Chemical contents and thermal stability of Madu bamboo (Gigantochloa albociliata) for natural-bonded fiber composites

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Abstract. The objective of this study was to evaluate the chemical contents and thermal stability of young (3 years old or less) and matured (more than 5 years old) Madu Bamboo (Gigantochloa albociliata). The comprehensive knowledge of these properties will help to promote the uses of this bamboo’s fiber for natural-bonded composite products. The different age levels of bamboo can be an indicator in evaluating the significant difference of the chemical contents and thermal stability of bamboo. The chemical contents were determined in accordance to the standard outline in Technical Association of Pulp and Paper Industry (TAPPI) test method, while thermal stability was conducted in accordance to Shimadzu TGA 50 analyzer. The culm exhibited different chemical contents between young and old age, in which, young bamboo showed higher hot water extractives and ash contents compared to mature bamboo. On the other hand, matured bamboo contained higher alcohol-toluene extractives, holocellulose, α-cellulose and lignin than young ones. Hence, more resin and possible wood gum in matured bamboo that is beneficially in natural bonded composite product. The thermal analysis of extracted bamboo fiber indicated the thermal degradation behavior of both young and matured bamboo with the same species. The maximum temperature degradation of both young and matured bamboos was 413°C and 404°C. Therefore, matured bamboo was degraded at lower temperature compared to young bamboo, which indicates lower thermal stabilities. The result of this study reported that young bamboo of G. albociliata species is acceptable to be harvested at young ages for reinforcement in natural bonded composite board, according to their thermal stabilities and chemical contents.

1. Introduction

The importance of bamboo’s material attributes such as anatomical features has to be understood, especially for fiber-based products. Low specific weight with excellent physical and mechanical properties caused the bamboo to present versatile structure which makes it be one of the natural fibers used by manufacturers. Anatomically, the structure of bamboo culm transverse section is characterized by numerous vascular bundles embedded in parenchyma tissue [1]. Kassim et al. [2] in their study have reported the anatomical features of Malaysian bamboo species, such as fiber length in vascular bundles. Quantity and distribution of fibers around vascular bundles affected the density of bamboo which varies from 500 to 800 kg/m³ as the maximum density obtained from 3 years old culm. Anatomical features influence the physical and mechanical properties of bamboo materials [3] and are thus often associated with its toughness, workability
and durability. Chemical compositions, size, shape, orientation and thickness of the cell walls affected the mechanical properties such as tensile strength, elongation at break and young modulus [4]. According to Wimmer et al. [5], fiber length has directly affected the bending stiffness of paper composite. It is also one of the factors controlling the strength properties of board, since the length of an individual fiber is associated with the number of bonding sites between fibers [5]. Mohmod et al. [6] have studied the inter-relationship of bamboo portion and age in relation to the anatomical properties of bamboo. In general, fiber dimensions increased with age, while fiber wall thickness and the runkle ratio decreased with bamboo height [6]. Higher density of fibers is predominantly found in the external layer compared to internal layer along the thickness in which the fiber sheath is distributed [7].

The selection of bamboo species for composite applications is not only related to anatomical features, but also chemical compositions. As reported by Abdul Razak et al. [8], the main chemical components of bamboo are holocellulose (60 – 70%), pentasons (20 – 25%), cellulose, hemicelluloses and lignin (each amounted to about 20 – 30%). Minor constituents are slimes, tannins, waxes and inorganic salt [9]. Compared to wood, however, bamboo has higher alkaline extractives, ash and silica contents [10]. This silica content affects the pulping properties of bamboo. The hydrophilic nature due to the presence of hydroxyl group throughout the structure especially for cellulose and hemicellulose portion becomes one of the limitations of the natural fibers [4]. Chemical compositions of bamboo varied with age within species [11]. Therefore, chemical compositions of bamboo can be correlated to the properties of composite products.

The thermal stability is an analytical technique used to determine the materials thermal stability and its fraction of volatile components by monitoring the weight change that occurs when the sample is heated at constant rate. Thermal stability of natural plant fiber is important and critical issue in reinforcement composite materials for various applications especially in aerospace industry [12]. In the process of bio-composite preparation, thermal analysis of natural fiber is important due to the fiber limited thermal stability during composite development [13]. Bamboo fiber composite are fabricated by various method especially hot press and cold press. Heat is used in different manners at all method; therefore, it is essential to ensure that bamboo fiber reinforced composite have the ability to conserve their properties and withstand the heat typical of composite preparation.

2. Materials and Methods

2.1 Material preparation
The preparation of raw material was carried out at the Bio-Composite Laboratory of the Faculty of Applied Sciences, Universiti Technologi MARA (UiTM) Shah Alam. Bamboo poles were split longitudinally into strips by using eight friction bamboo splitters to cut the bamboo. The bamboo strips were put through the stripper machine to remove the bamboo skin. The bamboo strips were crushed using hammer mill to reduce its size into particles and screened to classify the particles into medium (20-60 mesh) particle sizes.

