Distribution of permethrin on laminated bamboo after the preservative treatment using SC-CO$_2$ as a carrier solvent

Z Uslinawaty$^1$, M Muin$^2$, and Suhasman$^2$

$^1$Department of Forestry, Haluoleo University, Kendari 93232, Indonesia.
$^2$Department of Forestry, Hasanuddin University, Makassar, 90245, Indonesia

*Email: zakiahuslinawati@gmail.com

Abstract. This study was conducted to determine the presence of the insecticide permethrin and its retention gradients within the structure of laminated bamboo after treatment using supercritical carbon dioxide (SC-CO$_2$) as the carrier solvent. The presence of permethrin was based on functional group differences indicated by FT-IR analyses before and after the preservative treatment. Permethrin retentions in the treated bamboo materials ranged from 0.0020 to 0.0022%. This result indicated that the preservative treatment of laminated bamboo using SC-CO$_2$ as a carrier solvent produced evenly distributed chemical an effective level. There was no significant distribution gradient of the preservative observed over the layers of the treated laminated bamboo arranged with outer-inner surface laminations. The current treatment condition is potential to produce laminated bamboo products completely resistant to biodegradation.

1. Introduction

Laminated bamboo products are economically and environmentally attractive considered since bamboo is categorized as fast growing species that has better flexural strength than other raw materials [1-4]. However, bamboo has also low durability against biological degradation and therefore, some efforts have been made to overcome this unfavorable characteristic mostly with the use of preservatives [5]. Unfortunately, conventional preservatives treatments of bamboo product require liquid preservatives that potentially decrease mechanical properties due to the need to re-drying after treatment [2,6,7]. Conventional treatment has been also cause detrimental effects on environment because of chemical wastes [8-10]. In addition, conventional treatment method has a limited enactment in distributing preservative throughout the treated materials. In this case, the preservative was found mostly on the surface parts with higher concentration compared to the center parts [11,12].

One alternative approach to preservative treatment of composite products is the use of supercritical carbon dioxide (SC-CO$_2$) as carrier solvent. This method is environmentally friendly and can effectively increase the durability of the wood-based composite products [11-15]. SC-CO$_2$ is liquefied gas and able to easily penetrate into the inside of wood structure, maintaining wood dimension and stability. A previous study has indicated the feasibility of the SC-CO$_2$ treatment in producing bamboo laminates with high strength and durability properties [16]. However, the effectiveness of SC-CO$_2$ to impregnating and distributed preservatives in to bamboo-based composite products has never been evaluated. The current study intended to assess the distribution of permethrin within the matrix of bamboo products impregnated using SC-CO$_2$ as carrier solvent. Permethrin is commercially available and has been found
to be effective against white rot fungi *Pycnoporus sanguineus* and the termite *Coptotermes curvignathus* [5,17,18].

2. Materials and Methods

2.1 Materials

Three representative bamboo culms (age 4 years, diameter 22-25 cm, and thickness 1-1.5 cm) of *Dendrocalamus asper*, grown at Anduna Wolasi village, South Konawe district, South east Sulawesi, Indonesia, were harvested. Samples were taken at the distance of about 1 m from bottom of the bamboo culms. The samples were then axially cut into 2.5 cm width and 15 cm length. The outermost and innermost layers were laminated. Prior to treatments, all samples were then conditioned at 60°C for 24 hours.

Permethrin 100 EC (Bioindustries) in a liquid form with an active ingredient concentration 100 g/L permethrin. A preservative concentration of 0.5% was prepared for SC-CO₂ impregnation by addition of methanol p.a. (Merck) as a co-solvent. The preservative concentration was applied based on the manufacturer’s recommendation.

2.2. Methods

2.2.1. Bamboo lamination

Bamboo samples 1 (R) x 2.5 (T) x 15 (L) cm were assembled for laminations. Samples were arranged with different laminated surface areas of bamboo samples (outer-inner, outer-outer, and inner-inner surfaces). The laminated bamboo was produced by cold press method at the pressure of 10 kg/cm² for 3 hours after applying a glue type of isocyanates (polyurethanes) with the glue spread of 250 g/m².

2.2.2. Preservative treatment

Preservative treatments were applied in two separate ways, i.e. to bamboo raw materials (prefabrication or before lamination) and to laminated bamboo products (post-fabrication or after lamination). SC-CO₂ with 5 mL of permethrin 0.5% was impregnated using the procedure of Multi-Phase Carbon Dioxide (MPCO₂) treatment developed by Muin [19]. The treatment procedure in this study consisted of introducing the samples of six bamboo strips or three laminated bamboo products into the treatment vessel, setting the vessel temperature to 15°C, introducing CO₂ with the preservative at the pressure equal to the CO₂ source bomb approximately 6 MPa, gradually increasing the temperature and pressure to about 35°C and 8 MPa, and finally releasing the pressure to ambient atmosphere.

