Fabrication and tensile properties of bamboo micro-fibrils (BMF)/poly-lactic acid (PLA) green composite

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Abstract. In this research has been focused on the fabrication of green composites (GC) from emulsion-type poly-lactic acid (PLA) biodegradable resin with bamboo micro-fibrils (BMF) reinforcement. BMF were extracted by combination methods: chemical solution and mechanical treatment. The chemical solution: alkalization of 5% (weight/volume) sodium hydroxide (NaOH) for 72 hours and bleaching of 2.8% volume natrium hypoclorit (NaClO) for 12 hours. And for mechanical treatment: high speed-blender for up to 30 minute along with the alkalization process. The chemical structure of the resulting cellulose BMF was studied by Fourier Transform Infra-Red (FTIR) spectroscopy. The alkalization and bleaching treatment were affected by the BMF cellulose content. Fabrication of green composites with BFC loading from 0%, 20%, 30%, 40% and 50% of mass were prepared using hot-press molding at constant temperature of 170 °C, pressure of 10 MPa and time molding of 10 minutes. Tensile strength and elastic modulus was investigated using computerized Universal Testing Machines HT-2402 with crosshead speed of 5.0 mm/min. The measurement finding showed that the tensile strength and elastic modulus were affected by the BMF content. The results obtained emphasize the application of bamboo micro-fibrils composites (BMC), as a potential materials in biodegradable based or green composites (GC).

1. Introduction
Natural fibers used as a reinforcement in biodegradable polymer continuous to be subject of the research. Composites of biodegradable polymers such as polyhydroxybutyrate [1] or polylactide acid (PLA) with natural reinforcement is very promising for development as a friendly materials [2]. Biocomposites of PLA be attention of many researchers, PLA with microfibrillated cellulose [3][4], cellulose nanofibers [5][6], wood and bamboo fibers[7], short bamboo single fibers [8], agricultural waste [9] were prepared and studied recently. Applied and optimisation of natural fiber as reinforced [10]till modification of biodegradable polymers [11] continued to be done especially to get the desired properties as good in mechanical properties, low cost, recyclability and biodegradability [12].

Basically, plants have the main chemical composition such as cellulose, hemicellulose and lignin. In a studied, cellulose is a macro molecule formed by anhidro-betha-gluco-piranosa (β-(1-4)-gloco-sidic bond) which binded together form a linear chains and allowed the formation of hydrogen bonds (important in forming bonds between molecules)[13][14]. Hydroxil group in large amount gives natural fiber hydrophilic properties and when used to reinforce hydrophobic matrices will result very poor interface and poor resistance to moisture absorption. Many methods to getting fibers with good
interface and good resistance: chemical solution [15][16], mechanical treatment [17][18][19] till enzymatic [20][21]. In this research, combination between chemical solution with mechanical treatment have be done. The chemical solution is carried out in this research: alkalization (NaOH) and bleaching (NaClO) to remove amount lignin, hemicellulose, wax and oils covering the external surface of the fiber [22]. The alkalization process followed by mechanical treatment: high-speed blender [17]. That causes the plant cell wall consist of a multilayered which needs mechanical treatment to disintegrate the rigid structures. The aim of this research was: (i) to extract microfibrils from raw bamboo and optimize the cellulose content using combination methods: chemical solution and mechanical treatment (ii) to investigates the tensile properties of BMF/PLA composites with different BMF loading.

2. Materials and Methods
2.1 Preparation of Material
The bamboo used in this research was selected from one of the most usable bamboo species in Indonesia, *Gigantochloa Apus* (Schutz) Kurz. BMF was produced by chemical solution [15] and mechanical treatment [17]. The bundle bamboo fiber were cuts 10-15 mm in length and soaked in a NaOH solution (5% of weight) for 72 hours at room temperature and followed by mechanically treatment using blender with stir velocity of 12000 rpm for up to 30 minutes. Afterwards, the fiber were continuously washed with distilled water, removing any NaOH solution remaining on the fiber surface. Then, the fiber soaked in 2.8% (volume) sodium hypochlorite (NaClO) solution for 12 hours. The fibers was rinsed, then drained and dried under the sunlight for 12 hours. Finally, fiber blended using home-use mixer to get randomness finer BMF with average diameter of 8-10 µm and 3-4 mm in length, which free from soft cells powder attached on the BMF surface.