2.2 Characterizations
2.2.1 Chemical analysis
The component in chemical constituent of bamboo Gigantochloa albociliata or known as Buloh Madu were determined. The chemical composition of these species include extractive, holocellulose, α-cellulose, lignin and inorganic constituent. These was determined by several chemical testing in accordance with the standard outlined in TAPPI test methods. The determination of extractive content was carried out in according to the TAPPI T264, 1988 and T204, 1997 testing procedure [14]. The test procedure for holocellulose content and α-cellulose was determined following procedure of Le wise et al. 1946 and TAPPI
The lignin content in this species was determined according TAPPI T222, 1998 [14]. The inorganic constituent in lignocellulosic materials was referred to the ash content which is the residue remaining after combustion of extracted sample at 525±25°C according to procedure outline in TAPPI T211, 1993 method [15].

2.2.2 Thermogravimetric analysis
Thermal analysis is used to analyze the thermal stability and degradation temperature of materials. Thermogravimetric and Differential Thermogravimetric analysis (TGA/DTG) were carried out using (10.0±0.5)mg of bamboo powder. The experiment was performed at constant heating rate of 30°C/min, from room temperature up to 800°C, using Thermogravimetric analyzer (Shimadzu TGA 50), under inert atmosphere (pure nitrogen) with flow rate of 100 mL/min.

3. Results and Discussion/Results
3.1 Chemical Composition
The hot water procedure removes a part of extraneous component such as tannins, gums, coloring matter, sugar and starch. According to Table 1, the hot water solubility was estimated to be 12.04% at young age while 9.71% at old age. There is no significant difference between young and old bamboo culm. Alcohol-toluene extractives from bamboo consist of soluble materials not generally considered as part of the bamboo substances, which are primarily the waxes, fats, resin and some gums. The alcohol-toluene extractive content is higher at old bamboo culm with 2.09% while about 1.01% at young age. The epidermis of bamboo has an attractive green color due to presence of chlorophyll in its epidermis. The extraction with alcohol-toluene change the color of solution to dark green due to the extraction of chlorophyll [16]. The old bamboo generally darker green in color than young age, thus it has more chlorophyll substances in epidermis that easily degraded by alcohol-toluene solution, hence show higher alcohol-toluene soluble.

Holocellulose include alpha-cellulose and hemicellulose. It is normally consist about 50-70% in the bamboo [9]. From the result, the highest holocellulose content 57.33% was observed in old bamboo culm, whereas lowest holocellulose content 53.18% in young bamboo culm. Young bamboo culm had relatively lower holocellulose content in the epidermis due to its high extractive and ash content. Apart from that, old bamboo culm has heavy distribution of vascular bundle possess to higher holocellulose content. Previous study showed that epidermis consist of outer layer and inner layer; the inner layer appears to be highly lignified [17]. Since outer layer had higher extractive and ash content, it is seriously reduced the holocellulose in the bamboo epidermis [18].

Alpha cellulose is one of chemical constituents in the holocellulose. It is a dry substances approximately 40-55% main constituent in the bamboo [18]. Alpha-cellulose content between young and old bamboo culm were 42.98 % and 43.12% respectively, it is almost similar with the alpha-cellulose content in the softwood (42%) and hardwood (45%). There is no statistically significant difference on alpha-cellulose between the age level. The alpha cellulose content for cultivated bamboo on genus Gigantochloa is in ranged 33.79% to 51.76% [19]. Other study on the G.scortechinii and G.lagulata reported alpha-content about 46.14-46.53% and 48.4-56.45% respectively [20].

Lignin is polymer of phenylpropane units. It is acid insoluble that can be obtained after removing the polysaccharides from extracted wood by hydrolysis process with 72% sulfuric acid [21]. It constitutes 23% to 33% of wood substances in softwood and 16% to 25% in hardwood. Although lignin occurs in the wood throughout the cell wall, it is concentrated toward the outside of the cell and between the cell. The lignin content in the bamboo is almost similar with the softwood and hardwood. The young bamboo culm is significantly lower than old bamboo culm but the magnitude of difference is not statistically significant. From the result, old bamboo culm is suitable in construction because high lignin content contributes to high
heating value of bamboo and its structural rigidity makes it a valuable building material [22]. The high lignin content also contributes greatly to the strength properties of the outer layer of bamboo [18]. Previous study on genus *Gigantochloa* reported four species of these genus is in range 24.84% to 32.65% [19]. Hisham et al. [23] previously obtained *G.scortechinii* at range 23.40% to 29.00%. Ibrahim et al. [20] observed lignin content in *G.scortechinii* and *G.lagulata* about 16.12%-12.48% and 12.02%-11.69% respectively.

Ash is a term generally used to refer to inorganic components such as sulfates, silicates, carbonate or metal ions [24]. The inorganic component is generally expressed as percentage of ash, based on dry weight of the sample [19]. The young bamboo culm had high ash content but there is no significant different among both of the age level. Higher ash content means it contains more silica at the entire epidermis with hardly any silica in the rest of the wall [25]. Several common wood species have ash contents ranging from 0.43% (aspen) to 0.87% (white oak) [26]. Previous studies on the genus *Gigantochloa*, the bamboo has significantly higher ash content compared to these wood species and other genus of bamboo, but it is reported as similar with kenaf from 1.6-2.2% [27].

