Oxidation

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ABSTRACT

Indonesia is an agricultural country with the potential to grow many plants as natural fiber sources. In order to improve its properties, natural fiber needs to be treated by applying nanomaterial so that it can compete with the characteristics of synthetic fibers. The study aims to determine the influence of adding titanium dioxide (TiO_2) nanoparticles on pineapple leaf fiber (PALF) characteristics. The PALF was collected from the Subang plantation (Indonesia). The chemical treatment was carried out with pre-treatment using an alkalization process for 3 hours, and the oxidation process was carried out with TEMPO. TiO_2 nanoparticle grafting was carried out by adding a silane solution with a ratio of 1:10 with alcohol. The characteristics of PALF were observed using XRD, FTIR, SEM, and tensile tests. The results show that the crystallinity of the PALF increased after TEMPO treatment. PALF form Si-O-C bond identified at a wavelength of 1158 cm^{-1} after silane treatment. Ti – O – Si functional groups were identified in the 660 cm^{-1} – 670 cm^{-1} wavelength range. In the fiber surface, agglomerated TiO_2 nanoparticles are formed and increase with increasing TiO_2 nanoparticle concentration. The tensile stress of treated PALF is increased by 125%, with the highest tensile strength of 1279.18 MPa, obtained by TiO_2 nanoparticle concentration of 1.0%.

Keywords: *Pineapple leaf fiber, TEMPO, tensile strength, titanium dioxide*

I. Introduction

Technological developments in Indonesia, especially in materials, continue to increase yearly because composite materials are often used as a substitute for metal materials. Indonesia has a tropical climate and is known as an agricultural country. Compared to synthetic fibers, Indonesia has the potential to grow many plants that can be used as fiber for organic materials that can be decomposed or degraded by the environment. Natural fibers are widely used because they have low production costs, are environmentally friendly, are safe for human health, and can replace substitute synthetic fiber [1].

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The pineapple fruit is well-known among Indonesians. Pineapple accounts for 2.5 billion pineapples produced in Indonesia, making it one of the world's top 10 producers. According to the Indonesian Central Statistics Agency (BPS), pineapple production in 2020 will exceed 2 million tons [2]. Pineapple leaf fiber (PALF) has the potential to be used because it has a relatively high fiber content and a mechanical strength of 164.55 MPa when alkalized by NaOH 6% [3]. The other fiber was treated using alkali 5%, which increased its composite's flexural strength [4][5].

Natural fibers must be treated so that they can later bind to nanoparticles. The issue with cellulose-reinforced composites is that they are hydrophilic [6]. The hydrophilic nature of the fibers is opposite to that of the polymer to be used, namely hydrophobic as a matrix material. Hydrophilic is the property of a compound that can bond with water, whereas hydrophobic is the property of a compound that cannot bond with water [7]. Special treatment has been performed to improve the strength of natural fiber, including adding 6% alkali, which can increase tensile strength up to 82% [8]. Grafting using silane increases the interface shear stress of an epoxy composite by 129% at a silane concentration of 10% [1]. Using inorganic nanoparticles in natural fibers can also affect the fiber's natural properties, which range from hydrophilic to hydrophobic [9]. Introducing nanomaterials in natural fiber polymer composites may lead to fiber properties such as antibacterial [10][11], anti-static [12], UV protection [13], or superhydrophobic surface [14].

Titanium dioxide (TiO_2) is the element titanium's natural oxide with natural polymorphs such as brookite, anatase, and rutile [15]. They are recognized as among the most widely used nano-scale materials in various industries because of their widespread accessibility, lack of toxicity, affordability, biocompatibility, and strong chemical stability [16]. Incorporating TiO_2 nanoparticles into the polymer matrix could produce synergistic effects in their composite form. Adding TiO_2 nanoparticles to cellulose-based composites increases the composite elongation at break to 92% [17]. TiO_2 nanoparticles reinforced with natural fibers can also increase flexural strength because TiO_2 nanoparticle reduces the empty gaps between natural fibers and the epoxy matrix and increases tensile strength [18] and flexural strength up to 20% [19]. Grafting TiO_2 nanoparticles into natural fiber using the dip-coat method increases fiber tensile strength [20]. Silane-mediated grafting of TiO_2 nanoparticles into Sansevieria fiber slightly increases the strength of the fiber [1], so it needs to optimize the fiber surface so TiO_2 nanoparticles can grafted more efficiently into cellulose fiber.