Fabrication procedure of BMF/PLA green composite: Preliminary composites were prepared by mixed BMF and emulsion-type PLA (Miyoshi Oil & Fat Co., Ltd.; PL-1005) biodegradable resin was used as the matrix, followed by drying under the sunlight for 6 hours to obtain green composite performed sheet. Then composites were cutted with sized of 100 mm in length and 10 mm in width. The obtained sheets were laminated and pressed using hot pressing machine at 170°C under 10 MPa pressure for 10 minutes. The dimension of the green composite specimens of 100 mm in length, 10 mm in width and 5 mm in thickness (with BMF content was 0%, 20%, 30%, 40% and 50% of mass).

2.2 Characterization of BMF/PLA green composite
2.2.1 Chemical Properties
The bamboo fiber were characterized by Bruker Alpha ATR Fourier Transform Infra-Red (FTIR) (untreatment and BMF). The fiber samples were chopped into small particles using home-use mixer. And then infrared spectra of the above-mentioned samples were collected at room temperature. IR spectra were recorded in the region of 4.000–600 cm⁻¹ with resolution of 4 cm⁻¹.

Mechanical Properties
Tensile strength and elastic modulus of pure PLA and composites were measured according to universal testing machine HT-2402 with crosshead speed of 5 mm/min and a gauge length of 30 mm. Tensile strength and elastic modulus of the specimens were determined from the stress–strain curve.

2.2.2 Morphology
The micro structure and fractured surfaces of green composites were examined using scanning electron microscope Hitachi TM3030 with an acceleration voltage 5 kV.

3. Result and Discussions
3.1 Chemical Properties
The chemical effect of chemical solution (alkalization and bleaching) were investigated using FTIR spectroscopy. Figure 1 shows the FTIR spectra of bamboo fiber between 4000 and 600 cm⁻¹: (a) untreatment; (b) BMF. In the range between 1800 dan 800 cm⁻¹ there is evidence of fiber modification consisting with removal of lignin dan hemisellulosa and purification of crystalline cellulose. The stretching vibration C=O of carboxyl and acetyl groups in hemicelluloses at 1.755 cm⁻¹, while the
lignin at wave number 1.730 and 1.600 cm\(^{-1}\), it’s a carbon vibration and an aromatic vinyl propane, it’s just found in untreated fiber but not in BMF. Caused, BMF is a fiber that has undergone regeneration whose main component is cellulose.

**Figure 1(a).** FTIR spectra of untreated fiber

**Figure 1(b).** FTIR spectra of BMF
In addition, the bands positions and intensities were also shows BMF and untreated fibers. For instance, in the region of 1.200–800 cm\(^{-1}\), the bands at untreated fibers has eight at 900, 915, 925, 1.009, 1.052, 1.105, 1.160 and 1.240 cm\(^{-1}\), where the strong peaks at 925 and 900 cm\(^{-1}\). While the BMF has seven peaks at 896, 1.034, 1.057, 1.107, 1.133, 1.159, and 1.200 cm\(^{-1}\), and the strongest peaks appeared at 1.057 cm\(^{-1}\). Especially, peaks between 800–1.200 cm\(^{-1}\) has associated with stretching vibration of glycoside and C-O polysaccharides. The main absorptive bands of the fibers infrared spectra are summarized in Table 1[23][24][25].

