Effect of Citric Acid and Benzophenone Tetracarboxylic Acid Treatments on Stability and Durability of Short Rotation Teak Wood

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Abstract

Short rotation teak has been around 30 cm in diameter at the age of 15 years, however the wood is low quality especially in dimensional stability and durability. The short rotation teak wood was treated by non-biocide chemicals of Citric Acid (CA) and Benzophenone Tetracarboxylic Acid (BPTCA). The objective of this study was to improve dimensional stability and durability of the short rotation teak by modification treatment of CA and BPTCA. Short rotation teak sapwood was impregnated by 20% and 40% of both CA and BPTCA followed by heated in oven at 150 °C (HT150°C) for 2 h. Dimensional stability was characterized by anti-swelling efficiency (ASE), water uptake (WU), and termite durability was determined by weight loss and percentage of damage of the wood samples. The results show that the ASE values increased in the average of 46% and 50% after CA and BPTCA treatments, respectively. The WU values decreased in the average of 34% and 22% after CA and BPTCA treatments, respectively. These phenomena indicated a remarkable improvement in dimensional stability of the treated teak wood. Weight losses of treated teak woods due to termites were in the average of 1.0% and 1.5% after CA and BPTCA treatments, respectively, which categorized their durability to be class 1 (very durable). The results showed by Fourier Transform Infrared (FTIR) indicate that chemical reaction of wood lignin with CA and BPTCA chemicals was occurred. The CA and BPTCA treatment can be applied for improving the quality of short rotation teaks for high quality wood product utilization.

1. Introduction

High quality teak wood (Tectona grandis Linn. F.) from long rotation (60 to 80 years) plantation has been declining year after year. The amount of long rotation teak wood production in Indonesia in 2017, the first quarter was 134500 m³ and decreased in the fourth quarter to 115841 m³ (Badan Pusat Statistik 2017). Short rotation (10 to 15 years) teak plantation should be a promising solution to overcome the scarcity supply of teak wood from long rotation. Short rotation teak plantation has been increasing, in which the total area managed by state owned forest (PERHUTANI) is around 300 ha at 2021. The short rotation teak plantation has been recently also developed by other communities and private companies. Short rotation teak plantations produce tree diameters of 25 to 30 cm. These trees are lesser branches with straight and cylindrical trunks. However, the short rotation teak wood has low density, stability and durability, and high proportion of juvenile wood (Darmawan et al. 2015; Rizanti et al. 2018). Juvenile wood has shorter fibres with thinner walls, and larger microfibril angles, which lead to lower strength compared to mature wood (Evans et al. 2000; Koubaa et al. 2005; Clark et al. 2006). The present of high juvenile portion in the short rotation teak wood could affect its processing during production of end-product values. Therefore, a promising green wood modification treatment should be needed to improve the quality and finally to increase the utilization of the short rotation teak wood for high quality wood products.

Wood modification was proposed to improve the quality of wood (Hill 2006). Thermal modification has been the most important wood modification developed on industrial scale. An innovative eco-friendly thermal modification was investigated to improve the quality of short rotation teak (Martha et al. 2021a). The results indicated that anti-swelling efficiency (ASE) value after heat treatment is improved ranging
between 12.9% and 46.7%, indicating an improvement in dimensional stability. It was also reported in the study, the surface roughness and SFE values decrease as the heating temperature increased. The teak wood treated at 220°C provides the K-values (0.04 for acrylic and 5.04 for alkyd paint) larger than 0, which indicate a good wettability. However, heat treatment at the 220 °C decreases the MOE and MOR values of the short rotation teak, and does not provide any improvement in durability against termite (Pratiwi et al. 2019). It was reported in another study that heat treatment at 220 °C increases durability of the short rotation teak against decay fungi (Trametes versicolor) from moderate to very durable (Pratiwi et al. 2019).

In parallel to thermal modification, chemical modification constitutes another attractive alternative as promising wood treatment method. Even if a lot of methods have been proposed at laboratory scale for the chemical modification, only two of them have led to the development of industrial application, namely acetylation and furfurylation (Gérardin 2015). Chemical modification with furfuryl alcohol is a non-toxic alternative method to replace the toxic conventional preservation treatments. Esteves et al. (2011) treated wood with 70% furfuryl alcohol mixture and obtained anti-swelling efficiency (ASE) as high as 45% at a weight percent gain (WPG) of approximately 38%. Furfurylation treatment leads to an improvement of several wood properties like dimension stability, modulus of elasticity (MOE), modulus of rupture (MOR), hardness, decay resistance (Esteves et al. 2011; Sejati et al. 2016; Dong et al. 2015). Li et al. (2015) reported a slight improvement on MOE and MOR of furfurylated wood. The furfurylation treatment provides a more significant effect on compressive strength compared to MOE and MOR. Furfurylation treatment can improve durability against fungal decay (Lande et al. 2008; Esteves et al. 2011; Li et al. 2015), termites (Hadi et al. 2020), and marine borers (Lande et al. 2008). Recent studies regarding ecotoxicology and leachates of furfurylated wood indicate that the furfurylated wood has a low ecotoxicity (Lande et al. 2008; Pilgård et al. 2010).