Oxidation treatment on the fiber surface is conducted by adding oxygenated functional groups to the fiber surface [21]. The oxidation process mediated by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) presents a prospective approach for producing cellulose derivatives through surface modification. The utilization of oxidizing reactant, TEMPO, can change polysaccharide hydroxyl groups that are hydrophilic to carboxyl groups that are hydrophobic [22]. The TEMPO oxidation facilitates the complete dispersion of native cellulose in water, reaching individual nanofibrils or elementary fibrils. The resulting TEMPO-oxidized cellulose fibers incorporate negatively charged carboxyl groups onto the cellulose surface, forming uniform oxidized cellulose suspensions that are stabilized with surface charge [23]. These surface charges and reactivity play a dominant role in the sedimentation and aggregation of TiO_2 nanoparticles. So, this study aims to determine the influence of adding TiO_2 nanoparticles on PALF properties after being oxidized by TEMPO.

II. Materials and Methods

1. Materials

Natural fibers were obtained from pineapple fruit plants in Subang, West Java, Indonesia. In this study, the special treatment was oxidation with the reactant TEMPO followed by grafting by Silane (KH560, Sinoconvoy Materials, China) and TiO_2 nanoparticles (Sigma Aldrich, Singapore).

2. TEMPO Oxidation

PALF with a length of 10 cm and a mass of 3 grams were prepared, and an oxidation solution was prepared by mixing the compounds (0.1 gram of NaBr, 3.1 gram of NaClO, and TEMPO of 0.016 gram) into distilled water until a total solution volume of 300 ml was reached. Add the PALF 1%wt into the solution and stir for 1.5 hours with a magnetic stirrer. During the stirring process, 0.1 M HCl was added to the solution to begin the oxidation process, and the pH was adjusted to 10 using 0.5 M NaOH added to the solution on a regular basis. The solution was then sonicated for 15 minutes with a sonicator before being washed with distilled water until the pH returned to normal and dried in an oven at 70^{o}C for 4 hours.

3. Grafting TEMPO-oxidized PALF

TEMPO-oxidized PALF with a length of 10 cm and a mass of 2 grams were prepared. The grafting solution combined the silane solution with 96% alcohol in a 1:10 ratio. Prepare TiO_2 nanoparticles to be mixed into a Silane grafting solution prepared with a TiO_2 nanoparticle content of 0.25%, 0.50%, 0.75%, 1.0%, and 2.0%. Gently stir the TiO_2 nanoparticles into the grafting solution. TEMPO-oxidized PALF was sonicated for 15 minutes in a grafting solution containing TiO_2 nanoparticles. The fiber was washed with alcohol and distilled water for one hour before being dried in an oven at 75^{o}C for two hours.

4. Surface Morphology

The surface morphology of PALF was observed using a Scanning Electron Microscope (FEI, S50, USA). The magnification is 50,000x. The natural fiber's surface was covered with a layer of gold to increase the sample's conductivity prior to observation.

5. Crystallinity Analysis

Crystallinity Analysis was determined using X-ray Diffraction (XRD) (PAN Analytical E'xpert Pro). As described in Eq. (1), segmental equations were used to determine the fiber's crystallinity index (CI). The diffraction angle used for the scanning ranged between 10^o and 80^o.

$$\%CI = \frac{I_{002} - I_{am}}{I_{(002)}} \times 100\% \quad \ldots\ldots (1)$$

Where $I_{(am)}$ represents the diffraction intensity at 18^{o,} and $I_{(002)}$ refers to the highest diffraction intensity at 22^o-23^o.

6. FTIR Analysis

The modifications that occurred in the chemical bonding and intermolecular interactions of PALF-mediated TEMPO oxidation with the addition of TiO_2 nanoparticles were determined using Fourier Transform Infra-Red (FTIR) analysis. In order to observe bond issues of PALF

oxidation caused by TEMPO, spectra were obtained over a range of 500–4000 cm-1 and compared with an IR correlation table.