| Wave number (cm\(^{-1}\)) | Functional group assignment                              |
|---------------------------|----------------------------------------------------------|
| Bamboo fiber | Bamboo pulp fiber |                                           |
| 2.898         | 2.893            | C-H stretching in methyl and methylene groups          |
| 1.728         | -                | C=O stretching vibration of carboxyl and acetyl groups in hemicellulose |
| 1.635         | 1.645            | O-H bending of absorbed water                          |
| 1.433         | 1.423            | CH\(_2\) deformation in cellulose                     |
| 1.373         | 1.373            | C-H deformation in cellulose and hemicellulose         |
| 1.334         | 1.336            | O-H deformation                                       |
| 1.321         | -                | CH\(_2\) rock vibration in cellulose                   |
| -             | 1.263            | C-H bending in cellulose                               |
| 1.259         | -                | C-O stretching                                        |
| -             | 1.343            | C-OH bending in cellulose                              |
| 1.165         | 1.161            | C-O-C vibration in cellulose and hemicellulose         |
| 1.111         | -                | C-O stretching and ring asymmetric valence vibration   |
| 1.056         | 1.066            | C-O stretching                                        |
| 1.033         | 1.022            | C-O and C-C stretching                                |
| -             | 995              | C-O valence vibration                                 |
| 897           | 895              | C(1)-H(β) deformation                                 |

This result has supported by gravimetry test result with Chesson method to cellulose, lignin and hemicellulose content. Table 2.

| Chemical component       | Untreated fibers (%) | BMF (%) |
|--------------------------|----------------------|---------|
| Cellulose                | 61.25                | 84.35   |
| Lignin                   | 31.45                | 10.6    |
| Hemicellulose            | 7.26                 | 5.05    |

3.2. Mechanical properties

From Figure 2 (a) and (b) shows the tensile strength and elastic modulus were increases dependence on the BMF content, but it does not apply for specimens with mass more than 40%. In this study, could be observed the maximum value of GC tensile strength and elastic modulus were found to be 36.67±8.03 MPa and 121.40±16.9 MPa. These values were obtained for the GC at 40% of BMF content.
As compared to tensile strength of neat PLA (23.53 MPa) and tensile strength for BMF networks (2.3 MPa) [26]. After embedding the BMF in PLA tensile strength and elastic modulus were found increase till 100% and 150% (at optimum content of BMF, 40% of BMF mass). There is a decrease in tensile properties of GC more than 40% of BMF mass. It could be indicated for two condition such as voids and weak adhesion force between BMF and PLA. This results from interaction between MFC fibrils and PLA resin and tensile fracture, as shown in the SEM image. This improvement also confirms that BMF prepared from bamboo fibers using a combination between chemical solution and mechanical treatment can be used as reinforcement with PLA.

3. 3. Morphology
Internal structure of specimens with 20% of BMF mass content has BMF-rich and BMF-poor regions. Figure 3(a). The specimens with 40% of BMF mass content has evenly mixed between BMF and PLA, Figure 3(b). And the specimens with 50% of BMF mass content has inter-fiber bond each other with having resin and without having any resin Figure 3(c).
On the other hand, the fracture surface of tensile specimens with 20%, 40% and 50% showed in Figure 3(a), (b) and (c), respectively. In the Figure 3(a) shows the availability of fiber pull out without fiber fracture on the fracture surface, which is indicate weak interface bonding in this specimens. This indicate answered why this specimens weaker than the others. The experimental of tensile strength have been found maximum for the specimens with 40% of BMF content. The fiber pull out of this specimens accompanied with fiber fracture, Figure 3(b). This indicates that the BMF/PLA interface adhesion force of this specimens was higher than the other specimens. While, in specimens with 50% of BMF content, there was decreases in the tensile strength, Figure. In the Figure 3(c) shows there are fiber pull out without fiber fracture and fiber pull out with fiber fracture in this specimens. The existence of pull out without fiber fracture (weak interface adhesion force) in this specimen be the main causes of tensile strength decreases.

4. Conclusions
BMF was studied to know the potential reinforcement with goal of making green composites (GC). The GC from BMF/PLA were prepared and the chemical properties, mechanical properties and morphology were analysed. Combination between chemical solution and mechanical treatment to get BMF is effectively to used (removing impurities on the fibers and disintegrate a rigid structures). The resulting of embedded of BMF in PLA was increased the tensile strength by 100% and 150%. The maximum tensile strength and elastic modulus have been found in specimen with 40% of BMF
content. This indicates refer to interface adhesion force of this specimens higher than the other. BMF is a promising reinforcement of PLA composites as a GC and it could be developed further for various structural applications.

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