Furfurylation treatment was applied to improve technological properties of short rotation teak wood. The short rotation teak sapwoods were treated through impregnation process using 45% furfuryl alcohol (FA) and 5% of tartaric acid as catalyst followed by heating at 120 °C for 16 h under nitrogen atmosphere (Martha et al. 2021b). The results of the study showed that ASE increases in the average of 64%, and WU decreases in the average of 59%, which indicates the improvement in dimensional stability of the furfurylated short rotation teak. Weight losses of furfurylated teak woods due to fungal decay of Coriolus versicolor (CV), Pycnoporus sanguineus (PS), and Coniophora puteana (CP) are in the average of 2%, 1%, and 1%, respectively, which categorized their durability to be class 1 (very durable) (Martha et al. 2021b). Fourier Transform Infrared (FTIR) and Carbon 13 Nuclear Magnetic Resonance ($^{13}$C NMR) analysis indicated that the reaction of FA with lignin occurs after furfurylation treatment. The FA treatment can be considered as a promising method for improving the quality of short rotation teaks, though MOE and MOR are decreased after furfurylation.

Chemical modification has been performed by impregnation of non-biocide Glycerol-maleic anhydride (GMA) followed by heat treatment to improve technological properties of short rotation teak wood, especially dimensional stability and durability (Martha et al. 2021c). Impregnation with 10% w/w
aqueous solution of GMA followed by thermal modification at 150 and 220 °C under inert conditions was investigated on short rotation teak sapwood. The results of the study showed that chemical modification with 10% GMA combined with thermal modification increases ASE by 62.31% and 73.22% for 150 and 220 °C, respectively, indicating improved dimensional stability. Decay resistances of GMA-thermal treated teak wood against fungal decay of *Coriolus versicolor*, *Pycnoporus sanguineus*, and *Coniophora puteana* are categorized to be class 1 (very durable) (Martha et al. 2021c). Weight loss of GMA-thermal at 220 °C against termite attacks is 0.19%, which presented excellent durability (rating 10) against subterranean termites (Martha et al. 2021c). In addition, fourier transform infrared and carbon 13 nuclear magnetic resonance analyses indicated that the presence of reaction between GMA polymer with lignin occurs after thermal treatment at 220 °C. GMA-thermal treatment gave a significant improvement in dimensional stability and resistance to wood-decaying fungi and termite, however the MOE and MOR of the treated short rotation teak decrease up to 25% (Martha et al. 2021c). Mechanical and biological durability properties against soft-rot (soil bed test) and subterranean termites (grave-yard test) of beech wood modified with GMA at different curing conditions were also reported (Mubarok et al. 2021). The results revealed that GMA modified beech wood presents higher modulus of elasticity (MOE) value than untreated wood, however, modulus of rupture (MOR) decreases remarkably. In addition, biological durability in the soil bed test against soft-rot indicated that the GMA modified wood is specified as “durable” to “very durable”. However, among the treatments, the beech wood modified with GMA 20% heated at 150°C and GMA10% heated at 220°C present excellent durability against subterranean termites within a period of 328 days in the field.

The results presented above give an indication that the decrease in the strength of the modified woods could be caused by the high temperature (larger than 150 °C) imposed during the modification processes. A new innovation on environmentally friendly non-biocidal chemicals which could be cured at lower temperature need to be proposed. The present study was designed to investigate the effect of non-biocidal CA and BPTCA treatment of short rotation teak to develop further industrial valorization on physical properties (weight percent gain (WPG), density, and leachability), dimension stability (anti-swelling efficiency (ASE), water uptake (WU)), bending strength (MOE and MOR), termite resistance (weight loss, and defective samples), surface characteristics (wettability, surface free energy (SFE)). Location of CA and BPTCA in wood and in its different components was evaluated by Fourier Transform Infrared spectroscopy (FT-IR).

2. Materials And Methods

2.1 Sample Preparation

The sample trees of short rotation teak of 20 years with around 40 cm diameter were obtained from plantation forest managed by the state-owned enterprise (Perhutani) at Blora, Central Java (7°08’25.2”S/111°36’19.5”E). Blora, Central Java has an average rainfall between 1496-2506 mm/year
and dry conditions for 4–6 months with an average temperature of 27 °C. Log sections in length of 1 m were taken from each tree sample at the bottom part of the stem. The logs were transported to workshop and band-sawed into boards in thickness of 3 cm. Board samples were air dried up to a moisture content of 12–15% and then sawed into smaller samples for modification test and their characterisations. Test samples for CA and BPTCA treatment were prepared in size of 200 x 20 x 50 mm³ (longitudinal x tangential x radial). Impregnation of CA and BPTCA was performed on sapwood samples considering that heartwood presented sufficient natural durability and poor impregnability.

