Comparison of Natural Fiber Types as Reinforcement Material on Composite Mechanical Properties via Carbon Nanotubes Addition

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Abstract. Composites with natural fiber reinforcement have been widely used in various field. Natural fibers have the advantages of easy recycling, environmentally-friendly characters, renewable, non-toxic, inexpensive, high toughness, good insulation against heat and noise, and good thermal properties. The aim of this paper is to compare natural fibers used as reinforcing material on composite with an epoxy matrix and the addition of carbon nanotubes (CNT). The natural fibers used are oil palm empty fruit bunches (OPEFB), bagasse, and hemp fiber. Alkalization treatment with NaOH was carried out on natural fibers to remove impurities on the fiber surface and activate hydroxyl groups. CNTs need to be functionalized to achieve the desired compatibility. Functionalization is carried out by the mild acid oxidation method using nitric acid and hydrogen peroxide. Silane coupling agent treatment is carried out on natural fibers and CNTs to improve compatibility with the matrix. The result of the bending strength test of OPEFB, bagasse, and hemp fiber was 509.94 MPa, 36.22 MPa, and 18.12, respectively, in addition to CNT 0.5% mass. The bending strength of OPEFB fiber is more significant than bagasse and hemp fiber, so it has the opportunity to be developed in the automotive industry.

1. Introduction
The development of material technology has grown rapidly. The polymer has replaced many conventional materials such as metals in various applications due to advantages such as ease of processing, lightweight, higher productivity, and reduced costs. For many of these applications, polymer properties are modified using fillers and fibers to conform to high strength modulus requirements [1].

Composites with natural fiber reinforcement have been widely used in various fields such as automobiles, furniture, heating, and construction industries. Natural fibers have the advantages of low density, easy recycling, environmentally-friendly characters, renewable, non-toxic, inexpensive, high toughness, good insulation against heat and noise, good thermal properties, easy separation, and low abrasiveness[2]. The high content of chemical compounds in cellulose in natural fibers makes natural fibers suitable for modern applications [3]. Some natural fibers used as composite materials reinforcement are oil palm empty fruit bunch (OPEFB) [4], bagasse [5], and hemp fiber [6].

Engineering materials on the nanometer scale can produce various materials with various properties. One of the materials is carbon nanotubes (CNT) due to their excellent mechanical strength...
and electronic properties [7]. The CNT’s specific strength is 10 to 100 times stronger than the strongest steel [8].

The purpose of this paper is to compare natural fibers used as reinforcing materials to increase the mechanical strength of composites with the addition of carbon nanotubes and epoxy resin as a matrix. The natural fibers used are oil palm empty fruit bunches, bagasse, and hemp fiber. Natural fibers are first subjected to an alkaline treatment process then followed by surface treatment of the fibers with a silane coupling agent, after that the fibers are formed into chopped strands. CNTs need to be functionalized to improve compatibility with the polymer matrix [9]. After that, the CNT is mixed with liquid epoxy resin and then the epoxy/CNT-natural fiber composite is formed. FTIR characterization is carried out on natural fiber and CNT to analyze the functional group that exist in the substance. A bending test is carried out to see the performance of composites.

2. Materials and methods

2.1. Materials

2.1.1. Oil Palm Empty Fruit Bunch. The most massive waste produced from the oil palm industry is empty oil palm bunches and palm fronds [10]. The bunch is where the oil palm fruit sticks. After the oil palm fruit is separated for processing, it produces waste in the form of EFB. EFB waste can be used as a raw material for making composites because palm oil bunch fibers contain a lot of wood chemical components such as cellulose (45.8%), hemicellulose (31.6%), and lignin (22.6%) [11]. Cellulose can be used as a source of natural fibers in the formation of composite materials.

2.1.2. Bagasse. The main sugarcane product is sugar, but the by-product in the form of bagasse is 35-40% of each processed sugarcane [12]. Bagasse is a fibrous material that is obtained as a residue from sugarcane after being crushed for extraction. Bagasse contains chemical components such as cellulose 40-50%, hemicellulose 25-35%, lignin 17-20%, and several other components such as 0.8% wax and 2.3% ash [13], [14]. The use of bagasse as reinforcement in composite production is a good for increasing the bagasse’s economic value [15].

2.1.3. Hemp Fiber. Hemp is one of the long-lived plants, grows well in areas with warm and humid weather with rainfall that is almost evenly distributed throughout the year [16]. Hemp fiber is the bastfiber of the tree obtained from the inner bark of the hemp stem. Hemp has been used as a textile fiber in China and South Asia for centuries and has been known in Ancient Egypt [17]. Hemp fiber has good strength, durability, and absorption. One of the uses of hemp fiber is as an alternative material for cotton in using textiles to reduce cotton imports. Hemp fiber has chemical components such as cellulose (75.6%), hemicellulose (10.7%), and lignin (6.6%) [18].

