Determination of the Combined Effect of Chemical Modification and Compression of Agatis Wood on the Dimensional Stability, Termite Resistance, and Morphological Structure

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Agatis wood (Agathis lorantifolia Salisb.) was impregnated with a combination of styrene and methyl methacrylate and compressed to a strain of 50% to improve dimensional stability and termite resistance. The changes in cell structure were analyzed to determine the effects of the combination treatment. The results showed that densification of agatis wood with compression, impregnation, and a combination of treatments resulted in an increase in physical properties (density and dimensional stability) by changing the cellular structure and chemical components (i.e., cellulose crystallinity, microfibril angle, and preferred orientation of fibers) as well as degradation of cellulose. The chemical modification and combination treatment (chemical and compression) of wood generally led to a high resistance to dry wood termites.

Keywords: Agathis lorantifolia; Wood compressed; Wood impregnated; Wood compregnated; Dimensional stability; Microfibril angle; Termite resistance

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INTRODUCTION

Natural wood is subjected to large dimensional changes due to the presence of hydroxyl and other oxygen-containing groups in the cell wall polymers that react with moisture through hydrogen bonding (Rowell 1990). Chemical modification of wood can be defined as a chemical reaction between the reactive part of wood and the chemical reagent with or without catalyst (Rowell 1975). In chemical modification of wood, chemical reagents substitute hydroxyl groups with a stable covalently bonded and less hydrophilic group, which leads to an increased dimensional stability as a preservative agent.

There are several chemical agents utilized to chemically modify wood, including dimethyl sulfate (Matsuda 1996), carboxylic acid (Militz et al. 1997), acetic anhydride (Mohebby 2003), and epoxides (Militz et al. 1997; Abdul Khalil et al. 2013). Agatis wood (Agathis lorantifolia Salisb.) has low durability due to its low wood density. Agatis wood can be modified to improve its properties by following three different processes, namely densifying by impregnation, densifying by compression, and a combination of impregnation and compression (i.e., compregnation) (Kollmann et al. 1975). In the
impregnation process, wood cavity structure is filled with substances such as phenol formaldehyde resins, vinyl solution, liquefied natural resin, wax, sulfur, and lightweight metal so that the wood becomes more dense. Densifying by compression can also modify the properties of wood without damaging the cell structure of the wood (Stamm 1964). Densifying by compression also results in improved dimensional stability (McMillan and Wengert 1977; Dwianto et al. 1997; Kubojimo et al. 1998).

When wet wood is dried under pressure, the stress gradually decreases until it disappears and the material is fixed in the deformed state. Iida and Norimoto (1987) reported that densified wood can recover its original shape under the influence of moisture and heat. Tomme et al. (1998) suggested that densifying creates unstable wood. Densified wood expands at high temperature and humidity or when immersed in water. Expansion in the axial and/or radial dimensions of a wood material after an applied pressure is removed is called the springback effect. Therefore, permanent fixation of deformation after compression is the key to the success of this approach (Ayer et al. 2003; Dungani et al. 2014).

Many attempts have been made to stabilize the compressed deformation of wood permanently by resin treatment (Inoue et al. 1991; Dungani et al. 2014) and chemical modification (Inoue et al. 1994; Bhat et al. 2011; Chen et al. 2013). Several studies have been conducted on densifying wood by impregnation using the monomers styrene (ST), methyl methacrylate (MMA), and glycidyl methacrylate (GMA). This method can improve the mechanical properties, biological durability, dimensional stability, hardness, and UV-stability of wood (Takahashi et al. 1989; Feist et al. 1991; Sudiyani et al. 1999; Rashimi et al. 2003; Hadi et al. 2005; Yildiz et al. 2005). Furthermore, according to Abdul Khalil et al. (2010), modifications of Acacia mangium carried out with propianic anhydride and succinic anhydride in the presence of the catalyst sodium formate provided resistance to microbial attack.

To prevent densified wood from recovering its original shape and size, wood can be treated with water-repellent materials (Inoue et al. 1992). Inoue et al. (1992) found that compressed formaldehyde in Sugi (Cryptomeria japonica) was able to produce cross-linking among the wood components through the process of polymerization. Densified wood remained stable despite being exposed to steam for one hour (Inoue et al. 1992). Compressive deformation was well fixed by this method without any special post-treatment. There were limitations, considering formaldehyde pollution causes risks from the free formaldehyde remaining in the treated products.

Chemical modification or impregnation is an effective method of permanent fixation of compressed deformation of wood. There have been few studies conducted to determine the effect of the combination of chemical impregnation and compression. Therefore, the present study was conducted with the aim to investigate the combination effect of chemical modification and compression on the dimensional stability, termite resistance, and morphology structure of agatis wood.