2.2 Citric Acid and Benzophenone Tetracarboxylic Acid Treatment

Both CA and BPTCA were ordered in form of powder used as the impregnation solution. Both CA and BPTCA of 20% and 40% concentration each were prepared in aqueous solution. All test samples before treatment were dried at temperature 103 ± 2 °C, the weight (m₀) and volume (V₀) were measured. The impregnation process was initiated with vacuum conditions 8–10 kPa for 5 min in an autoclave and followed by introduction of the aqueous CA and BPTCA solution. Afterward, the test samples in the CA and BPTCA solutions were exposed to a pressure of 1200 kPa for 10 min. The impregnated samples were kept at room temperature for 48 h to evaporate the excess of water. The impregnated samples were wrapped in aluminium foil to avoid CA and BPTCA evaporation during curing and placed again in an oven for polymerization. The oven temperature was slowly increased by 0.5 °C min⁻¹ from ambient to 100 °C and maintained at this temperature for 1 h. After this period, the oven temperature was increased by 0.5 °C min⁻¹ to 150 °C (HT150°C) and was maintained for 2 h. Heating was then stopped and treated wood samples were allowed to cool down to room temperature under inert atmosphere. All treated woods were measured for their weight (m₁) and volume (V₁).

2.3 WPG and density measurement

WPG was calculated using the following equation (Eq. 1):

\[
\text{WPG} (%) = \left( \frac{\text{m}_1 - \text{m}_0}{\text{m}_0} \right) \times 100 \quad (1)
\]

where WPG is the percentage of weight gain due to the Citric Acid and Benzophenone Tetra Cyclic Acid treatment, m₀ is the initial mass of wood at 103 °C before treatment, m₁ is the mass of wood after treatment.

Density was calculated from the following equation (Eq. 2):

\[
\text{Density (gr cm}^{-3}\text{)} = \frac{\text{m}_0}{\text{V}_0} \text{ or } \frac{\text{m}_1}{\text{V}_1} \quad (2)
\]

where m₀ is the initial mass of wood at 103 °C before treatment, m₁ is the mass of wood after treatment, V₀ is the initial volume of wood at 103 °C before treatment, V₁ is the volume of wood after treatment.

2.4 Leaching test
The leaching tests of untreated and treated short rotation teak woods were carried out according to a procedure adapted from NF X 41-568 (2010). Test samples of 30 × 15 × 5 mm$^3$ (L, R, T) were prepared in six replications for both untreated and treated woods. The leaching test samples were submerged in test tubes containing distilled water with a quantity of distilled water representing 5 times the volume of the introduced samples. The leaching test for the samples were carried out in leaching periods 24 h at 25 °C. Between the periods of 12 h, the used distilled water was removed and the wood samples were kept without water for 16 h in tube test. After leaching periods were completed, samples were dried at 103 °C for 48 h and reweighed ($m_2$).

Weight loss due to leaching ($WL_L$) was calculated from the following equation (Eq. 3):

$$WL_L (%) = \left( \frac{m_1 - m_2}{m_1} \right) \times 100$$  \hspace{1cm} (3)

where $WL_L$ is the percentage of weight loss of untreated or treated wood due to leaching, $m_1$ is the mass of wood after treatment, $m_2$ is the mass at 103 °C of untreated and treated wood after leaching process.

### 2.5 Fourier Transform Infrared (FT-IR) Spectroscopy

FT-IR spectrums were recorded on an ATR-FTIR Perkin Elmer Spectrum 2000 instrument in the range of 600 - 4000 cm$^{-1}$ at a resolution of 4 cm$^{-1}$ with an ATR cell both for untreated and treated samples.

### 2.6 ASE and WU measurement

The ASE and WU were measured by the method developed by Pfriem et al. (2012). Dimensional stability test samples in dimension of 10 × 20 × 20 mm$^3$ (L, R, T) were prepared in five replications from untreated and treated wood. The untreated and treated wood were dried at 103 °C and their weights ($W_d$) and volumes were recorded ($V_d$). The samples were directly immersed in distilled water and placed under vacuum condition (10 kPa) for 1 hour. After 24 h imposed in the vacuum, the samples were released from the distillate water and their green weight ($W_w$) and volume ($V_w$) were measured. Four cycles (1, 2, 3, and 14 days) of drying-soaking system were conducted and their weigh and volume ($W_{di}$, $V_{di}$, $W_{wi}$, and $V_{wi}$) for each cycle were recorded. The volumetric swelling ($S_v$) and ASE were calculated. The volumetric swelling ($S_v$) was determined using formula by equation (Eq. 4):

$$S_v (%) = \left( \frac{V_w - V_d}{V_d} \right) / V_d$$  \hspace{1cm} (4)

where $S_v$ is the percentage of volumetric swelling of wood sample, $V_w$ is the wet volumetric sample of the wood sample, and $V_d$ is the dry volumetric of the oven-dried sample at 103 °C.

