Changes in chemical components with NIR spectroscopy and durability of samama wood treated with boron, methyl methacrylate and heat treatment

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Abstract. Wood quality modifications have the potential to degrade the wood's chemical components, especially those using heat treatment. In fact, wood quality improvement should be identical with the durability improvement and the other specific purposes, such as fixation improvement of preservative materials. This research was aimed to examine changes in chemical components and durability of Samama wood gradually impregnated with boron, methyl methacrylate (MMA) and heat treatment (HT). Each of borax and boric acid was impregnated in pressure tank, continued with MMA impregnation. A 5-atm pressure is applied for 4 hours to both borax and MMA impregnations. The next stage is HT at 90°C and 180°C. The analysis on chemical components was conducted using NIR Spectroscopy and the durability was tested using drywood termites. The results showed that there were changes in lignin, cellulose and hemicellulose components of the wood, as indicated with clear differences in spectra between impregnated and non-impregnated woods. The most significant difference was found on wood impregnated with borax, MMA and HT at 180 °C. This tested sample evidently had the best durability among the tested samples.

1. Introduction

Strengthening mechanism of boron bond with wood has been presented by previous researches. This strengthening may be classified into three parts. First part is chemicals addition. Addition of polyflavanoid tannins evidently improves boron resistance to leaching up to threefold [1]. Boron residue inside the wood after leaching increases in line with enhancement of the quaternary ammonium compounds concentration [2]. A synthesis of vinyl ester of 4-carboxyphenylboronic acid and its test as reactive reagent which is able to maintain boron fixation permanently have been conducted [3]. Second step is bulking agent addition in order to keep boron inside the wood [4, 5]. Third step is finishing quality modification [6]. In addition, the other mechanisms include the application of oil heat treatment [7-9], vapour boron treatment [10] and heat treatment [11, 12].

Heat treatment changes wood colour darker, improves wood’s mechanical properties and dimension stability. If boron fixation phases start with monomer impregnation, heat treatment also helps polymerization process [13]. Heat treatment changes wood’s chemical components, including
cellulose, hemicellulose and lignin [14]. No substantial change occurs to lignin, but hemicellulose is degraded and cellulose’s crystallinity index increases [15]. These changes to chemical components are expected to contribute to boron leaching inhibition.

The stronger the boron’s bond in wood, the better its resistance to wood destroying agent. Boron effectively serves to be insecticide and fungicide, so that although it is a long used preservative, but it is still relevant to analyse the issue of improvement of its bond quality in wood, moreover, for woods of fast growing species[16-18]. Second, three-phase modification to improve boron fixation inside wood, which is impregnation, addition of bulking agent as well as heat treatment is infrequently used. Therefore, this research aims at examining the change in wood’s chemical components using NIR and resistance of modified Samama wood to drywood termites.

2. Materials and methods

2.1. Materials

The samama wood was chosen from a tree which is free from defect and has straight and cylindrical trunk. The plant was 9 years old, originated from community forest in Bogor, West Java, Indonesia. After cutting down the plant, the wood was brought to the laboratory in the form of fresh log to be dried with kiln drying until moisture content of 10-12%. The samples were taken at 8 cm from the pith in size of 0.5 cm x 1.5 cm x 1.5 cm (length, width and thickness) for NIR test and 5 cm x 2.5 cm x 2.5 cm for drywood termites test.

2.2. Methods

2.2.1. Material preparation. Boron impregnation was conducted in three phases. First, each of boron solutions in the form of Borax (Sodium tetraboratedecahydrate) and Boric Acid (Trihydrooxidoboron) were impregnated into wood using pressure tube with a concentration of 5% and at 5 atm for 4 hours. The second phase was impregnation with methyl methacrylate (MMA) using catalyst Mepoxi M (Methyl Ethyl Ketone Peroxide) with a ratio of 10:1 (v/v). The pressure used was equal to that in the first phase. The third phase was heat treatment process at 90 °C and 180 °C, each for 4 hours.

2.2.2. Near Infrared Spectroscopy Measurement. The impregnated samama wood is scanned using spectrum at wavelength 1,000 mm to 2,500 nm. The measurement is performed for 30 seconds with three repetitions. The calibration and validation models of NIR spectroscopy are with multivariate calibration method (PLS) [19-21].

2.2.3. Comply’s durability against drywood termites’ attacks. The standard test used is SNI 01-7207-2006 [22]. A glass tube with height 3 cm and diameter 1.8 cm is placed on the surface of Samama wood where 50 workers termites are put in the glass tube and placed in a dark and clean place, free from any other insects. After 12 weeks, an observation is conducted on any change in the weight of test samples, damage and number of surviving termites.

3. Results and discussion

3.1. Change in chemical components

The spectra of the 36 test samples of Samama wood are presented in Figure 1. The type of absorption presented conforms to the spectroscopic diffusion reflectance characteristics of lignocellulosic materials. The chemical contents are shown from the peak and valley of wave absorption. Absorption will increase when the chemical content gets higher. The number and type of atom bonds as well as particle size of test samples influence absorbance value [23].

Hydrogen atom is the most powerful to absorb NIR wave. The implication is most of NIR spectra are dominated by hydrogen bonds. It seems that the different peak of absorption at wavelength 1910 nm influences the spectra’s profile as the result of water content [24]. The OH group contained in
water is absorbed at wavelength 1,916 to 1,940 nm [25]. Fig. 1 also presents difference in peak of absorption at wavelength 1,664 nm to 1,689 nm. The test sample which shows this symptom is one impregnated with MMA, especially when using HT at 180° C. Lignin chemical component is absorbed at wavelengths 1,170 nm by CH=HC, 1,672 nm and 1,685 nm by CH, and at 2,134 nm by CH and CC. The increased absorption at such wavelengths shows an increase of lignin content.

