Effect of mercerized surface treated natural fiber to the tensile properties of green composite

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Abstract. This research deals with fabrication and tensile properties characterization of green composite (GC). In this research, GC was made from ramie, coir and bagasse fiber as reinforcement with polylactic acid (PLA) biodegradable resin. To improve the adhesion between fiber and PLA also increasing tensile properties of GC, mercerization or NaOH fiber treatment is used. This is aimed to observe the effect of NaOH fiber surface treatment on the tensile properties of GC. Ramie, bagasse, and coir fiber were chopped (2-3mm) and immersed in 5 wt% NaOH for 2, 3 and 4 hours respectively. The GC with ten wt% fiber loading was prepared by pouring the fiber in a melted PLA at 170°C and stirring them for a homogenizing process. Then pour it in a metallic mold, the pressure at 10MPa was applied for 10 minutes. Six types of GC were obtained, such as R/PLA, C/PLA, B/PLA, RC/PLA, RB/PLA, and RCB/PLA, both of untreated and NaOH treated fiber. The tensile test was done to observe the effect of NaOH fiber surface treatment on the tensile properties of GC. The entire result showed that the tensile properties of GC were affected by fiber surface treatment and meaningless existence. The highest tensile strength and modulus of elasticity were obtained from GC with untreated R/PLA, 56.88±1.17 MPa and 363.37±11.44 MPa respectively.

1. Introduction
Green composites (GC) are promising materials in recent years. Consist of natural resources materials, both of the fiber and matrix make the GC materials more favorable to produce continuously [1], [2]. Biodegradability and renewability of GC refer to the environmental issues of “sustainability” and “environmental impact” [2] and thus agree with the 2030 agenda for sustainable development [3]. Growing environmental awareness and new regulation in the manufacturing process have driven a more significant effort and research to the GC materials [4], [5]. One of them, the new provision in the manufacturing process was made because of the abundant effect on the environment from the waste product based synthetic materials [6]. Previously, synthetic materials are widely used in the manufacturing process to improve the mechanical characteristics of products. Unfortunately, synthetic materials are toxic, high CO2 emission and non-biodegradable, so they have caused environmental damage, through increasing CO2 emission and pollution from waste materials accumulation on landfill. Consequently, the use of natural resources is necessary to replace synthetic materials, minimize the dependence of synthetic materials and reduce environmental damage [7]–[9].

This research deals with the utilization of plant fibers and biodegradable resin as the constituent materials in GC fabrication. Plant fibers are favorable materials for a manufacturing process, due to they
are abundantly available over the world, lightweight and high specific strength than synthetic fibers. Biodegradable resin, like polyactic acid (PLA) is frequently used as a matrix with natural fibers reinforcement. PLA is thermoplastic biopolymer and has been widely used as a matrix for biodegradable materials reinforced with natural or synthetic fiber. It can be naturally decomposed and satisfied environmental effect. Also, the mechanical properties are comparable with the synthetic polymer[1], [10]. As compared with polypropylene (PP), PLA has higher tensile strength and modulus of elasticity [4][11].

Natural fibers have been more full used in reinforcing thermoplastic resin and applied in several industries because of the cost-effective and environmentally friendly [12],[13]. Natural fibers are generally used as a yarn in the textile industry [13]–[15]. As the increasing of natural fiber value, a new improvement of natural fiber as reinforcing materials has been developed in many industries, such as automotive industry [16],[17]. The previous research on GC has been carried out with various fibers such as ramie [18], bamboo [4], [19], coir [6], [20], bagasse [21], banana [16] and hemp [22]. In addition, to the enriching of GC research, ramie, coir and bagasse fibers can be utilized through compounding into fiber-reinforced PLA. These three different fibers were selected to investigate their benefits as a reinforcing agent in a PLA. In recent years, the use of PLA in GC fabrication become increase cause of the biodegradable, non-toxic and higher tensile properties [1].

It is well-known however natural fibers are hydrophilic in nature, while the matrix is hydrophobic. It creates difficulties in achieving a good interaction between the fiber and matrix [9]. As a result, a poor fiber-matrix interface is often seen. Hence, research about fiber surface modification become important to improve interfacial between fiber and matrix. The previous report said that chemical treatment could be applied as fiber surface modification, and develop the fiber-matrix interface [5], [7], [23]. Mercerization is one of the chemical treatment which used NaOH solution as fiber surface modification. NaOH solution will remove parts of natural fiber like hemicellulose and wax. So, the fiber surface becomes rough and interaction between fiber-matrix will increase. In the scope of this study, coir, ramie, and bagasse fiber were used as reinforcement with PLA, and mercerized treatment has been chosen as a simple method but effective to modify the fiber surface and to improve adhesion between fibers and matrix [5], [19]. The purpose of this study is to investigate the use of different natural fiber to the tensile properties of GC, with or without mercerization.