ASE was calculated by equation (Eq. 5):

$$ASE (%) = \left[ \frac{(S_{vu} - S_v)}{S_{vu}} \right] \times 100$$  \hspace{1cm} (5)
where ASE is the percentage of anti-swelling efficiency of treated wood, \( S_{vu} \) is volumetric swelling of untreated wood, and \( S_{vt} \) is the volumetric swelling of the treated wood.

WU was determined using the following equation (Eq. 6):

\[
WU(\%) = \left(\frac{(W_w - W_d)}{W_d}\right) \times 100
\]

(6)

where WU is percentage of water uptake, \( W_d \) is the weight of the air-dried sample at 103 °C before immersion and \( W_w \) is the weight after immersion in water.

### 2.7 MOE and MOR

MOE and MOR were measured following the standard procedure of EN 310 (1993) with the sample size of 200 x 20 x 5 mm\(^3\) (L, R, T). Wood samples of both untreated and treated were conditioned at the room with a temperature of at 22 ± 2 °C and relative humidity of 65 ± 5% RH, until constant mass. MOE and MOR of static bending were determined by device INSTRON 4467 universal testing machine (Buckinghamshire, UK).

### 2.8 Field test for termite resistance

The untreated and treated stakes (200 x 20 x 10 mm\(^3\) (L, R, T)) were oven-dried at 60 °C until constant weight (\( W_0 \)). All stakes were embedded in-ground to determine their resistance against subterranean termite at the research field of Faculty of Forestry, IPB University, Indonesia. The dominant subterranean termite species identified in this area has been *Macrotermes gilvus* Hagen. The stakes were buried vertically 150 mm below ground level and placed randomly in a distance of 300 mm among each other. The tests began between mid-December 2021 and mid-March 2022 (period of 3 months). The stakes were removed after 12 weeks, washed with water and cleaned with a brush, dried under sunlight, followed by drying in the oven at 60 °C until constant weight (\( W_1 \)). Stakes mass loss and rating due to termite attack were calculated. The tested stakes were evaluated according to SNI 7207 (2014) (Table 1). The mass loss (ML) was measured according to Eq. (7):

\[
ML(\%) = \left(\frac{(W_0 - W_1)}{W_0}\right) \times 100
\]

(7)

where ML is percentage of mass loss, and \( W_0 \) and \( W_1 \) are dry weight of the samples before and after field exposure, respectively.

The tested stakes were also investigated according to ASTM D 1758 (2006) (Table 2). The wood damage grading system in Table 2 are classified based on the percentage of damages of cross-section due to attacked by subterranean termite.

### 2.9 Surface roughness and wettability measurement
The measurement of surface roughness of wood specimens was performed perpendicularly to the fibre direction at five different positions on tangential surface of each sample using Mitutoyo type SJ-210 tester. The measurement according to ISO 1997 was performed with a diamond tip radius of 5 µm, tracing length of 6 mm, the cut off of 0.8 mm and speed of 0.5 mm/s. The variable evaluated was the arithmetical mean roughness (Ra) value. The dynamic contact angles of alkyd and acrylic varnishes for measurement of wettability were performed with video measuring system with a high-resolution CCD camera. During measurement, teak wood specimen (untreated and CA BA treated) was placed on the top of a table in front of the CCD video camera. The drop of selected standard liquids and the acrylic paint with volume of 20 µl were dropped by a syringe with a screw method to obtain the same droplets. The drop shapes on the wood surface were captured by the CCD camera and saved for the duration of 180 s. Five droplets per sample was captured for each standard liquids and acrylic paint for the measurements of contact angle. Each of the captured video images was cut to an individual image at intervals of 10 s for total duration of 180 s. The Image-J 1.46 software with drop-snakes plugin analysis was used to measure the contact angle (θ) of the individual image of the drop. The contact angles of each droplet on the surface of wood specimen were measured both on the left side and the right side of the droplet and then the values were averaged. The contact angle tests were conducted at the room with temperature of 23°C±2°C and relative humidity of 80% ± 5%.

3. Results And Discussions

3.1 Retention, WPG, Density, and Leachability

The retentions of CA and BPTCA were in the average of 24 kg/m$^3$ and 19 kg/m$^3$, respectively. The results in Fig. 1 indicate that the retention by 20% and 40% concentration was almost the same both for CA and BPTCA. Slightly lower retention of the BPTCA could be due its higher molecular weight (226.23 g/mol) compared to that of CA (192.12 g/mol). However, these values were larger than the minimum retention of 8 kg/m$^3$ recommended for commercial preservatives used in conventional preservation treatment. The results in Fig. 1 also show that the WPG of the teak wood treated by CA and BPTCA was in the average of 28% and 25%, respectively. The increases in the WPG were due to the CA and BPTCA polymers filling cell cavities and the void spaces within the cell wall as presented by the profiles of FTIR results among the untreated and the treated wood samples (Fig. 2). Similar WPG value was also reported by Marta et al. (2021b). It was noted in the study that treated teak wood presents WPG value around 20% after furfuryl alcohol treatment, and the polymerization of furfuryl alcohol is identified and chemical interaction occurs between furfuryl alcohol and lignin.