### Table 1. Chemical composition of *G. albociliata* at different bamboo age levels.

| Chemical components (%) | Gigantochloa albociliata age levels |
|-------------------------|----------------------------------|
|                         | Young bamboo culm | Old bamboo culm |
| Hot water solubility    | 12.04              | 9.71             |
| Alcohol-Benzene solubility | 1.01               | 2.09             |
| Holocellulose           | 53.18              | 57.33            |
| α cellulose             | 42.98              | 43.12            |
| Lignin content          | 22.82              | 24.67            |
| Ash content             | 1.87               | 1.59             |

### 3.2 Thermal Properties

The differences in thermal degradation for this bamboo species (*G. albociliata*) characterized by the peak temperature and weight loss between young and old age levels as shown in Figure 1 and Table 2. The first stage of degradation is the dehydration phase (25 < T < 150°C). This phase was attributed to moisture and some extractive evaporation in the fiber [28]. As the result, young age bamboo has higher weight loss with 1.31% while old age bamboo is lowest with 0.86%. this is due to more moisture and bound water release from the bamboo fiber [13].

Next zone degradation is known as active pyrolysis where the rate of mass loss was rapid correspond to the decomposition of hemicellulose, cellulose and lignin. The first degradation stage, the mass losses that began in young and mature bamboo negligible between temperature of 114°C to 216°C. At this stage the TGA curve displayed the decomposition of hemicellulose and followed by the breakdown of cellulose [13]. Young bamboo at first degradation show a mass loss about 1.24% while mature bamboo mass loss about 1.15%; therefore, young bamboo degrades more hemicellulose than mature bamboo. On the other hand, second degradation stage show that young bamboo mass loss about 1.70% lower than mature bamboo mass loss about 1.86%. From Table 2, both bamboo age degraded cellulose at high temperature at range 215°C to 272°C. The degradation of cellulose take place at higher temperature due to its complex structure will cause higher stability compared hemicellulose. Therefore, cellulose content is in contrast with hemicellulose between young and mature bamboo.

From Figure 1, it can be seen that thermal degradation for both, young and mature bamboo occurred at higher temperature but within the range due to the thermo-chemical changes of hemicellulose of same
species within different ages level. Hemicellulose is a heterogeneous polymeric network which has an amorphous structure and has lower molecular weight compared to cellulose; therefore, it can decompose easily at low temperature [29]. Cellulose is in contrast with hemicellulose as it has long chain of polysaccharides which is more thermally stable. From Figure 1 and Table 2, mature bamboo degraded more compared to young bamboos. Hence, more cellulose degraded will cause less thermal stability in mature bamboos.

Table 2. Thermal degradation data of bamboo *G. albociliata* between young and old age levels.

| Bamboo ages | Dehydration | Active pyrolysis | Passive pyrolysis |
|-------------|-------------|------------------|-------------------|
|              | Weight loss (%) at temperature (25-150 °C) | 1st degradation | 2nd degradation | 3rd degradation | Char residue (%) at temperature (600 °C) |
| Young       | 1.31        | 114-215          | 1.24              | 215-270          | 1.70              | 270-413                      | 34.72      | 61.86 |
| Old         | 0.86        | 119-216          | 1.15              | 216-272          | 1.86              | 272-404                      | 45.20      | 49.13 |

Following the degradation of cellulose, the degradation of lignin take place at range 270°C to 413°C. The decomposition of lignin in matured bamboo is 45.2% higher than young bamboo about 34.72% weight loss. Lignin is a component that contain aromatic compound unlike hemicellulose and cellulose, which is main component of the cell wall [30] It has complex structure, which is bonding the hemicellulose and cellulose together. Therefore, the decomposition of lignin is slow and more difficult during entire temperature range up to 700°C [31]. The higher mass loss in third stage decomposition will cause less thermal stability due to more lignin degraded. Therefore, matured bamboo is less thermal stability as the strong component that bind cellulose and hemicellulose is less.

The residual char of *G. albociliata* within young and mature bamboos was 61.86% and 49.13% respectively. The diversity in amount of residual char existed due to differences in chemical composition in bamboo [31]. From Figure 1, matured bamboo degraded at lower temperature than mature bamboo, which indicated that the thermal stabilities of matured bamboo were lower than young bamboo.
4. Conclusion
The chemical composition of *G. albociliata* or known as Buloh Madu of young (3 years old or less) and mature (5 years old) was determined. The young bamboos reported higher composition in hot water solubility and ash content while matured bamboos have higher composition in alcohol-toluene solubility, holocellulose, alpha-cellulose and lignin content. The TGA analysis shows that young bamboos (3 years old or less) have better thermal stability compared to mature bamboos; hence, it is acceptable and suitable to harvest within 3 years old culm to be used in development of natural bonded composites. Thus, both young and matured bamboo are suitable to be used in natural bonded board, but matured bamboo is more favourable. On the other hand, due to time consuming, young bamboo also acceptable based on its good thermal stability.

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