2.2. Methods

2.2.1. Alkalization Treatment. Cellulose and hemicellulose in the plant body are generally physically encased by lignin and pectin [19]. Lignin is insoluble in water and stable in nature and acts as adhesive connecting cellulose and hemicellulose [20]. Alkalization is the most widely used method to remove the lignin and oil content covering the fiber’s outer surface [21] and increase the number of free hydroxyl groups, thereby increasing the fiber and resin’s interface bond [22]. The alkalization process is carried out by immersing the fibers in an alkaline solution (NaOH) with different treatments at time and temperature [23]. The alkalization process will raise cellulose and remove impurities on the surface of natural fibers such as lignin and pectin to improve the fiber’s mechanical properties [24]. Plant fiber can be obtained more easily from the plant body after the adhesive components in the form of lignin and pectin dissolve in the cooking solution. Cooking fiber with a 10% weight NaOH solution at 100°C can dissolve most of the lignin found in plant components so that the fibers can be easily separated
[11]. The high-temperature of NaOH can damage the fiber’s hydrogen bond structure to increase the surface area of the fiber[25].

2.2.2. Natural Fiber Surface Treatment. The effectiveness of cellulose fiber strengthening in polymers is very dependent on the compatibility between the two materials. Chemical treatment such as acid etching and a coupling agent can be applied to increase the surface interaction of the composite’s constituent materials. The hydroxide group produces the hydrophilic nature of natural fibers and the hydrophobic nature of the matrix makes the two combinations incompatible. In this case, silane surface treatment can improve the interface adhesion between natural fibers and the matrix. Silane molecules have bifunctional groups, where one of them reacts with the fiber and the other with the polymer. Therefore, the silane surface treatment reduces the number of hydroxyl groups on the fiber’s surface, and one part of the other will bind to the matrix [27]. The tensile and flexural strength of the composite with modified fibers is increased when the silane coupling agent is used [28]. The fiber treatment and functionalization CNT using a silane coupling agent increase the matrix’s compatibility. Good interfacial bonding between the reinforcement and the matrix provides improved mechanical properties [29]. Alkali treatment of fibers and CNT functionalization with the mild acid oxidation method is first carried out to activate the fiber and CNT’s hydroxyl groups, which will then bind to the silane coupling agent [30]. Surface treatment using a silane coupling agent increase mechanical strength due to good dispersion and adhesion to the epoxy matrix [31].

2.2.3. Carbon Nanotube Treatment. CNTs can act as reinforcing agents in polymers. The conductivity, strength, elasticity, robustness, and resistance of the composites formed can be increased substantially with the CNT’s [32]. The surface energy of CNTs is significantly different from matrices such as organic solvents or polymers, and CNTs have no chemical affinity for the organic matrix [33]. Pure CNT is a hydrophobic and have low solubility in solvent. Therefore, CNT needs to be functionalized to make CNT dispersible in solution [34]. The CNT functionalization method can be carried out in 2 ways; the first is mild acid oxidation using HNO3 and H2O2 to oxidize pure CNT, which will form a hydroxyl functional group on the CNT surface which functions as a reaction site [35]. Oxidation with acid can perform CNT purification, disperse, and surface activation simultaneously. Oxidation with 3M HNO3 and 30% v/v H2O2 and ultrasonic vibrations have been shown to functionally function CNT surfaces without damaging the structure of the nanotubes [36]. The second method used is CNT silanization using a silane coupling agent by dissolving the silane coupling agent solution in ethanol so that it forms a silanol group due to hydrolysis, then forms a covalent bond with the OH group on the CNT surface to form a Si-O-C bond [37]. CNT surface treatment with a silane coupling agent has also been shown to increase the flexural strength and crack strength of epoxy matrix-based composites [38] to increase composite’s tensile strength with an epoxy matrix [39].

3. Results and discussion
FTIR characterization was carried out on natural fibers and CNT, in its pure and modified form to analyze functional group in those substance. A bending test is done to analyze mechanical strength of composite.

3.1. Surface Modification
Transmittance graphs of natural fiber obtained from FTIR spectroscopy, both pure and modified with GPTMS.
Figure 1. Transmittance graph of OPEFB (a) pure, (b) modified [40].

Figure 1 shows several peaks that prove the functional group characteristics, -OH at 3442 cm$^{-1}$, C-H at 2061 cm$^{-1}$, CH$_2$ 1427 cm$^{-1}$, C-O 1043 cm$^{-1}$. FTIR spectra of modified OPEFB not only showed the same peak as pure, but also increasing intensity of peak at 1000-1200 cm$^{-1}$ wavelength [40] which means there is indicating the presence of Si-OH bonds on natural fiber [31].

