Research on Optimization of Impregnation Conditions of Eucalyptus Veneer with Modification of Fire Retardancy

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Abstract. The waterborne composite modifier was employed to treat Eucalyptus veneer to obtain fire retardancy. By response surface methodology (RSM), the effects of vacuum time, impregnation pressure, and impregnation time were investigated. The optimized impregnation conditions were obtained through RSM. The vacuum time, impregnation pressure, and impregnation time were 39 min, 0.9 MPa and 79 min, respectively. After validation test, under the optimized conditions, the average LOI of Eucalyptus veneer was 28.2\% with the percentage error 4.49\%. Therefore, this predictive model for the preparation of treated Eucalyptus veneer was accurate and reliable for practical manufacturing. Moreover, the SEM analysis illustrated that the cavity of wood was filled with modifier after impregnation under optimized conditions.

1. Introduction
With the depletion of forest resources and the increasing attention attracted to the protection of natural resources in the world, the application of high-value plantation wood has been paid more and more attention by researchers and market [1, 2]. As one of the most widely used wood materials for interior decoration, wood-based panel is of great importance for its high value application and large-scale production. As a widely used veneer in multi-layer plywood and blockboard, the study on the flame retardancy of Eucalyptus veneer is of great significance. In this study, Eucalyptus veneers were treated with water-based composite flame retardant by vacuum-pressure impregnation. Response surface methodology (RSM) was used to optimize the impregnation conditions and a mathematical model was established between the impregnation process and the limit oxygen index (LOI) of Eucalyptus veneer. In addition, SEM analysis was performed to verify the effects of impregnation. This study provided reference for flame retardant treatment and high-value applications of Eucalyptus veneer.
2. Materials and methods

2.1. Materials
Eucalyptus veneer was purchased from Hunan Fusen Bamboo & Wood Technology, Co., Ltd. The dimension of test samples was 200 mm × 200 mm × 6 mm (length × width × thickness), with initial moisture content 8% - 13%. Ammonium polyphosphate (APP), polyvinyl alcohol (PVA) and all other chemicals were analytically pure.

2.2. Experimental methods
100 g distilled water was preheated to 95 °C, and 1% PVA was added into the water for 30 min until PVA was completely dissolved. The solutions were then cooled to room temperature, and 5% APP was added into the solutions which were stirred for 60 min until completely dissolved. The Eucalyptus veneer was dried in an air-blast drying oven to reach an absolute dry state. Then put these veneers into a treating tank, and sealed the tank. The vacuum in the tank was set to -0.089 MPa. The treatment solutions were pumped into the tank by negative pressure, and then the pressure in the tank was increased to a set value by a pressurizing device. After treatment, the wood was stored at room temperature for 24 hours. The moisture content of the wood was controlled from 6% to 10% in the air blast drying box. The test method referred to the Chinese standard GB/T 2406.2-2009.

2.3. BBD
The main factors affecting the permeation of wood modifier are the type of modifier, concentration of modifier, vacuum time, impregnation pressure, and impregnation time. The types of modifiers are generally classified into water and oil. Because of the good water-solubility, water-based modifier can enter the wood more quickly, fill the wood cavity, and fix in the cell wall. Therefore, water-based composite modifier is selected as flame retardant in this study. After adding the modifier, the amounts of the modifier entering the cell lumens of the wood interior are relatively larger with longer vacuum time. However, the vacuum time affects the actual production cost. Therefore, it is necessary to optimize the appropriate vacuum time for wood pretreatment. The impregnation pressure has an important influence on the entry of the modifier into the wood [3, 4]. However, if the pressure was too high, it could cause physical damage to the wood. The impregnation time also has an important influence on the amount of the modifier fixed within the wood. The longer the impregnation time, the bigger weight gain of treated wood. If the time was too long, it could seriously affect the treatment efficiency, which would rise the modification cost [5]. Therefore, on the basis of previous studies this study mainly selected three factors such as vacuum time, impregnation pressure, and impregnation time to modify Eucalyptus veneers. Firstly, the single factor experiment of 3 factors was carried out, and the optimum interval level was preliminarily selected. Then the response surface experiment was designed according to the optimum level, and the optimum impregnation parameters were obtained. In the single factor experiment design, the vacuum time interval was set to 10 - 50 min, the immersion pressure and the immersion time were fixed to 0.8 MPa and 60 min respectively; the pressure interval was set at 0.4 - 1.2 MPa, the vacuum time and the immersion time were fixed at 20 min and 60 min respectively; the time interval was set at 20 - 100 min in the single factor experiment, the vacuum time and immersion pressure were fixed at 20 min and 0.8 MPa, respectively. Each factor was set at 5 levels.