Heating of the teak wood samples at 150 °C (HT150°C) after CA and BPTCA impregnation caused the occurrence of their chemical interaction with lignin, cellulose or hemicellulose. Figure 2-left presents the FTIR spectra for the untreated, 20% CA, 20% CA followed by thermal at 150 °C, 40% CA, and 40% CA followed by thermal at 150 °C over the 600 to 4000 cm$^{-1}$ wavenumber range. The absorption bands in the range of 3000–3600 cm$^{-1}$ are assigned as the stretching vibration of the -OH in polysaccharides, which
indicate the water bond or moisture absorption (Gupta et al. 2015). The FTIR spectra of all treatments in Fig. 2-left indicated a relative decrease in intensity compared to untreated wood. The peak intensity decreased with increasing citric acid content and curing temperature. In the finger print area, the absorption bands in the spectra of untreated and treated woods were different. On the spectra of treated wood, the spectra presented the increase in absorption band at 1715 cm\(^{-1}\) corresponding to the carbonyl stretching band associated (ester bonds). This result indicates that a complete polymerization of CA and wood lignin occurred. Notably, the peak intensity increased along with increasing citric acid content from 20–40% and increasing curing temperature. These observations confirmed that citric acid has reacted with the hydroxyl groups of short rotation teak wood to form ester linkages and contribute to reduce hygroscopicity.

Figure 2-right shows the FTIR spectra of the untreated 20% BPTCA, 20% BPTCA followed by thermal at 150 °C, 40% BPTCA, and 40% BPTCA followed by thermal at 150 °C over the 600 to 4000 cm\(^{-1}\) wavenumber range. The FTIR absorbance at around 3000–3600 cm\(^{-1}\) for the treated wood, which assigned as the stretching vibration of the hydroxyl group in polysaccharides, showed a relative decrease in intensity compared to untreated teak wood. Similar behaviour was observed for the peak intensity of hydroxyl groups. The peak intensity decreased with increasing BPTCA content and curing temperature. The decrease in the intensity of the hydroxyl groups caused the wood more hydrophobic. The absorption band in the spectra between untreated and treated wood were different especially in fingerprint area. The absorption bands of the treated woods showed a different after 40% BPTCA treatment and 40% BPTCA followed by thermal at 150 °C treatment. The increase in absorption band at 1650 cm\(^{-1}\) associated to C = O stretching. Three small bands were observed at 856, 769 and 721 cm\(^{-1}\) for 40% BPTCA treatment and 40% BPTCA followed by thermal at 150 °C treatment. These small bands are assigned to aromatic C-H out-of-plane deformation (Gupta et al. 2015). The different absorbance bands observed in the spectra of 40% BPTCA treatment and 40% BPTCA followed by thermal at 150 °C treatment indicates that the chemical interaction occurred between polycarboxylic acid and wood lignin.

Variation of density among the untreated and treated teak woods are presented in Fig. 3. Density of the untreated teak wood was 0.56 g/cm\(^3\) and of the treated woods was in the range between 0.60 to 0.63 g/cm\(^3\). The increase of density in the average of 5% was caused by the increase in the WPG of 26%. The deposition of the CA and BPTCA in the cell cavities and in the void spaces within the cell wall increase the density and impart new properties on the treated wood. It was reported in another study that furfuryl alcohol treatment improves density wood because its cell walls are filled with polymerized furfuryl alcohol (Dong et al. 2016). Impregnation of wood with a polymer causes penetration of polymer and strengthen cell walls (Hill 2006). The results in Fig. 4 show that the leachability of treated teak wood was in the average of 1.65% for CA treatment and 1.19% for BPTCA treatment, which indicated a good fixation of CA and BPTCA in the teak woods. The results in Fig. 4 also indicate that the values of leaching decreased slightly after the CA and BPTCA treatment followed by heating at 150 °C. In another study, leaching value was reported to be 0.20% for teak wood after glycerol-maleic anhydride treatment followed
by heating at a higher temperature of 220 °C (Martha et al. 2021c). This slightly lower leaching is caused by the occurrence of polymerization of the glycerol-maleic anhydride and lignin at the 220 °C.