Figure 2. Transmittance graph of bagasse (a) pure, (b) modified [5].

Figure 2 shows C-O wavelengths at 1250 cm$^{-1}$, C=O at 1735 cm$^{-1}$, and -OH at 3300 cm$^{-1}$. Surface treatment of sugarcane pulp fiber showed the presence of Si-O-Si and Si-O-C groups in waves 1000-1200 cm$^{-1}$ [5]. Si-O-Si bonds are formed due to cross-links between coupling agents, while Si-O-C bonds are formed due to chemical reactions between coupling agents and fibers [41].

Figure 3. Transmittance graph of hemp fiber (a) pure, (b) modified [6].
Figure 3 shows the functional group’s wavelength -OH at 3331 cm\(^{-1}\), C=O at 1242 cm\(^{-1}\), and Si-O-Si and Si-O-C bonds at 1000-1200 cm\(^{-1}\) [6]. There is a reaction between hydrolyzed silane and hemp fiber to produce a Si-O-C strain in the hemp fiber [42].

The Si-O-C covalent bond will react with the polymer matrix thereby increasing the fiber-matrix interface [43]. Treatment of the fiber surface with a silane coupling agent forms a covalent bond between the silane and the fiber surface, thus forming a composite that has better mechanical strength because it has good stress transfer between the fiber and the epoxy matrix [29].

3.2. Functionalization CNT

FTIR analysis was carried out on the CNT before and after the functionalization process. The CNT transmission graph in figure 4 shows the wavelength of -OH at 3455 cm\(^{-1}\), C=O at 1654 cm\(^{-1}\), and C-O at 1171 cm\(^{-1}\) so it can be confirmed that functionalization CNT by acid has OH group [40]. Silane coupling agent GPTMS will react rapidly with water forming silanol group. This group react rapidly with OH group at the surface of oxidized CNT to form polymeric bond Si-O-Si [41]. The presence of Si-O-Si bonding was confirmed by FTIR analysis where there are peaks at 1000-1200 cm\(^{-1}\) wavelength [40].

![Figure 4. Transmittance graph of functionalization CNT (a) pure, (b) mild acid oxidation treatment, (c) silane coupling agent treatment [40].](image)

3.3. Composite Molding and Bending Test

CNT addition 0.5% and fiber form chopped strand are done to make effective composition for composite. The standard used for the bending test is ASTM D790 using 3 point loading. Specimens were prepared to be 80 mm x 25.4 mm x 3.2 mm for OPEFB [4] and 125 mm x 12.7 mm x 3.2 mm for bagasse and hemp fiber [5],[6]. The specimen is supported by two cantilevers in a determined support span. The pressure is applied in the middle part of the specimen; by a metal bar until the specimen gets fatigued and cannot hold any more pressure load.
Table 1. Bending Test Result.

| Natural Fiber | Epoxy + Natural Fiber | Epoxy + 0.5% CNT + Natural Fiber | Reference |
|---------------|-----------------------|----------------------------------|-----------|
| OPEFB         | 464.14                | 509.94                           | Syahrudin, U. P, 2016 |
| Bagasse       | 14.45                 | 36.22                            | Daffa, M, 2020 |
| Hemp fiber    | 35.55                 | 18.12                            | Raihan, S. D, 2020 |

Table 1 shows the bending strength of each composite. The addition of CNT can increase the bending strength of the OPEFB fibers and bagasse [4],[5]. The bending strength of bagasse was 150.65%, more significant than OPEFB, which increased by 9.86%. However, the increase in bending strength in bagasse does not exceed the bending strength of the OPEFB fibers. The addition of CNT to hemp fiber decreased mechanical strength by 48.96% [6]. The addition of a smaller number of CNTs harms the interface bond between the CNT and the matrix and the Van der Waals bond between the fiber and matrix. Likewise, adding too much CNT can show negative results [45]. So we need an optimal point for adding CNT to the hemp fiber composite. The bending test results show that the formed composite can be applied to the automotive industry, especially as a car bumper.

4. Conclusion
Surface treatment of natural fibers and CNTs with a silane coupling agent successfully modifies the surface and helps strengthen the bonds between composite components. The addition of 0.5% CNT to OPEFB increases the bending strength by 9.86% and bagasse by 150.65%. Meanwhile, the addition of 0.5% CNT to hemp fiber reduces the bending strength by 48.96%. The bending strength of CNT composites with OPEFB fibers was 509.94 MPa, bagasse 36.22 MPa, and hemp fibers 18.12 MPa. CNT-OPEFB composites have greater bending strength than bagasse and hemp fibers and can be developed in the automotive industry.

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