Optimization of SC-CO$_2$ Time Conditions and Permethrin Concentration in Laminated Bamboo Production Using Surface Response Methodology

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Abstract. Supercritical carbon dioxide method has starting to be used as environmental friendly method in preserving wood. It is expected to maintain physical and mechanical properties of bamboo. The purpose of this study was to determine the effect of the duration times of supercritical conditions and permethrin preservative concentrations on optimization of shear strength of laminated bamboo impregnated by using supercritical carbon dioxide in the initial process (blades) and final process (laminated bamboo). The RSM-CCD experimental design was used to determine the effect of duration times of supercritical carbon dioxide for 20, 25, 30, 35, 40 minutes and the effect of permethrin concentrations 0.1, 0.3, and 0.5% against the shear strength of laminated bamboo. Response surface analysis, using 10 version of design expert software, has been done to get the optimum condition which would produce maximum of shear strength. The results showed that permethrin concentrations have stronger influenced (based on RSM analysis) on the shear strength and durability of laminated bamboo than the times of supercritical carbon dioxide conditions. Optimization of the two combinations of increasing shear strength and endurance were supercritical conditions = 22.71 minutes, and preservative permethrin concentration = 0.24%. Shear strength of shear strength and decrease in combination weight is 85 kg / cm$^2$ and 0.38%.

1. Introduction
Many preservation efforts have been carried out to improve bamboo’s durability against powder beetles [1, 2, 3, 4]. The preservation methods that have been carried out have several disadvantages, including: decreased mechanical physical properties of laminated bamboo (mainly shear strength), the amount of preservative used, and produces waste that causes pollution to the environment [5, 6]. Therefore the preservation of environmentally friendly methods need to be developed.
One method of preservation that is environmentally friendly and does not cause dimensional changes in some types of wood, composite wood and laminated bamboo is supercritical carbon dioxide impregnation (SC-CO2) [7, 8, 9]. Preservation of wood and composite wood using the SC-CO2 impregnation method produces unchanging physical and mechanical properties. So preservation with the impregnation method SC-CO2 as a solvent is expected not to reduce the mechanical properties (mainly shear strength) and increase the durability of laminated bamboo. This study sought to optimize the time of supercritical conditions and permethrin preservative concentration to produce quality laminated bamboo.

2. Method

2.1. Sample Preparation
Bamboo used is Petung bamboo (Dendrocalamus asper) with an age of ± 4 years. Stem diameter is ± 25 cm with a thickness of 1-1.5 cm. The bamboo stem used is that is ± 1 m from the base of the stem. 4 stems of bamboo were taken from 4 bamboo clumps from Anduna village, Wolasi sub-district, South Konawe district, Southeast Sulawesi province. Bamboo is cut to a length of 15 cm, width 2.5 cm, and thickness according to the thickness of the bamboo wall. The outer and inner parts are removed. Before gluing, the splits bamboo is air dried at a temperature of 60 °C for 24 hours.

2.2. Laminated Bamboo
Laminated bamboo is made with the inner outer bonding area. The adhesive used is an isocyanate adhesive prepared according to the technical standards specified by the manufacturer. Before being applied, the two adhesive components, namely resin and hardener were mixed and stirred until blended in a ratio of 100: 15 (based on weight). Before the gluing process, the blade surface is smooth, cleaned of all dirt. All adhesive resurfacing systems are carried out using a spatula, and are applied to both the double spread surface of the lamina with a weight of 250 g / m2. The laminated bamboo is cold pressed / clamped with a 3 hour press time and a pressure of 10 kg / cm².

2.3. Preservation with SC-CO2 and permethrin impregnation
Preservation with CO2 impregnation uses the Multi-Phase Carbon Dioxide (MP-CO2) [7]. The impregnation treatment of SC-CO2 is applied to the bamboo blade before being laminated. In the production of laminated bamboo. Impregnation begins by inserting the blade in the vessel at 15 °C and a pressure of about 6 MPa. After the temperature and pressure reach 35 °C and 8 MPa, the sample is left to stand with various times of supercritical conditions and permethrin concentration. Then the sample was removed from the ship and stored in the desiccator for ± 1 hour. Before testing shear strength and testing resistance to beetle powder, samples were stored for a week.

2.4. Experiment Design
This study uses a central composite design (CCD) with factorial experiments consisting of supercritical conditions and permethrin preservative concentrations. Factor level observed: supercritical condition (A), which consists of three levels, namely 20 minutes, 30 minutes, and 40 minutes and permethrin (B) concentration consisting of three levels of 0.1%; 0.3%; and 0.5%. The level of experiment on each factor (independent variable) is coded to simplify the calculation, with the value of code 1 at the largest level, the value -1 at the smallest level, 0 for
the center point, and the axial point ($|\alpha| = 1.414$). Each factor combination is repeated 2 times, except the center point factor is repeated 3 times.