7. Mechanical Strength Test

The nanocomposite's mechanical strength was evaluated using an ASTM D3379-75 tensile test. At a maximum load of 50 N, tensile testing was carried out using a tensile test apparatus (Techno Lab, Indonesia). In accordance with ASTM D3379-75, the samples were cut using scissors and placed between holders for tensile testing.

III. Result and Discussion

1. Morphology Analysis

Figure 1 shows the results of SEM observation on TEMPO-oxidized PALF with the addition of TiO_2 nanoparticles at 50k magnification.

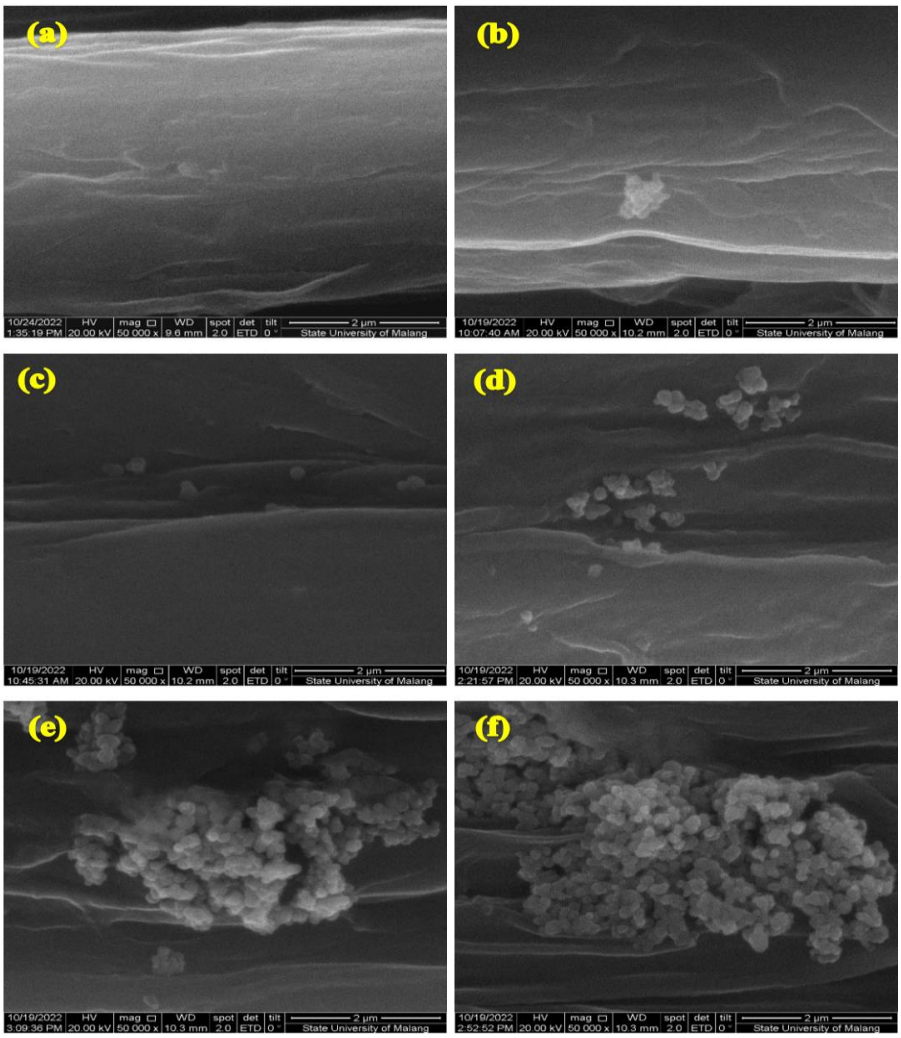

Fig. 1. Surface Morphology of PALF-mediated TEMPO oxidation (a) TEMPO+Silane, (b) T.S + TiO_2 0.25%, (c) T.S + TiO_2 0.5%, (d) T.S + TiO_2 0.75%, (e) T.S + TiO_2 1%, and (f) T.S + TiO_2 2%