The LOI of modified Eucalyptus veneers was measured according to GB/T 2406.2-2009. The primary and secondary factors of LOI were +1, 0, -1 represented high, middle and low levels respectively. The response surface analysis of 3 factors and 3 levels was performed by Design-Expert 10.0.2 (Trail version) with BBD design and LOI as the response value. Based on the analysis of the experimental results, a quadratic polynomial mathematical model was established to obtain the optimal impregnation conditions and the corresponding prediction of LOI.
Table 1. Experimental factor level and coding.

| Factors          | Level |
|------------------|-------|
| \(X_1/\text{min}\) | -1    | 0    | +1   |
| \(X_2/\text{MPa}\) | 0.6   | 0.8  | 1    |
| \(X_3/\text{min}\) | 40    | 60   | 80   |

2.4. Validation test

In order to verify the accuracy and reliability of the optimal conditions, six parallel validation experiments were carried out under the optimal conditions, and the results were verified and compared with the predicted values.

3. Results and analysis

3.1. Single factor experiments

![Fig. 1](image_url)

**Fig. 1** Effects of (a) vacuum time, (b) impregnation time, and (c) impregnation pressure on LOI.

Figure 1 shows the effects of the factors on LOI of modified Eucalyptus veneer. As can be seen from Fig. 1(a), the LOI of Eucalyptus veneers increased with the rising of vacuum time. However, when the vacuum time reached 40 min, the LOI of Eucalyptus veneers increased little with the further increase of time. It could be that when the vacuum time reaches a certain value, the air in the wood cavity has been basically exhausted through the vacuum and reached a stable state, even if the further increase of time showed no obvious improvement on the modification effect. Therefore, the optimum range of vacuum time was 20 – 40 min.

Figure 1(b) shows the effect of impregnation pressure on LOI of modified Eucalyptus veneer. The LOI of Eucalyptus veneers increased with the increase of impregnation pressure. This was because the impregnation pressure had a direct effect on the modifier penetrating the wood. In the impregnation process, the modifier was pressurized into the wood. But the impregnation pressure was too large and easily causes damage to the wood, which has a negative impact on impregnations. Considering the cost and effect of the modification process, 0.6 - 1 MPa was selected as the optimum range for RSM.

Figure 1(c) shows the effect of soaking time on LOI of modified Eucalyptus veneer. The LOI of Eucalyptus veneers increased with impregnation time. This may be because the modifier was water-based, under the same conditions, the modifier easily entered the cell lumens through the pressure, with the increase of impregnation time. The modifier infiltrated the cell wall and entered the cell wall interior, which made weight gain increase. Therefore, the LOI of Eucalyptus veneer is higher. The optimum impregnation time was 40 - 80 min, considering the cost and effect of the modification.

Based on the single factor experimental results of vacuum time, impregnation pressure and impregnation time, the economy and feasibility of impregnation process were considered, the LOI of modified Eucalyptus veneer was better when vacuum time, immersion pressure and immersion time were between 20 - 40 min, 0.6 - 1 MPa and 40 - 80 min, respectively.
3.2. Response surface experiments

The experimental results of BBD design are shown in Table 2. The results of further analysis of variance for the optimized experimental results are shown in Table 3. The results of variance analysis showed that the effects of X2 and X3 on LOI of modified Eucalyptus veneer were very significant. Impregnation pressure and impregnation time were important controlling factors for LOI of modified Eucalyptus veneers. The influence of other factors and their interaction effects was not significant.

Table 2. The experiment results of response surface.

| Running No. | X1/min | X2/MPa | X3/min | (Y, LOI)% |
|-------------|--------|--------|--------|-----------|
| 1           | 20     | 1      | 60     | 28.5      |
| 2           | 40     | 0.6    | 60     | 27.1      |
| 3           | 20     | 0.8    | 80     | 28.4      |
| 4           | 30     | 0.8    | 60     | 27.9      |
| 5           | 30     | 0.8    | 60     | 28.1      |
| 6           | 30     | 0.8    | 60     | 27.8      |
| 7           | 30     | 0.6    | 40     | 24.8      |
| 8           | 30     | 0.8    | 60     | 27.4      |
| 9           | 30     | 1      | 80     | 29.5      |
| 10          | 30     | 1      | 40     | 28.9      |
| 11          | 30     | 0.8    | 60     | 27.7      |
| 12          | 40     | 0.8    | 80     | 28.8      |
| 13          | 40     | 0.8    | 40     | 26.5      |
| 14          | 40     | 1      | 60     | 29.2      |
| 15          | 30     | 0.6    | 80     | 27.6      |
| 16          | 20     | 0.6    | 60     | 26.3      |
| 17          | 20     | 0.8    | 40     | 26.2      |

The order of influence on LOI of Eucalyptus veneer was ordered as follows: impregnation pressure, impregnation time, and vacuum time. The lack of fit represented the fitness that the actual experimental data didn’t match the predictive data [6, 7], which indicated that the misfit between the real data and the model prediction data. The p value of the lack of fit was 0.1617, which showed that there was no significant abnormal value in the data and it was accurate and reliable. The R2 value of the model was 0.9641, which showed that the model equation could explain 96.41% of the variation of the LOI of treated Eucalyptus veneer. It also showed that the quadratic regression equation fitted well, which proved the reliability of the model [8, 9].