### 3.2 Dimensional Stability (ASE, WU)

The ASE and WU of the untreated and treated teak wood are shown in Fig. 5. The increase ASE value was followed by the decrease in WU value after CA and BPTCA treatments. ASE of CA and BPTCA treated teak wood reached 46% and 48%, respectively. The results in Fig. 5 indicate that remarkable differences on the value of ASE were not observed between unheated and heated CA and BPTCA. The increase of the ASE values suggested that impregnation of the CA and BPTCA polymers can improve dimensional stability of the short rotation teak wood. Reduction of void volume in wood due to filled by CA and BPTCA polymer could stabilize the teak wood dimension. FTIR analysis in Fig. 2 confirm that the CA and BPTCA treated teak wood were difficult to absorb water due to decreasing in hydroxyl groups lead to the increase in dimensional stability. Slightly higher ASE values were reported in other studies. ASE of furfurylated teak wood is in the average of 60% (Martha et al. 2021b), and ASE of glycerol-maleic anhydride unheated and heated at 150 °C for teak wood is 40% and 62% respectively (Martha et al. 2021c). ASE of furfurylated beech wood containing 50% of furfuryl alcohol and 5% of tartaric acid is approximately 66% (Sejati et al. 2016). The WU value of the untreated teak wood was 65%, and decreased to be 31% after CA treatment and to be 42% after BPTCA treatment. The WU decreases after CA and BPTCA treatment could be due to the polymers filling void spaces in wood and blocking the water absorption. The WU value for untreated teak is 94% and decreases to be 37% after furfuryl alcohol treatment (Martha et al. 2021b). The WU of untreated teak wood is to be 92% and decreases to be 52% after glycerol maleic anhydride and thermal treatment at 150 °C (Martha et al. 2021c). The decrease in the WU value indicates reduction in wood hygroscopicity due to the decrease of free hydroxyl groups. The WU and ASE are improved due to the decrease in crystallinity (Dong et al. 2014; Rahayu et al. 2020). This may be attributed to the penetration of furfuryl alcohol into the amorphous region of the wood cell wall (Dong et al. 2014), and filling empty cell as a bulking agent (Baysal et al. 2004; Hill 2011). It can be considered that the CA and BPTCA came in into the empty space in the cell wall as bulking agents to replace water, then the treated teak wood dimension became more stable.

### 3.3 MOE and MOR

MOE and MOR of the untreated and CA and BPTCA treated short rotation teak are presented in Fig. 6. The mean MOE values for untreated, CA and BPTCA treated were 11769.13 MPa, 9947.04 MPa, and 10807.50 MPa respectively. This result indicates that the MOE decreased 15% after CA treated and 8% after BPTCA treated. The values of MOE for the 20% and 40% of CA and BPTCA were almost the same. However, the values of MOE of the CA and BPTCA treated teak wood decreased slightly as the CA and BPTCA treated teak wood were heated at 150 °C. It was noted that the MOE value of furfurylated teak wood decreases by 14% (Martha et al. 2021b), and of glycerol maleic anhydride treated teak wood decreases by 3% (Martha et al. 2021c). The decrease in MOE value was also reported for furfurylated beech wood catalyzed by maleic anhydride (Mubarok et al. 2021). The reason for the decrease in MOE has been clearly reported due to the depolymerisation of wood polymers (Martha et al. 2021a, b, Mubarok et al.
The MOR of untreated wood was 90 MPa, the MOR values of CA and BPTCA treated teak wood were 80.35 MPa and 74.64 MPa, respectively. This result indicates that the MOR decreased 11% after CA treated and 17% after BPTCA treated. The same phenomenon as in the MOE, the values of MOR for the 20% and 40% of CA and BPTCA were almost the same. However, the values of MOR of the CA and BPTCA treated teak wood decreased slightly as the CA and BPTCA treated teak wood were heated at 150 °C. It was reported that MOR of teak wood treated by glycerol maleic anhydride followed by heating at 150 °C decreases 29% (Martha et al. 2021c), and treated by furfuryl alcohol followed by heating at 120 °C decreases 20% (Martha et al. 2021b). The decrease in MOR of the teak wood after CA and BPTCA can be explained due to the acidic property of the CA and BPTCA solution and of the heat imposed which caused the degradation of chemical compounds (Mubarok et al. 2019; Martha et al. 2021a, b; Mubarok et al. 2021).