**EXPERIMENTAL**

**Materials**

Agatis lumber was prepared from mature (> 25 years old) agatis trees collected from a community forest in West Java, Indonesia. The agatis trees were sawn using the polygon sawing method to obtain the dense homogenous lumber of agatis wood. Wood
was sawn radially at a thickness of 35 mm to obtain samples. The samples were initially dried for 24 h at 50 °C in an oven to reach 15% moisture content (MC) and a specific gravity between 0.25 and 0.45 before compregnation, and finally cut to samples with dimensions of 10 mm (L) x 20 mm (T) x 20 mm (R). The compregnated wood was then steamed at 180 °C for 8 min according to the method of Inoue et al. (1993) to produce densified wood with stable deformation.

Methods

**Chemical impregnation and compression treatment**

A monomer solution of styrene (ST) was prepared by mixing methyl methacrylamide (MMA) (65/28 w/w%) with a 2% benzoyl peroxide catalyst (polymerization) and a 5% divinyl benzene. The cross-linker was prepared by adding monomer solution to benzene at a ratio of 2:3 (w/w). The mixture was perfectly incorporated into a chamber to begin the process of impregnation. The wood was impregnated with the monomer solution by vacuum-pressure, with an initial vacuum of 3 bar for 30 min, pressure at 7 bar for 60 min, and subsequently at 3 bars for 10 min.

After the impregnation process, the polymerizing samples (semi-curing) were compressed for 15 min using a TOM-5000x press machine (Shinkoh Communication Industry Co., Japan) at 190 °C in the radial direction to a strain of 50% (10 mm) with a constant strain rate of 10 mm/min. The wood specimens were impregnated with ST/MMA to produce wood polymer composites (WPCs), compressed to produce wood compressed composites (WC), and impregnated and compressed to produce wood compregnated composites (ICW).

**Density and dimensional stability properties**

Samples between the tangential sections were used for density measurement, as determined by the ASTM D2395 (2002) method. Dimensional parameters such as volumetric swelling were calculated according to the method reported by Schneider and Brebner (1985). Briefly, the samples were submersed in distilled water evacuated in a vacuum desiccator. Excess water was drained, and the volume of the samples was determined. The soaking process was continued until samples attained a constant volume. The volumetric swelling coefficient (SC) was calculated by Eq. 1,

\[
SC = \left( V_w - V_{u,t} \right) \times \frac{100}{V_{u,t}}
\]

where \( V_w \) is the swollen volume of wood sample after treatment (cm\(^3\)) and \( V_{u,t} \) is the oven-dried volume of either treated or untreated samples (cm\(^3\)).

**Termite resistance**

The testing procedures were referring to those of modified Indonesian National Standard (SNI) No. 01-7207-2006. The wood samples 50 mm (R) x 25 mm (T) x 25 mm (L) were air-dried for one week prior to analysis. In the experiment, PVC tube transparent (30 mm in height and 18 mm in diameter) was used instead of a glass tube. The samples were placed horizontally under the vertically installed tube, so that the larger surface of the sample came into contact with the lower mouth (hole) of the PVC tube transparent. Fifty worker drywood termites of Cryptotermes cynocephalus Light were added to the tube. After 12 weeks, samples were removed from the tube, cleaned thoroughly, and weighed to determine their oven-dry weights. The condition \( i.e. \) protection level of the test specimens with respect to termite damage was determined based on the percentage
weight loss of each test specimen following termite exposure. The samples were prepared for observation with an SEM before and after the termite damage. The resistance class of the treated agatis wood was determined according to the Indonesian Standard SNI 01.7207 (2006).

*Morphological structure analysis*

Scanning electron microscopy (SEM) (LEO Supra 50 Vp, Germany) was used to characterize the morphology of the wood samples. The samples were attached to an aluminum stub, sputter-coated with gold (Polaron SC515, Fisons Instruments; UK), and analyzed at an accelerating voltage of 5 kV. X-ray diffraction (XRD) analysis, carried out on a Philips PW 1050 X-pert (Netherlands), was used to determine the change in microfibril angle (MFA), preferred orientation of fiber (PO), and wood crystallinity (WC).