2.2.3. Analysis of preservative distribution

The presence of preservative permethrin within the structure of the treated bamboo materials was determined using Fourier Transform Infra-Red (FTIR) Spectroscopy (Shimadzu IR Prestige 21 type with 8400 S). FTIR spectroscopy has been found appropriate to determine the intensity of specific bonds and functional groups within the polymeric structure. It was used in this study to indicate the changes of functional groups on bamboo products before and after permethrin impregnation using SC-CO₂ as carrier solvent. For the analysis of the preservative distribution, the treated bamboo samples of either bamboo strip or bamboo laminations were sliced into four sections with a proportional thickness. As the use of conventional method using weight gain in determining preservative retentions is thought to be unappropriate, the permethrin concentrations within the treated bamboo products were analyzed using spectrophotometer (Perkinelmer Type Lamda 25). The treated sample was milled to pass a 40-mesh screen. Two grams of the milled materials were dissolved in 10 mL of KI 5% and 10 mL of AgNO₃ 0.25% and then macerated for 30 min. The permethrin concentration was analyzed using UV-VIS spectrophotometer employed at the wave length of 339 nm.
3. Results and Discussion
Results of this study showed that the use of SC-CO$_2$ as a carrier solvent was found to have capability in introducing preservative permethrin into the treated bamboo products. It is indicated by the results of FTIR analysis showing the changes of existing functional groups as shown in Figure 1. There was no different functional groups between bamboo samples with and without the SC-CO$_2$ treatments, indicating there was no chemical interaction between CO$_2$ and bamboo materials during the impregnating process. However, results of FTIR analysis on the bamboo samples before and after the preservative treatment indicated the changes of existing functional groups. Figure 1 clearly demonstrates the presence of different compositions in the functional groups of bamboo samples before and after impregnated with the preservative permethrin. The presence of the preservative compound after treatment is shown by C-Cl linkage functional groups of permethrin. This fact was associated with the solubility of permethrin in SC-CO$_2$ ranging from 0.1765 g/L (without co-solvent) to 0.6497 g/L (with a methanol co-solvent).

![Figure 1. FTIR spectra of bamboo products: (a) bamboo strip without treatment; (b) laminated bamboo after SC-CO$_2$ impregnation with permethrin to bamboo strips (before lamination); (c) laminated bamboo after SC-CO$_2$ impregnation with permethrin (after lamination)](image)

Figure 1 shows that the FTIR spectra pattern is generally unchanged as indicated by the peak of 1512 cm$^{-1}$, 1514 cm$^{-1}$, and 1739 cm$^{-1}$ on the tested bamboo specimens. These conditions are related to the nature of lignin and hemicellulose, respectively, characterized by the presence of C=C groups around the wavelength of 1505-1512 cm$^{-1}$ [21] and the peak of 1739 cm$^{-1}$ [22,23]. However, new peaks of 763.81 cm$^{-1}$ and 761.88 cm$^{-1}$ in the FTIR spectrum were found to occur on laminated bamboo products after treatment, indicating the presence of permethrin in the specimen. The peak of 763.81 cm$^{-1}$ occurred at the specimens of laminated bamboo with permethrin treatment before lamination, while the peak of 761.88 cm$^{-1}$ occurred at the specimens of laminated bamboo with permethrin treatment after lamination.

Further analysis on the presence of permethrin within the treated bamboo samples demonstrated that the preservative was distributed with different levels of signficancy, depending on the treated bamboo materials (Table 1). The retentions of the preservative permethrin were significantly different from outer to inner layers (layer 1 to layer 4) of the treated bamboo splits. The significant differences of gradient retentions were also found in the laminated bamboo with outer-out and inner-inner laminations, but
not in the outer-inner laminated bamboo. Overall, the retention values of the preservative in all treated samples were approximately 0.002% It was comparable to the findings of Cookson [20] showing the permethrin retention of 0.005% on Eucalyptus oblique after treatment using SC-CO$_2$ at the pressure of 15 MPa and temperature of 50°C. These results suggest that the SC-CO$_2$ treatment condition in the current study requires the application of higher amount of the preservative to be able to transport the same concentration of 0.005%. However, it is important to further test the effectiveness of the preservative retention found in this study since permethrin is becoming increasingly used as components in low retention wood preservative [24]. Results also showed that there was no significant difference in overall permethrin retention among the different surface areas of bamboo laminations as shown in Table 1.

Table 1. Retentions of permethrin bamboo products after SC-CO$_2$ impregnation

| Specimen                        | Retention (%) |                  |                  |                  |          |
|---------------------------------|---------------|-----------------|-----------------|-----------------|----------|
|                                 | Layer 1       | Layer 2         | Layer 3         | Layer 4         | Average  |
| Bamboo splits                   | 0.002         | 0.002           | 0.0028          | 0.0023          | 0.0022   |
| Outer-outer laminated bamboo    | 0.0018        | 0.0021          | 0.0023          | 0.0021          | 0.002    |
| Outer-inner laminated bamboo    | 0.0021        | 0.0021          | 0.0021          | 0.0021          | 0.0021   |
| Inner-inner laminated bamboo    | 0.0021        | 0.0023          | 0.0022          | 0.0021          | 0.0021   |

4. Conclusion
Preservative treatment with SC-CO$_2$ as a carrier solvent is feasible with laminated bamboo products. The current condition of SC-CO$_2$ treatment proved effective in solubilizing and transporting a sufficient amount of permethrin into laminated bamboo prevent biological attacks. In this study, permethrin retentions on the treated bamboo products were approximately 0.002% without any significant difference among the surface laminated areas. The preservative permethrin within the samples of outer-inner laminated bamboo was more evenly distributed compared to those of outer-outer and inner-inner laminated bamboo products, indicating the importance of considering surface layer laminations in the manufacture of biological resistant laminated bamboo.

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