2. Methods

2.1. Materials

Ramie, coir, and bagasse fiber were used as reinforcing materials. Ramie fibers were purchased from “Balai Penelitian Tanaman Pemanis dan Serat” (BALITTAS) Malang. Coir fibers were obtained from CV. Sumber Sari Jember, while bagasse fibers were taken from sugar waste product in Sugar Factory Semboro Jember. The fibers were chopped 2-3mm in length and washed using tap water, then dried at 100°C for 1 hour before the mercerizing process. The dried ramie, bagasse, and coir fiber were mercurized by immersing the fibers in the alkali solution (NaOH 5 wt%) for 2 hours, 3 hours, and 4 hours respectively. The different time in mercerization for each fiber was agreed with the optimum fiber cellulose that obtained after the mercerizing process. Mechanical treatment was applied at the end of the mercerizing process using home-mixer for 30 minutes, to get the cellulose of the fiber.

Thermoplastic biopolymer PLA with 31.74 MPa tensile strength was used as a matrix in green composite fabrication. It has been widely used as a green composite matrix with natural or synthetic fiber reinforcement. Some advantages of using PLA are good mechanical properties, environmentally friendly, biodegradable, recyclable and non-toxic.

2.2. Fabrication of GC

The “green” composite (GC) were reinforced by untreated, and NaOH treated fiber in randomly fiber oriented. The fiber content in the composites was prepared as indicated in table 1. Firstly, the prepared PLA were melted in the hot plate at temperature 170°C. After the PLA melting completely, the prepared natural fiber poured in the melting PLA and stirred them up until the mixture blended homogeneously.

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Table 1. PLA and fiber composition of “green” composites (GC)

| Fiber           | Code  | Fiber fraction (wt%) | PLA (wt%) |
|-----------------|-------|----------------------|-----------|
| -               | -     | -                    | 100       |
| Untreated/ NaOH treated fiber |       |                      |           |
| Ramie           | R/PLA | 10                   | 90        |
| Coir            | C/PLA | 10                   | 90        |
| Bagasse         | B/PLA | 10                   | 90        |
| Ramie-coir      | RC/PLA| 5:5                  | 90        |
| Ramie-bagasse   | RB/PLA| 5:5                  | 90        |
| Ramie-coir-bagasse | RCB/PLA | 5:2.5:2.5          | 90        |

Secondly, the homogenous mixture poured into the metallic mold, and the pressure of 10 MPa was applied for 10 minutes for the molding process. Then, the mold was finally removed from the pressure machine and allowed to cool down to room temperature without any pressure. The GC perform sheet was removed from the mold and cut in the small sizes with dimensions of 100.00 mm in length and 10.00 mm in width. The R/PLA, C/PLA, B/PLA, RC/PLA, RB/PLA, and RCB/PLA composites were obtained both of untreated and NaOH treated fiber reinforcement.

2.3. Tensile testing of GC

The tensile properties of GC specimens reinforced with randomly oriented fiber were carried out by tensile testing. Universal testing machine HT 2404-10KN did the tensile testing of the GC samples. Tensile testing of GC samples was done by gripped the rectangular GC samples at a 30.00 mm gauge length, and the crosshead speed was set at 1.00 mm/min. In this study, tensile testing was done to characterize the tensile strength, modulus of elasticity and strain at break of the GC materials. The software of the machine determined tensile strength, strain at break, and modulus of elasticity of the samples. The linear slope of the tensile stress-strain curve identified as the modulus of elasticity of the materials. Meanwhile, the maximum stress and strain of the samples were identified as the tensile strength and strain at break of the elements respectively.

2.4. Microstructure investigation

Scanning Electron Microscope (SEM) was used to investigate the internal structure of the GC. This is used to know the existence of voids in the specimens which given an impact to the tensile properties of the specimens. To observe the existence of voids in the specimens, the scanning electron microscope (SEM) TM3030Plus, Merck HITACHI was used. The specimens were cut into the small pieces with 2mm in thickness, then placed at the holder and insert in the SEM machine to do the observation process. The results were investigated to represent the meaningless existence and their effects on tensile properties.
3. Results and discussion

3.1 Internal structure of GC

The internal structure of GC was evaluated using a scanning electron microscope (SEM). Figure 1 shows the SEM images from the cross-sectional area of R/PLA and C/PLA, both untreated and NaOH treated fiber. Based on the pictures, we can see the different microstructure of GC. The void existing in the samples cause the different images. No more void that exists in the sample both of untreated R/PLA and C/PLA (figure 1a and 1d). Meanwhile, we can see some voids that exist in the NaOH treated R/PLA and C/PLA (figure 1b and 1c). It means, there is air which is trapped in the materials when applied pressure. The void exists in the samples also indicated the matrix capability to displace all peculiar materials, like the air that exist within the fiber or between the fiber and matrix while the pressure is applied during fabrication process [24], [25].