PALF, after oxidization by TEMPO and grafting by Silane, shows a smooth surface (Figure 1A-B). TiO_2 nanoparticles indicate the presence on the fiber surface (Figure 1C-1D). Increasing TiO_2 nanoparticle content increases the agglomeration of TiO_2 nanoparticles (Figure 1E and 1F). These agglomerated TiO_2 nanoparticles were formed due to previous chemical treatments, such as alkali treatment and TEMPO oxidation, which made the fibers more reactive and caused agglomeration [24]. The reactive side for the silanol groups on the silane is the hydroxyl group on the surface of the TiO_2 nanoparticles, which will react with the hydroxyl groups on the PALF. In contrast, other silanol groups will combine with the TiO_2 nanoparticles to form Ti - O - Si and Si - O - C structures, as evidenced by the FTIR test results [25]. Silane grafting is an effective method for reducing surface energy and enhancing dispersion properties. Still, when the amount of nanoparticles was too high, it led to nanoparticle agglomeration, which might impact some properties.

2. Crystallinity Analysis

TiO_2 nanoparticles were added to the peak of crystallinity in TEMPO-oxidized PALF. XRD testing was performed to determine the differences and compare the crystalline phase in the fiber. The peak of crystallinity of TEMPO-oxidized PALF occurred at 2θ 22º-23º for crystalline material and 2θ 18º for amorphous material. According to Figure 2, the diffraction peaks are [011], [002], and [400] at 21.6, 22.7, and 34.4° [26], indicating that cellulose is included in cellulose I or α cellulose [27].

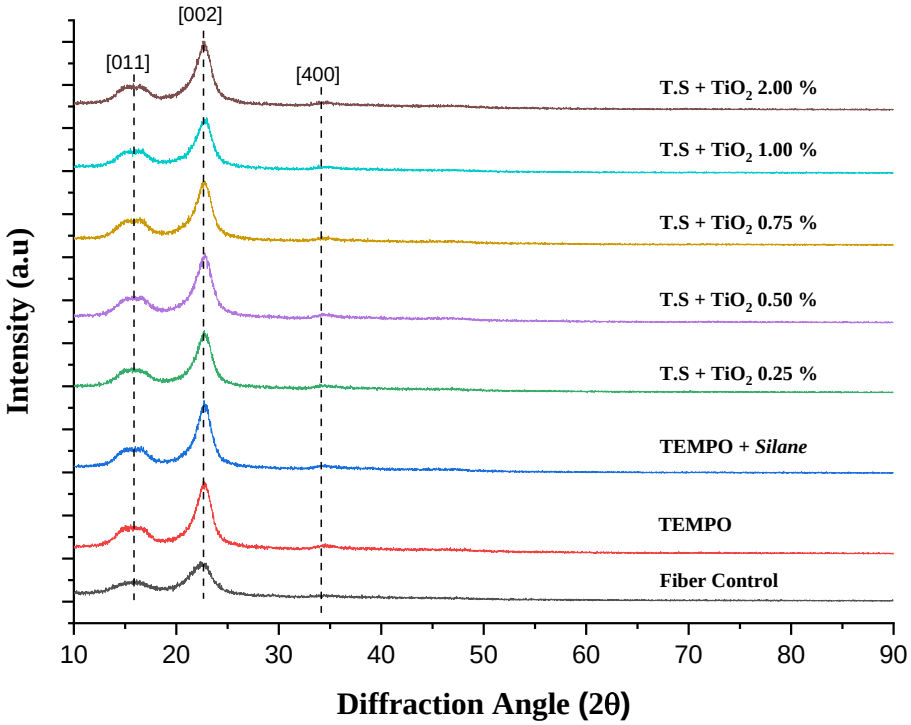

Fig. 2. X-ray diffraction angle of PALF-mediated TEMPO oxidation

The crystalline index (CI) values of PALF increased from 73% to 84.8% before and after treatment, owing to chemical treatments such as alkalization and the grafting silane, which

dissolved the amorphous content in the fiber, causing it to crystallize more and increase the percentage of cellulose I. Increased crystallinity in chemically treated fiber content due to improved moisture resistance and chemical reactivity over raw fiber [27]. A slight decrease in the crystallinity of TEMPO-oxidized PALF was caused by the deposition of TiO_2 nanoparticles on the fiber's surface, as shown in Table 1. The agglomeration of TiO_2 nanoparticles in the SEM test results was confirmed [28].