The difference in peak of absorption by Samama wood impregnated with MMA and HT 180°C also occurs with absorption characterizing polysaccharide. The peak at 2,336 nm is classified in stretching and deformation of C–H of frequency of polysaccharide group [20]. Absorption by cellulose occurs at wavelength 1,428 nm by OH functional group, at wavelength 1,780 nm by CH, 2,080 nm by OH and CH bonds, 2,291 nm by CO and OH, 2,335 nm and 2,361 nm by CH bond. Hemicellulose is at wavelength 1370 nm and 1,724 nm with the existence of CH bond. Meanwhile, extractive substance exists at wavelength 2,220 nm with CH and CO functional groups. The absorption rate of cellulose seems to increase and there is no change to hemicellulose. Extractive content is hardly noticeable since it coincides with lignin at wavelength 1,410nm [25]. In addition, various extractive contents in wood make spectra reading more difficult with highly varied functional groups.

3.2. Resistance of treated Samama wood to drywood termites
Samama wood’s weight loss resulted from drywood termites’ attack decreased after heat treatment. This is consistent with all tested samples (Table 1). In addition, MMA application also effectively holds the attack. The results of analysis of variance shows that the applications of MMA, boron and heat treatment result in reduction of drywood termites’ attack. Further, Duncan’s test shows that treatment with 5% Boron, MMA and HT at 180°C results in the least weight loss.
Untreated Samama wood presents the highest weight loss, but only about 2%. With such an attack level, according to SNI 01-7207-2006, it is classified as resistant. This is confirmed by previous study that drywood termites’ attack level on Samama wood ranges from 2 % to 3 % [26]. On the contrary, the least attack level occurs with Samama wood modified with Borax, MMA and HT of 0.6 ± 0.03 % (Table 2). In comparison with untreated Samama wood, the effectiveness of inhibiting drywood termites’ attack is up to 71%.

**Table 1.** Mortality and weight loss of Samama wood modified with Boron, MMA and heat treatment

| Treatment                  | Mortality (%) | Weight Loss (%) |
|----------------------------|---------------|-----------------|
| Untreated, 90 °C           | 98±2.31       | 2.10±0.80       |
| Untreated, 180 °C          | 96±5.77       | 1.09±0.21       |
| Untreated, MMA, 90 °C      | 98±2.31       | 1.50±0.28       |
| Untreated, MMA, 180 °C     | 100±0.00      | 1.01±0.31       |
| 5% BA, 90 °C               | 100±0.00      | 1.43±0.16       |
| 5% BA, 180 °C              | 100±0.00      | 1.26±0.17       |
| 5% BA, MMA, 90 °C          | 100±0.00      | 1.31±0.23       |
| 5% BA, MMA, 180 °C         | 100±0.00      | 0.92±0.16       |
| 5% B, 90 °C                | 100±0.00      | 1.73±0.10       |
| 5% B, 180 °C               | 100±0.00      | 1.50±0.13       |
| 5% B, MMA, 90 °C           | 100±0.00      | 1.02±0.11       |
| 5% B, MMA, 180 °C          | 100±0.00      | 0.60±0.03       |

**Table 2.** Results of Duncan’s test, treated Samama wood’s weight loss

| Type                | N  | 1     | 2     | 3     | 4     | 5     |
|---------------------|----|-------|-------|-------|-------|-------|
| 5% B, MMA, 180 °C   | 3  | 0.6019|       |       |       |       |
| 5% BA, MMA, 180 °C  | 3  | 0.9198| 0.9198|       |       |       |
| Untreated, MMA, 180 °C | 3 | 1.0076| 1.0076| 1.0076|       |       |
| 5% B, MMA, 90 °C    | 3  | 1.0196| 1.0196| 1.0196|       |       |
| Untreated 180 °C    | 3  | 1.0898| 1.0898| 1.0898|       |       |
| 5% BA, 180 °C       | 3  | 1.2632| 1.2632| 1.2632|       |       |
| 5% BA, MMA, 90 °C   | 3  | 1.3076| 1.3076| 1.3076|       |       |
| 5% B, 90 °C         | 3  | 1.4297| 1.4297| 1.4297|       |       |
| Untreated, MMA, 90 °C | 3 | 1.5008| 1.5008|       |       |       |
| 5% B, 90 °C         | 3  | 1.5016|       | 1.7293| 1.7293|       |
| Untreated 90 °C     | 3  |       | 1.7293| 1.7293|       | 2.1033|

**Sig.**

|     | 0.077 | 0.072 | 0.084 | 0.096 | 0.130 |

Means for groups in homogeneous subsets are displayed.
Based on observed means.
The error term is Mean Square(Error) = 0.085.

There are different types of attack between destroying organisms. For example, white rot fungi only attack lignin but do not attack cellulose. Brown rot fungi only destroy cellulose but do not attack...
lignin. Differently from the two types of destroying organisms, drywood termites destroy wood components entirely, in which they attack wood surface and slowly attack other parts of wood [27-29]. Therefore, the changes in chemical components presented with NIR analysis are not substantially correlated with drywood termites’ attack level. The direct correlation is that, in case of toxic impregnant, attack will be inhibited and high mortality will be up to 100%.

4. Conclusions
An increase of lignin component was found after Samama wood modification process using Borax, MMA and heat treatment at 180°C. Besides lignin, there were spectra which indicate that cellulose also increased. On the contrary, no change was found in the composition of hemicellulose and extractive substance. Drywood termites’ attack level on Samama wood modified with borax, MMA and heat treatment at 180°C decreased up to 71%.

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