### 2.5. Shear Strength Test
Making test samples for shear strength testing is carried out at least 7 days after gluing bamboo slats. For each replication made 6 examples of press shear test. Testing of bamboo stickiness for each treatment was carried out according to Japanese Standards [10]. The stickiness test is done by giving the load placed in the parallel direction of the fiber by placing the test sample vertically. The maximum load value is read when the test sample has a 0.5 cm damage to the adhesive line.

### 2.6. Weight Loss Test
In plastic tubs measuring 50 x 25 x 5 cm bamboo is inserted which has been attacked by powder beetles. Then covered with wire sheets measuring 0.5 cm x 0.5 cm. On the wire sheet, sample samples were 19 samples based on the run of the CCD design. Then closed using a mosquito net so that the beetle does not come out. Every week a plastic tub is observed for signs of a powder beetle attack. After 12 weeks the sample was dismantled based on the presence of a powder beetle of 30% in the control sample ie non-treatment sample. The test sample is cleaned of fine powder, then weighed.

### 3. Results and Discussion
The value of shear strength of laminated bamboo impregnated with SC-CO2 in the initial process ranged from 8.15 MPa - 8.87 MPa. The value of shear strength of laminated bamboo is better than some laminated bamboo which has been preserved with certain preservatives [4, 5]. The shear strength of laminated bamboo is different based on the type of bamboo, age, and also the adhesive used.

Bamboo durability can be seen in the value of heavy loss due to the attack of microorganisms. The value of weight loss in this study was very low, ranging from 0% - 3.02%. The value of weight loss of laminated bamboo with impregnation of SC-CO2 is equivalent to the weight loss of several types of wood preserved with permethrin and using SC-CO2 as a solvent [4]. The effectiveness of permethrin was very good even at a concentration of 0.04% with a value of weight loss of 0%. Permethrin is a synthetic pyrethroid-based on natural pyrethrins chemistry. This preservative was developed to replace harmful organochlorine insecticides. This pesticide has a very low toxicity in the environment. It was developed Permethrin has been used in wood preservation since 1980 because it is beneficial for the environment, its spectrum of poisoning is extensive, stable in wood and has dual action as repellent and contact insecticides.

Based on Annova's analysis, a suitable model for shear strength response in the initial process is a linear model with a p-value of 0.0001 (0.01%), which indicates that the probability of a model error of less than 1% or a linear model has a significant (significant) shear strength response initial process. The lack of fit value of the linear model has a p-value of 0.1610 (16.10%) which shows this model is not significantly different at p > 5%. This value indicates that the linear model is suitable for predicting the effect of supercritical conditions and preservative concentration on shear strength. The model developed is suitable for shear strong responses in the initial process and produces the following equation:
Encoded equation:
\[ Y = 8.42 - 0.076 X_1 - 0.207 X_2 \] (1)

Actual equation:
\[ Y = 8.69 - 0.0076 A - 1.0348 B \] (2)

Description: \[ X_1 = A - 30 \]
\[ X_2 = B - 0.3 \]

Based on the model equation it is known that the shear resistance of laminated bamboo impregnated in the initial process will increase as the supercritical condition decreases (A) and decreases the concentration of preservatives (B).

The effect of each factor on the shear resistance of bamboo lamination in the initial process can be seen in the Annova. The factors that influence are the time of encoded supercritical conditions (X_1) and the concentration of preservatives (X_2). The R-value for the laminated bamboo shear response model that was SC-CO2 pre-impregnated in the initial process was 0.8519. This value means that the effect of variables X_1 and X_2 on changes in the response variable is 85.19% while the remaining 14.8% is influenced by other variables.

Analysis of variance in weight loss in the quadratic model (order polynomial model 2) obtained a Lack of fit value of 36.54 or p <0.001. This value indicates the model is not suitable to explain the effect of treatment on heavy losses, so it is necessary to revise the model stepwise and produce a value of lack of fit that remains significant. This indicates that there are some components that have not been added. So that from the order 2 polynomial model it is changed to the 3rd order polynomial model by adding a cubic component for the time of encoded supercritical conditions and concentration preserved concentrations of the encapsulated. Then the order 3 polynomial model was revised again to eliminate non-significant components. The choice of order 3 without interaction is the most appropriate model (addition of A^3 and B^3) so that the value of lack of fit is not significant. The Lack of fit value is 0.71 with p-value 0.51 or p> 0.05, indicating that the model does not significantly affect the model, meaning that the model is suitable to explain the effect of treatment on the weight loss of laminated bamboo. So the equation for losing weight in the initial process is as follows:

Encoded equation
\[ Y = 0.009 + 0.29 X_1 - 0.94 X_2 +0.23 X_1 X_2 + 0.75 X_2^2 - 0.30 X_1 X_3 - 0.059 X_2 X_3 \] (3)

Description: \[ X_1 = A - 30 \]
\[ X_2 = B - 0.3 \]
\[ X_3 = 10 \]
\[ X_3 = 0.2 \]
A = time of supercritical condition

B = Permetrin preservative concentration

Actual equation:

\[ Y = 12.69 - 0.92 A - 18.10 B + 0.029 A^2 + 25.59 B^2 -0.0003 A^3 - 7.38 B^3 \] (4)

The most influential factors in losing weight of laminated bamboo after testing with beetles are the length of time encoded supercritical conditions (X₁), encoded preservative concentration (X₂), quadratic length of the supercritical condition encoded (X₁)², quadratic concentration of coded preservative (X₂)², cubic length of encoded supercritical condition (X₁)³ and cubic encoded preservative concentration (X₂)³. The R-value for the weight loss response is 0.9976, this value means that the effect of variables X₁ and X₂ on the change in the response variable is 99.76% while the remaining 0.24% is influenced by other variables.

Based on the description above it is known that the shear resistance of laminated bamboo impregnated in the initial process will increase with decreasing the time of encoded supercritical conditions (X₁) and decreasing the concentration of encoded preservatives (X₂). but weight loss will increase in decreasing the preservative concentration, the cubic time of supercritical conditions and the cubic concentration of preservatives. Both of these are problematic because laminated bamboo which is expected from the results of preservation are those that have a high shear strength and heavy loss from low microorganism attacks. So to get the optimization of the two criteria above, a combination process is carried out. The optimization of the two combinations of increasing shear strength and durability was the time of supercritical conditions = 22.71 minutes, and the concentration of preservative permethrin = 0.24%. The shear strength of the shear strength and weight loss of the combination is 85 kg / cm² and 0.38%. This condition indicates that the permethrin laminated bamboo preservation using the SC-CO₂ impregnation method in the initial process can be carried out only with the time of supercritical conditions 22.71 minutes and with a concentration of 0.24%.

The relationship between dependent and independent variables is illustrated in the form of a three-dimensional response surface curve constructed based on the analysis of shear strength and weight loss due to the attack of the powder beetle. The three-dimensional graph of the surface response of the shear strength of laminated bamboo is presented in Figure 1, and a three-dimensional graph of the surface response to the weight loss of laminated bamboo in the initial process is presented in Figure 2.

Figure 1. explained that when the supercritical conditions of the concentration of preservatives both play a role in reactively decreasing the shear strength. The higher the concentration of preservatives causes the shear strength to decrease. The higher time for supercritical conditions (20-40 minutes) also causes shear strength to decrease (Figure 1).
The optimum condition of shear strength was predicted at the time of supercritical conditions of 20 minutes and preservative concentration of 0.1%, with a shear strength of 8.87 MPa. Then after adding time to 40 minutes with a fixed concentration, the shear strength decreases to 8.59 MPa. While the lowest shear strength at the time of 40 minutes of supercritical conditions and 0.5% preservative concentration with a value of 8.15 MPa. This condition shows that the concentration of preservatives plays a role in reactively decreasing the shear strength. Increasing the time of supercritical conditions and increasing concentration, the shear strength will be smaller.

On the three-dimensional curve in Figure 1(a), it will be seen that the concentration of preservatives plays a role reactively reducing weight loss. the higher the concentration of preservatives, the lower the value of weight loss. Conversely, if the preservative concentration decreases, then the weight loss will increase. A good preservation method is a preservation method that is able to increase the resistance of bamboo to the attack of destructive microorganisms and is able to maintain the value of shear strength similar to laminated bamboo which does not undergo a process of preservation.

At the time of 40 minutes supercritical conditions and 0.5% concentration. Bamboo laminates do not experience a heavy loss (0%). When the concentration of 0.5 when the supercritical condition is lowered to 20 minutes, the weight loss occurs at 0.008%. Weight loss increases when the preservative concentration is reduced to 0.1% and the time of supercritical conditions is 20 minutes, weight loss increases to 1.9%. The weight loss value increases again when the supercritical condition is increased to 40 minutes and the concentration is 0.1% to 2.1%.

4. Conclusion
- Higher concentration of permethrin preservation, decreased the shear strength but on contrary increased the durability of laminated bamboo,
- RSM used to determine optimal condition of time condition of SC-CO₂ and
- The results of this research can be applied to the laminated bamboo industry.
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