Table 1. Crystallinity and peak of PALF-mediated TEMPO oxidation

Samples	Diffraction Angle (°)	I_{002}	I_{amorf}	CI (%)
Control	22.39	467	126	73.0
TEMPO (T)	22.63	854	134	84.3
TEMPO+Silane (T.S)	22.71	853	125	85.3
T.S + TiO_2 0.25%	22.73	730	120	83.6
T.S + TiO_2 0.50%	22.77	821	130	84.2
T.S + TiO_2 0.75%	22.79	753	121	83.9
T.S + TiO_2 1.00%	22.95	651	115	82.3
T.S + TiO_2 2.00%	22.69	809	123	84.8

3. Functional Group Analysis

Based on the FTIR test results, TEMPO-oxidized PALF with variations in the addition of TiO_2 nanoparticles are shown in Figure 3. The first peak shows a peak at a wavelength of 3100 cm^{-1} – 3600 cm^{-1} associated with the free O-H stretch vibration of the OH group in cellulose molecules [29]. The second peak occurs at a wavelength of 2914 cm^{-1} to 2897 cm^{-1}, indicating the presence of cellulose, hemicellulose, and organic components for those not chemically treated [27]. The silane grafting results in the formation of a Si-O-C bond with a wavelength of 1158 cm^{-1}. The hydroxyl groups on the surface of TiO_2 nanoparticles are the reactive side for the silanol groups. Other silanol groups will join the TiO_2 nanoparticles on PALF [25]. The increase in transmittance in the TiO_2 1% content as TiO_2 nanoparticles are added to the fiber is shown at a wavelength of 670 cm^{-1} to form Ti–O–Si bonds [30].

According to Figure 4, there was an increase in the tensile stress of PALF after being treated with TEMPO before the silane grafting. Fiber tensile strength starts to increase with the addition of TiO_2 nanoparticles to PALF at 0.5% TiO_2, with a value of 679.65 MPa. The fiber strength increases with the increasing TiO_2 nanoparticle content with a value of 1279.18 MPa at TiO_2 content of 2% or an increase of 125%. This result is better than the previous study, which found that silane treatment only increases the tensile strength of flax fiber by 23% [25] and *Sansevieria cylindrica* fiber by 37% [1]. These results indicate that TEMPO treatment before silane grafting on the surface of the PALF filled with TiO_2 nanoparticles can improve the bonding of the silane layer, and the FTIR results show the formation of a Ti-O bond at a wavelength of 669 cm^{-1}, which supports this result. Improving the grafting efficiency after TEMPO oxidation was also reported at ethylene glycol methyl ether acrylate grafted in the cellulose sponges [31].