Like the previous report, the void existence causes some disadvantage to the interface between fiber and matrix and makes the mechanical properties of materials become lower [25]. It can be proven by evaluating the result of the tensile test that obtained from this research thoroughly.
3.2. Tensile properties of GC
The tensile characteristic of GC is represented through the stress-strain curve. Stress-strain curve of the GC indicated the ability of the samples to elongate during the tensile testing process. When the loads were applied to the samples of GC, the sample will elongate to sustain the loads before they are broken into two parts. Each sample has different behavior during the tensile testing process. It causes of the different constituent that used as reinforcement, so the tensile stress-strain characteristics of the samples are different. There is some information which can be observed from the stress-strain curves, such as tensile strength, modulus of elasticity and strain at break. Based on figure 2, we can see how long each sample elongates during the tensile testing process. The end of the stress-strain curve gives the meaning that the samples have been broken into two parts, and it can be indicated as the maximum stress that can be sustained by the samples. The maximum stress of the samples is shown as the tensile stress of the samples. As we can see, RCB/PLA has the highest strain with the maximum stress as near as the maximum stress in R/PLA. It means the tensile testing of RCB/PLA almost has the same value with R/PLA with a higher capability to elongate than R/PLA, and so not easy to break into two parts. For RCB/PLA the time that needed to be broken into two parts is longer than R/PLA. It also indicated that R/PLA is brittle materials, while RCB/PLA is ductile materials [26].

Figure 2. Stress-strain curve of GC (NaOH treated)

Figure 3 and 4 illustrate the effects of fiber types when applied as reinforcement in neat polyactic acid (PLA) on the tensile properties of GC. Addition of any fibers to the PLA, either ramie, coir or bagasse fiber both of NaOH treated or untreated, yield a GC material with a higher tensile strength compared to neat PLA. This result has an agreement with other research which has been reported [1]. In this research, tensile properties among GC will compare based on the NaOH treatment, the use of different kind fiber both of individual and combination (hybrid). The result of tensile strength shows that GC with NaOH surface fiber treatment giving a high tensile strength than the untreated GC. But the void existence (figure 1) makes an exception for NaOH treated R/PLA which shows the lower tensile strength than untreated R/PLA, as seen as at figure 3. Based on the void, we also can see there is some void that presences in NaOH treated C/PLA. It also makes the tensile strength of C/PLA is lower than B/PLA. Whereas, coir fiber is higher in tensile strength than bagasse fiber [6]. Same as the previous research, which is said that the void presence in the materials will decrease the mechanical properties of the materials, include the tensile strength [25].

For the entire type of individual fiber, GC with ramie fiber reinforcement (R/PLA) has higher tensile strength among others. Untreated R/PLA results from the most upper tensile strength, that is 56.88±1.17 MPa. This result makes an agreement with the natural tensile properties of individual fiber, where ramie fiber is plant fiber with the highest tensile strength than others coir and bagasse fiber. Naturally, the tensile strength of ramie, coir, and bagasse fiber are 500 MPa, 220 MPa, and 70.9 MPa respectively [8],
In the other case, we can see the increase of tensile strength also resulted when the fibers are combined in a PLA. The tensile strength of GC with fiber combination including NaOH treated RC/PLA, RB/PLA, and RCB/PLA are 51.77±4.29 MPa; 49.50±0.22 MPa; and 50.77±1.86 MPa respectively. Based on the fiber combination, GC reinforced with ramie and coir fiber (RC/PLA) has the highest tensile strength.

![Figure 3. The tensile strength of GC](image)

Mercerization or NaOH treatment to the fibers affect not only the tensile strength of the GC but also the modulus of elasticity of the GC. As a result of tensile strength, the highest modulus of elasticity of the GC has been obtained from untreated R/PLA, that is 363.37±11.44 MPa as seen as in figure 4. Both of tensile strength and modulus of elasticity show to us how is mercerized of surface fiber treatment or NaOH treatment to the natural fiber affect the tensile properties of GC. Generally, the use of NaOH as surface fiber chemical treatment is the effective one to improve the tensile properties of GC including tensile strength and modulus of elasticity.

![Figure 4. Modulus of elasticity of GC](image)

4. Conclusions
The GC materials reinforced with natural fiber (ramie, coir, and bagasse) both of untreated and NaOH treated fiber had been successfully fabricated. The tensile properties of GC materials were affected by
the NaOH treatment or mercerization, types of fiber and voids. NaOH treatment can increase the tensile properties of GC. The presence of voids in NaOH treated R/PLA decrease the tensile properties. Hence, the experimental value of the GC’s tensile testing found that the GC materials reinforced with untreated R/PLA have the highest tensile strength and modulus of elasticity. Meanwhile, the treated RC/PLA is a good combination of plant fibers in PLA with highest tensile properties among other combination.

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