**RESULTS AND DISCUSSION**

The hydroxyl groups of the wood macromolecules can react with chemical agents. As a consequence of the functionalization of the -OH groups, the natural hydrophilicity of wood is reduced. The blocking of the cell wall micropores, the occupied spaces within the cell wall, is the most representative modification technique. The reaction with cellulose and ST/MMA with the aid of benzoyl peroxide after impregnation process is shown in Fig. 1.

\[
\text{Wood} + \text{OH} \rightarrow \text{Wood} \text{polymer}
\]

**Fig. 1.** Coupling reaction of agatis wood with styrene and methyl methacrylamide (Source: Rahman et al. 2013)

The untreated wood fibers soaked in water, without chemical modification and compression, exhibited an initial high rate of moisture absorption (Fig. 2a). This is due to the fact that natural fiber contains hydroxyl groups, which may form further layers on top of the water molecules that have already been absorbed (Nabi Saheb and Jog 1999). Figure 2b shows that the water absorption process ceased due to the presence of polymerisable chemicals within the wood. Figure 2c shows the chemical reaction of monomers ST/MMA in agatis wood before the compression treatment. The hydroxyl groups within the wood were replaced by the ST/MMA reagents, which led to improved dimensional stability. Similar results have been reported by Rahman et al. (2013), who reported that chemical modification with styrene and methyl methacrylate (ST/MMA) causes permanent swelling of the cell walls. Compression treatment of agatis wood revealed the mechanism of permanent fixation of deformation (Fig. 2d). However, wood
fixed by the compregnate treatment showed higher density than modified and compressed wood.

Fig. 2. Modification process of agatis wood. (a) untreated wood, (b) wood compressed composite (WC), (c) wood polymer composite (WPC), and (d) wood compregnated composite (ICW)

Properties of Modified Wood

The wood density, volumetric swelling coefficient (SC), and termite resistance after modification of agatis showed a range of variation (Table 1). Compared with the untreated control, the density of WC and WPCs each increased by 17% and 26.87%, respectively. Both impregnation and compression made a contribution to the density increase. A combination of treatment impregnation and compression (compregnation) increased the density by 36.36%. Under normal conditions for the modified wood, a higher density causes dimensional stability and an increase in termite resistance.

<table>
<thead>
<tr>
<th>Table 1. Density, SC, and Termite Resistance of Modified Agatis Wood</th>
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<tr>
<td>Density (kg/cm³)</td>
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<tr>
<td>SC (%)</td>
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<tr>
<td>Termite resistance</td>
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* Data reported as ± standard deviation

The increase of density due to compression occurs because the wood cell cavities and cell walls become denser and contain low cellulose in the primary wall and middle lamella. Increased density of wood due to heating causes degradation of wood components (Dwianto et al. 1997). Agatis wood impregnated with monomers to fill the void space by compression treatment led to an increase in density. Polymer-filled wood yielded higher density compared to compressed wood because co-polymerization of the cell wall in the wood produced permanent fixation by the presence of ST/MMA, as shown by Rahman et al. (2013). They reported permanent fixation of the wood matrix due to ST/MMA crosslinking with the wood cell wall. The rate of change in the
volumetric swelling of the WPCs is very low due to the presence of monomers in the cell cavities that are bulking.

**Termite Resistance**

Figure 3 shows the SEM micrographs of the treated and untreated agatis wood. It was observed that dry wood termites attacked the untreated wood control. The surface of agatis was no longer intact, indicating a large amount of damage to the cells of wood (Fig. 3a). From the present experiment, it was observed that modification of agatis wood cannot completely protect against drywood termite attack (Figs. 3b, 3c, and 3d). The WPCs and ICW were placed in resistance class I (high resistance), while WC was placed in resistance class III (moderate resistance). The untreated control was placed in resistance class V (poor resistance). This may be due to the relatively higher hardness of these modified agatis woods. Thus, the unmodified agatis wood is not environmentally suitable for drywood termites. In addition to the higher density, a change in the chemical micro environment and structure of the wood affects the complex mechanism of enzymatic and non-enzymatic processes of the termite attack. Hadi *et al.* (1998; 2005) investigated the termite resistance of chemically modified softwood and hardwood by impregnation treatment. They showed that modified wood had more resistance toward the dry wood termites.

![Fig. 3. Low magnification SEM micrographs showing drywood termite damage to modified agatis wood. (a) untreated control, (b) wood compressed composite (WC), (c) wood polymer composite (WPC), and (d) wood compregnated composite (ICW)](image_url)

**Morphological Structure**

The change in morphology can be seen by comparing the SEM cross-section of the fracture surface of the control and modified agatis wood. The bulk of softwood consists of long narrow hollow cells, or tracheids, that fit closely together (Fig. 4a). Figure 4b shows the change in cell shape on the cell structure of the compressed wood. Dwianto *et al.* (1997) reported that shape changes of softwood involve the tracheid cells. In addition to considering the cell shape, Fig. 4b also shows that the compression
treatment only affected the shape of the cell cavity on the surface of the wood. This is consistent with the results of the Dwianto et al. (1999), who determined that tracheid cells in WC collapse, while on the inside did not change significantly.

Figure 4c shows that the monomer had filled the cavity so that the cavity cells had shrunk. It appears that the cavities in the parenchyma tissue were full, so impregnation had occurred. The high density of the pores in the wood after impregnation with monomer shows that the mixture of monomers was symmetrical and achieved homogeneity, resulting in improved mechanical and physical properties (Dwianto et al. 1999).