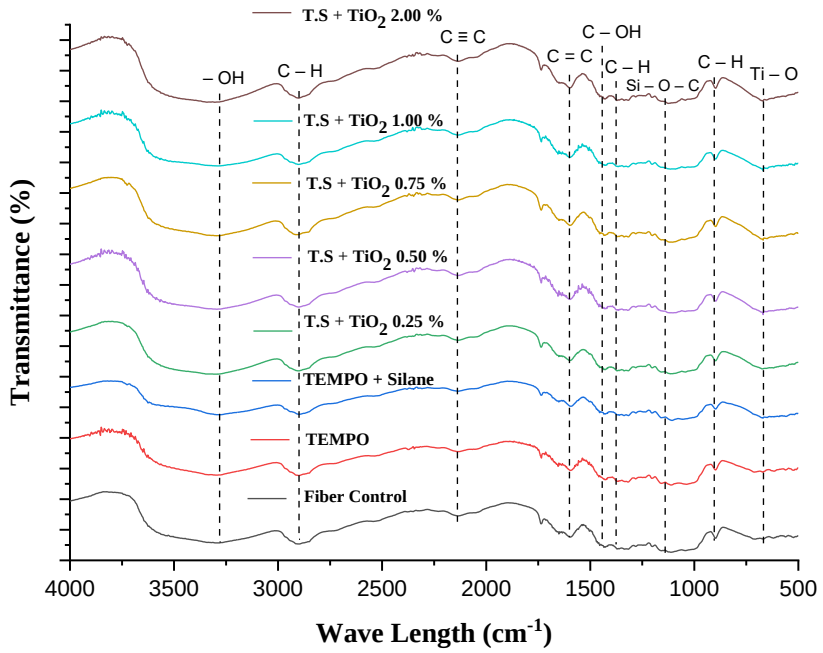

Fig. 3. FTIR spectra of PALF-mediated TEMPO oxidation

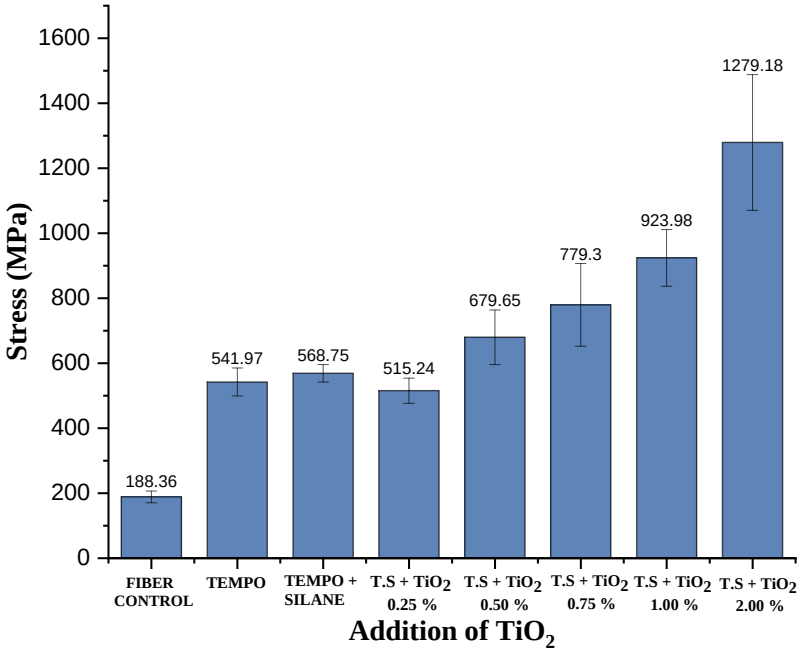

Fig. 4. Comparison of tensile strength of PALF-mediated TEMPO oxidation

Introducing TiO_2 nanoparticles engages in a chemical interaction with the fiber surface. This interaction involves the bonding of free hydroxyl groups on each glucose unit in the cellulose chain with the oxygen of TiO_2, leading to a secondary hydrogen interaction [32].

TEMPO oxidation of cellulose increases the grafting efficiency, but when TiO_2 nanoparticle concentrations are low, minimal interaction takes place. Increasing TiO_2 nanoparticle content increases entrapped nanoparticles in the fiber microfibril due to a mechanical interlocking mechanism. The presence of numerous widely distributed particles bonded to the fiber results in robust adhesion to the fiber, strengthening the network bond. The incorporation of TiO_2 nanoparticles within the mechanical interlocking mechanism restricts microfibril movements. The membrane's strength is correlated with this mechanical interlocking mechanism, which acts as a barrier in the nanocomposite matrix, enhancing structural integrity and improving mechanical properties.

IV. Conclusions

The study of PALF-mediated TEMPO oxidation with a variation of TiO_2 nanoparticles has been completed properly. Surface treatment using TEMPO causes the fiber to become more reactive, as evidenced by agglomeration in the SEM observation, and the mechanical strength of the PALF has been improved by the addition of TiO_2 nanoparticles. This arose in the formation of TiO_2 nanoparticle-filled silane layer on the PALF surface, which enhanced the layer's mechanical characteristics and decreased the amount of stress distributed on the fiber surface during the tensile test. In the future, this treatment will have the benefit of preparing PALF fiber to increase the composite strength by applying TiO_2 nanoparticles.

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