3.4 Durability against subterranean termite in the field test

Weight losses of untreated, CA and BPTCA treated teak wood against subterranean termite were 17.00%, 1.03%, and 1.56%, respectively (Fig. 7). The results in Fig. 6 show that the concentration of 20% and 40% of both CA and BPTCA of unheated and heated generated almost the same weight loss against termite. This result indicates that the use of CA, and BPTCA with or without thermal treatment could be valuable to protect the short rotation teak wood both against termite. The CA and BPTCA resulted in the fixation with wood components and/or wood degradation products formed, leading to a new material that was unable to be digested by termite. According to the SNI 7207 standard (2014), the termite resistance of untreated was classified as poor (class IV), and that of CA and BPTCA treated teak wood was classified as very resistant (class I). The results in Fig. 8 show that the untreated samples after three moths tested in the field suffered severe damages along their cross sections due to attacked by termites. The damages on their sections reached 22% of their volume (Table 3). The damages were mostly on the buried part of the samples which indicated the attack of subterranean termites. The species of the subterranean termites was Macrotermes sp and Microtermes sp. The damages of the CA and BPTCA treated teak samples were due to slight attacks by the subterranean termites. The percentage of the damages on the CA and BPTCA treated samples was less than 3%. According to the ASTM D 1758 standard (2006), the termite resistance of untreated was classified as grade 7, and that of CA and BPTCA treated teak wood was classified as 9–10 (Table 3). It was reported that the weight losses of untreated, and glycerol maleic anhydride treatment with thermal at 150 °C were 34.13%, 19.49%, respectively (Martha et al. 2021c). In addition, though the glycerol maleic anhydride-thermal at 150 °C treatments of the short rotation teak produces better resistance against fungal decay, however the glycerol maleic anhydride followed by thermal at 150 °C treatments suffers high mass loss against termite (Martha et al. 2021c). According to the SNI 7207 standard, the termite resistance of the glycerol maleic anhydride-thermal at 150 °C teak wood was classified as very poor resistance (class V). This result indicates that the use of CA and BPTCA combined with thermal treatment could be valuable to protect the short rotation teak wood both against fungus and termite.

3.5 Surface roughness and wettability
Figure 9 shows the variation of surface roughness as presented by the arithmetical mean roughness (Ra). The Ra values of untreated, CA and BPTCA treated teak wood was in the average of 14.85 µm, 17.69 µm, and 18.59 µm, respectively. The slightly higher in roughness of the CA and BPTCA treated teak wood could be important in determining their wettability for water-based acrylic and oil-based varnishes wettability. The values of the contact angle of the water-based acrylic and oil-based alkyd are shown in Fig. 9. The untreated teak wood with slightly lower in Ra value generated higher contact angle of 56.29° for acrylic varnish, and of 3.46° for alkyd varnish. The contact angle of the CA and BPTCA treated teak woods were almost the same in the average of 44.31° for acrylic varnish, and 0.24° for alkyd varnish. This result indicates that the CA and BPTCA treated teak wood tended to provide a lower contact angle. The treated teak woods with a lower contact angle caused the water-based acrylic and oil-based alkyd varnish liquid to spread and penetrate easier in their surfaces. Fortunately, the CA and BPTCA treated teak woods in this work presented the water-based acrylic and oil-based alkyd contact angle values lower than 90° which indicate their high wetting ability against the varnish liquids.

Considering the results presented above, the treated short rotation teak wood should be expected to exhibit remarkable dimensional stability, wettability and durability compared to other wood species. Its higher stability and termite resistance would promise its utilization to some extent. The treated short rotation teak should be superior to many other timbers of fast-growing plantations like Indonesian Sengon (Paraserianthes falcataria) and Jabon (Anthocephalus cadamba) (Rahayu et al. 2014), and could be homogenized with long rotation teak wood, which is widely used. The future for short rotation teak wood modification by thermal and chemical methods looks very promising. There are already many new wood substitutes for solid treated wood, including engineered wood composites like wood-plastic composites and products such as preserved oriented strandboard (OSB), laminated veneer lumber (LVL), and parallel strand lumber (PSL). All these products will require both new and existing preserving technologies to prevent the colonization by decay organisms and infestation by wood-destroying insects. Evaluation of engineered wood composites already in service has demonstrated that those without preservation have exhibited both decaying and fruiting bodies after exterior exposure.

4. Conclusion

The non-biocide citric acid and benzophenone tetracyclic acid allows to improve the properties of short rotation teak wood. Dimensional stability of the citric acid and benzophenone tetracyclic acid treated teak wood is increased, though the MOE and MOR are slightly decreased. Durability against subterranean termites of the citric acid and benzophenone tetracyclic acid treated short rotation teak wood is classified as very durable (class I and grade 9 to 10). FT-IR analysis indicates the presence of chemical bonds between benzophenone tetracyclic acid with the teak wood cell wall polymers. The treatments of citric acid and benzophenone tetracyclic acid produce good wettability of both acrylic and alkyd varnishes on the teak wood surface, promoting a good bonding quality of varnish and paint. The citric acid and benzophenone tetracyclic acid treatment can be eco-friendly and valuable method for improving the
quality of short rotation teaks for high quality wood product utilization both interior and exterior purposes.

Declarations

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Competing Interests

The authors declare that there is no conflict of interest. The authors have no relevant financial or non-financial interests to disclose.

Author Contributions

All authors contributed to the research work during the conception, design, performing the work. Material preparation, data collection and analysis were performed by Efrida Basri, Nisrina Hanif, Resa Martha and Istie S Rahayu. The first draft of the manuscript was written by Wayan Darmawan and all authors read and commented on the previous versions of the manuscript. All authors read and approved the final manuscript.