Figure 4d shows changes in agatis wood structure due to a combination of chemical modification and compression. During chemical modification, the cell wall thickness increased since it had become filled by the chemical agents. Changes in agatis wood caused by compression treatment (Fig. 4b) were similar to those of the dimensional stability and strength in chemically modified wood (Fig. 4c). However, the libriform fibers were highly affected by the compression treatment from all other agatis wood anatomical elements.

**Changes of Microstructure**

The chemical modification of agatis wood had notable effects on the change of microstructure relevant to the microfibril angle (MFA), preferred orientation (PO), and gradient crystallinity (GC), as shown in Table 2. As can be seen in Table 2, untreated agatis wood had a higher MFA than modified agatis wood. This suggests that the
compression process decreased the microfibril angle by 50% to improve the properties of agatis wood.

**Table 2. Change in Microstructure of Modified Agatis Wood**

<table>
<thead>
<tr>
<th></th>
<th>Control (untreated)</th>
<th>modified Agatis wood</th>
<th>modified Agatis wood</th>
<th>ICW</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFA (°)</td>
<td>19.67</td>
<td>11.74</td>
<td>11.47</td>
<td>11.10</td>
</tr>
<tr>
<td>PO (%)</td>
<td>38.80</td>
<td>51.80</td>
<td>70.40</td>
<td>71.30</td>
</tr>
<tr>
<td>GC (%)</td>
<td>49.36</td>
<td>51.81</td>
<td>37.47</td>
<td>36.91</td>
</tr>
</tbody>
</table>

Figure 5 shows the MFA curves of modified agatis wood. The value of MFA in modified wood decreased notably compared with the untreated agathis wood (control). The MFA shows a variable relationship with wood density (Lin and Chiu 2007), and dominant parameters such as orientation and crystallinity of cellulose microfibrils in the cell wall along the fiber axis (Hein and Brancheriau 2011) affect shrinkage and shrinkage anisotropy (Harris 1977). The results revealed the increased dimensional stability and strength of treated wood with low MFA values for WC, WPCs, and ICW.

**Fig. 5.** MFA curves of modified agatis wood. (a) untreated control, (b) wood compressed composite, (c) wood polymer composite, and (d) wood compregnated composite

Compression causes the preferred orientation to become more pronounced. The phenomenon that occurs in wood compacted at a compression rate of 50% shows that the
inner layer is more regular than the outside fiber (Fig. 6). Meanwhile, the impregnation process caused there to be irregular fibers. Changes in the value of preferred orientation are shown in Table 2.

Chemical modification is the process to change from hydrophobic to hydrophilic in the wood. If there are changes in the shape regularity structure, flexibility will be lower because wood density increases. This phenomenon shows that cells in wood filled with chemical agents changed the preferred orientation of wood by replacement of hydroxyl groups with monomers that polymerize with wood (Chen et al. 2013).

Fig. 6. PO curves of agathis modified wood. (a) untreated control, (b) wood compressed composite, (c) wood polymer composite, and (d) wood compregnated composite

Wood modification results in an increase in the crystallinity of modified agatis wood, as shown by X-ray diffraction (Fig. 7). In WC, the compression process using heating causes softening of matrix components and reduced water molecules, resulting in damage to the H-bonds between the molecules can reach the crystallites. The primary component of wood is cellulose, and generally cellulose is in a crystalline form. Cellulose crystallinity is reduced after impregnation, because the monomer groups interact with the groups in the volume of wood and occupy a larger space in the wood. This process causes a change to the arrangement of wood fibrils, to cause a reduction in crystallinity so fibrils become more rigid.
CONCLUSIONS

1. Modifications to the compression process successfully improved the physical properties of agatis wood. At 50% compression, an increase of the gradient density and a decrease in the volumetric swelling in agatis wood was observed. Both impregnation and compregnation also increased the dimensional stability of the treated wood (density and specific gravity).

2. Chemical modification and compregnation of agatis wood showed high resistance against dry wood termite attack, while wood modified by compression treatment showed moderate resistant to drywood termites. Notable termite resistance was observed in agatis wood treated by chemical modification.

3. Process modification by impregnation and compression resulted in a small increase in the value of microfibril angle (MFA). Densifying the wood by compression resulted in an increase in the crystallinity of wood and degradation of some chemical components of the cell wall. Impregnation resulted in a decrease in the crystallinity of wood and tended to result in a reduction of cell wall chemistry.

ACKNOWLEDGMENTS

The authors would like to thanks to the Universiti Sains Malaysia (USM) for their financial support by providing the Research University Grant (RUI) No. 1001/PTEKIND/811195.

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Article submitted: June 20, 2014; Peer review completed: August 17, 2014; Revised version received and accepted: September 4, 2014; Published: September 15, 2014.