Table 3. The variance analysis of response surface.

| Source       | Sum of square | Df | Mean square | F-value | p-value | Significance |
|--------------|---------------|----|-------------|---------|---------|--------------|
| Model        | 23.14         | 9  | 2.57        | 20.91   | 0.0003  | **           |
| X1           | 0.61          | 1  | 0.61        | 4.92    | 0.0620  |              |
| X2           | 13.26         | 1  | 13.26       | 107.88  | <0.000  | **           |
| X3           | 7.80          | 1  | 7.80        | 63.46   | <0.0001 | **           |
| X1X2         | 2.5×10⁻³      | 1  | 2.5×10⁻³    | 0.020   | 0.8906  |              |
| X1X3         | 2.5×10⁻³      | 1  | 2.5×10⁻³    | 0.020   | 0.8906  |              |
| X2X3         | 1.21          | 1  | 1.21        | 9.84    | 0.0164  |              |
| X1²          | 0.056         | 1  | 0.056       | 0.45    | 0.5225  |              |
| X2²          | 0.051         | 1  | 0.051       | 0.41    | 0.5402  |              |
| X3²          | 0.15          | 1  | 0.15        | 1.24    | 0.3029  |              |
| Residue error| 0.86          | 7  | 0.12        |         |         |              |
| Lack of fit  | 0.59          | 3  | 0.20        | 2.95    | 0.1617  |              |
| R²           | 0.9641        |    |             |         |         |              |

Note: ** means the statistical result is very significant (p < 0.01).

By using Design-Expert software to analyze the experimental data, the quadratic regression equation of response value LOI was obtained by polynomial fitting of three factors.
$$Y=27.78+0.28X_1+1.29X_2+0.99X_3-0.025X_1X_2+0.025X_1X_3-0.55X_2X_3-0.12X_2^2+0.11X_2^2-0.19X_3^2$$

3.3. Response surface of interactions among factors of LOI

According to the response surface optimization model, the data is fitted and the three-dimensional response surface and contour maps of LOI of treated Eucalyptus veneer are shown in Figure 2. The three-dimensional response surface diagram was the interactive influence diagram of the LOI and the various factors. Each small figure corresponded to the interactive response surface diagram of two different factors, the other two factors were fixed at zero level. The response surface plots of impregnation pressure and impregnation time were relatively steepest, indicating that the interactions of impregnation pressure and impregnation time on the LOI of modified Eucalyptus veneer was significant [9, 10]. This was consistent with the results of variance analysis in the previous section Because the effect of vacuum time on the LOI of modified Eucalyptus veneers was not significant, the main factors influencing the LOI of modified Eucalyptus veneers were impregnation time and impregnation pressure. The corresponding three-dimensional response surface was relatively smooth. In the analysis of variance, the statistical results of p-values corresponding to $X_1X_2$ and $X_2X_3$ were not significant, which corresponded with the shape of response surface curve.

3.4. Validation test

By solving the fitting equation of LOI, the predicted value of LOI was 29.525%. The vacuum time, impregnation pressure and impregnation time were 35.412 min, 0.998 MPa and 79.093 min, respectively. According to the predicted optimal process parameters and considering the operation feasibility and economy, the vacuum time, the impregnation pressure, and the impregnation time were rounded to 35 min, 0.9 MPa and 79 min, respectively. Under this condition, the modified Eucalyptus veneers were impregnated with flame retardant, and LOI of the modified Eucalyptus veneers was measured and analyzed. The results showed that the average value of LOI as 28.2% and the percentage error was 4.49%. On this basis, the prediction of the optimal process by the response surface optimization model was verified to be accurate, reliable, and feasible.

3.5. SEM analysis

![Fig. 3 SEM images of pristine and treated Eucalyptus veneers.](image-url)
Figure 3 displays the SEM images of Eucalyptus veneer before and after modification under the optimum conditions. The cavity of the treated wood was filled with a large number of regular particles. These particles were crystalline particles formed by APP, which filled and fixed on the cell lumens and cell wall of the treated wood. The feasibility and reliability of the optimal process conditions predicted by RSM were further verified by SEM analysis.

4. Conclusion and discussion
(1) The influence of impregnation pressure and impregnation time on LOI was very significant, but other factors and their interaction effects were not significant.
(2) By establishing the quadratic multiple regression model between the independent variables and the response, the optimum conditions were obtained as follows: vacuum Time 39 min, impregnation pressure 0.9 MPa, and immersion time 79 min.
(3) The average value of LOI of modified Eucalyptus veneer was 28.2% and the error rate was 4.49%, which showed that the model was accurate and reliable for prediction.
(4) The cell lumens of Eucalyptus veneer was filled with modifier by analysis of SEM, which showed the modifier had entered the wood and deposited in the cell walls under the optimum conditions.

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