Data Availability

The datasets generated during and/or analysed in this study are available from the corresponding author on reasonable request

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Tables

Table 1

The grading system based on weight loss of stakes by attacked subterranean termite (SNI 7207-2014)

<table>
<thead>
<tr>
<th>Durability Class</th>
<th>Resistance</th>
<th>Mass loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Very resistance</td>
<td>&lt; 3.52</td>
</tr>
<tr>
<td>II</td>
<td>Resistance</td>
<td>3.52 – 7.50</td>
</tr>
<tr>
<td>III</td>
<td>Moderate</td>
<td>7.50 -10.96</td>
</tr>
<tr>
<td>IV</td>
<td>Poor</td>
<td>1. – 18.94</td>
</tr>
<tr>
<td>V</td>
<td>Very poor</td>
<td>&gt;18.94</td>
</tr>
</tbody>
</table>

Table 2

The grading system based on percentage of damages stakes attacked by subterranean termite (ASTM D 1758-06)
Table 3

Durability Rating of the untreated and treated woods based on percentage of damages stakes attacked by subterranean termite.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Percentage of Damages (%)</th>
<th>Rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>22.70</td>
<td>7</td>
</tr>
<tr>
<td>CA20%</td>
<td>0.00</td>
<td>10</td>
</tr>
<tr>
<td>CA20% HT150°C</td>
<td>0.00</td>
<td>10</td>
</tr>
<tr>
<td>CA40%</td>
<td>0.44</td>
<td>9</td>
</tr>
<tr>
<td>CA40% HT150°C</td>
<td>0.66</td>
<td>9</td>
</tr>
<tr>
<td>BPTCA20%</td>
<td>1.49</td>
<td>9</td>
</tr>
<tr>
<td>BPTCA20% HT150°C</td>
<td>1.49</td>
<td>9</td>
</tr>
<tr>
<td>BPTCA40%</td>
<td>1.18</td>
<td>9</td>
</tr>
<tr>
<td>BPTCA40% HT150°C</td>
<td>0.54</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 4

Durability class of the untreated and treated woods based on weight loss
<table>
<thead>
<tr>
<th>Treatments</th>
<th>Weight Loss (%)</th>
<th>Durability Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>8.80</td>
<td>III</td>
</tr>
<tr>
<td>CA20%</td>
<td>1.00</td>
<td>I</td>
</tr>
<tr>
<td>CA20% HT150°C</td>
<td>0.62</td>
<td>I</td>
</tr>
<tr>
<td>CA40%</td>
<td>1.03</td>
<td>I</td>
</tr>
<tr>
<td>CA40% HT150°C</td>
<td>1.32</td>
<td>I</td>
</tr>
<tr>
<td>BPTCA 20%</td>
<td>1.53</td>
<td>I</td>
</tr>
<tr>
<td>BPTCA20% HT150°C</td>
<td>1.28</td>
<td>I</td>
</tr>
<tr>
<td>BPTCA40%</td>
<td>2.05</td>
<td>I</td>
</tr>
<tr>
<td>BPTCA40% HT150°C</td>
<td>1.00</td>
<td>I</td>
</tr>
</tbody>
</table>

**Figures**

**Figure 1**

![Graph showing Retension (kg/m^3) and WPG (%)](image)
Retention and WPG of CA and BPTCA treated teak wood without and with heat treatment at 150 °C

**Figure 2**

FT-IR spectra of untreated and CA treated (left), untreated and BPTCA treated (right) of the short rotation teak wood. Note: A = untreated, B = 20% concentration, C = 20% concentration followed by thermal at 150 °C, FT-IR spectra of untreated and CA treated (left), untreated and BPTCA treated (right) of the short rotation teak wood. Note: A = untreated, B = 20% concentration, C = 20% concentration followed by thermal at 150°C
Figure 3

Variation of density among the untreated and treated short rotation teak wood
Figure 4

Leachability of CA and BPTCA treated teak wood without and with heat treatment at 150 °C (HT150°C)

Figure 5
Dimensional stability (ASE and WU) of CA treated (left) and BPTCA treated (right) teak wood without and with heat treatment at 150 °C (HT150°C)

**Figure 6**

MOR and MOE values of CA and BPTCA treated teak wood without and with heat treatment at 150 °C (HT150°C)
Figure 7

Weight loss of untreated, CA and BPTCA treated teak wood without and with heat treatment at 150 °C (HT150°C)
Figure 8

The appearance of untreated and treated teak wood samples after 3 months of grave yard test. Note: a = untreated, b = CA20%, c = CA20% HT150°C, d = 40%CA, e = 40%CA HT150°C, f = BPTCA20%, g = BPTCA20% HT150°C, h = 40%BPTCA, i = 40%BPTCA HT150°C
Figure 9

Ra and Contact angle of untreated, CA and BPTCA treated teak wood without and with heat treatment at 150 °C (HT150°C)