Influence of Mesoporous Inorganic Al–B–P Amphiprotic Surfactant Material Resistances of Wood against Brown and White-Rot Fungi (Part 1)

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Abstract: This study describes the application of aluminum sulfate Al₂(SO₄)₃, boric acid H₃BO₃, phosphoric acid H₃PO₄ (Al–B–P) and amphiprotic surfactant material synthesis by the sol-gel process, which were adopted as novel precursors for wood modification. The efficacy of Al–B–P-treated wood was tested against Poria placenta and Coriolus versicolor. Untreated wood samples had higher mass losses (>40%) compared to the treated sample, which had the lowest wood mass losses (of 4%) against P. placenta and C. versicolor. To analyze the reaction mechanism of Al–B–P wood, the mechanical properties, chemical structure, crystallinity, thermal analysis, binding energy and wettability was examined by modulus of rupture (MOR), modulus of elasticity (MOE), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD), Thermogravimetric analysis (TG) and X-ray photoelectron spectroscopy (XPS), respectively. Scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) confirmed the wood colonization by fungi, and was used to identify the microstructures and morphologies changes that occurred in the cells during degradation by white and brown-rot fungi. At the same time, X-ray photoelectron spectroscopy (XPS) was employed to analyze the physical and chemical properties of the samples. Therefore, the study confirmed that Al–B–P and amphiprotic surfactant could replace the traditional wood preservative products, and have the potential to extend the service life of wood, particularly in soil contact and outdoor usage.

Keywords: white-rot fungi; Poria placenta; Coriolus versicolor; fiber reinforced; inorganic sol-gel process; wood modification

1. Introduction

Wood is renewable by excellence and is an environmentally friendly material; nevertheless, as a biological material, it suffers to the same extent as many other natural materials, namely degradation, due to its composition and anatomical structure.

The foremost problems are the facts that white-rot fungi use non-enzymatic and enzymatic systems to degrade all cell wall components [1]. Coriolus versicolor and Poria placenta fungi degrade wood in the crystalline region by cellulolytic and ligninolytic enzymes [2]. P. placenta fungi colonize wood by the sequential decomposition of lignin and cellulose using their extracellular enzyme system [3-5]. Wood decayed by P. placenta has been further chemically characterized by a number of β-xylosidases and endo-xylanases [2]. C. versicolor fungi are known to degrade polysaccharides efficiently [6].
The most widely used wood chemical preservatives include; copper azole alkaline (CAA) and copper quaternary cresote (CQC), etc. They protect wood bio-deteriorating agents after application; however, their uses pose a threat to the environment, due to the presence of heavy metals that are toxic to the mammals and other organisms in the environment.

In the same way, \textit{C. versicolor} and \textit{P. placenta} are also tolerant to copper, a commonly used active ingredient in wood preservation products \cite{7}. Environmental and health concerns are related, which in turn closes the loop by encouraging the use of materials that contain recycled content, reducing their leaching into the environment \cite{8,9}. Moreover, more recently, studies conducted by Saka have been testing inorganic sol-gel, such as TiO$_2$ and SiO$_2$, which, combined with other reagents as Na$_2$OSiO$_2$ gel, can be useful for wood preservation, and the study results showed that integrating inorganic compounds into the wood cavity wall can enhance the characteristics of the wood, such as against fungi (white and brown-rot fungi) and termites \cite{10,11}.

Some novel inorganic chemical combinations, based on boron compounds (B), aluminum sulfate compounds (Al), phosphoric acid (P) and amphiprotic surfactant as a reinforcing agent, through a sol-gel process, have been shown to be an excellent anti-fungal agent process, and was a promising and environmentally friendly method to enhance the wood properties against fungi and molds \cite{11}. For this reason, there are significant efforts to investigate the replacement of copper as an active ingredient in protecting wood against copper-tolerant fungi.

Thus, the Al–B–P and the amphiprotic surfactant is perfect for wood preservative, and would not only inhibit the growth of wood-destroying organisms, but would also have low water solubility, which would reduce their leaching into the environment. The decrease hygroscopicity of the wood can also improve dimensional stability because of the presence of aluminum sulfate, which combines with boric acid \cite{12}. The treatment decreases the hygroscopicity of the wood sample, and can also improve the dimensional stability due to the incorporation of the combination of aluminum sulfate and boric acid agents. The application of inorganic sol-gel for wood modification treatment to both enhance and improve resistance to fungi has attracted the attention of many researchers \cite{13,14}.

The development of new wood preservatives is aimed to reduce environmental pollution, is cost-effective, and has low viscosity and excellent fungal resistance properties. In recent years several investigations attract the focus of researcher concern on wood surface morphology changed by inorganic agents. Especially Hübert (2018) describes the behavior of nanoparticles compounds against brown-rot fungi \cite{15}. Based on maintaining the characteristics of wood porous structure, it can improve the wood performance on many aspects, including mechanical properties, dimensional stability, being antibacterial, waterproof, and improving the anti-loss of preservatives such as copper and boron, etc. \cite{16-18}. Anti-fungi treatment is vital for the efficient utilization of wood raw material \cite{8}. Sol-gel based on aluminum and copper sulfate can lead to an improved resistance against decay degradation and reduced fungal colonization \cite{19}. The deterioration of wood by biological organisms is a definite disadvantage when the wood is used in service. However, the cross-linking mechanism of the chemical bonds formed after impregnation could improve the wood service life \cite{20}. Many studies have reported that \textit{Poria placenta} mycelium penetrates inside wood cells and causes enormous impact and thus has a higher fungal activity morphology of the mycelium. Novel inorganic aluminum borate and nano metal compounds could improve the antifungal performance of wood, which is in agreement with previous studies \cite{21,22}.

Therefore, aluminum sulfate (Al$_2$(SO$_4$)$_3$), boric acid (H$_3$BO$_3$) and the amphiprotic surfactant are considered non-toxic, and also has relatively very low-risk to animals and is non-toxic for humans to significantly improve wood against white-rot fungi and termites, including being low-cost and renewable \cite{23}. Aluminum sulfate and boric acid products are effective against both fungi and termites if used below the limit stated in biocidal products, and have emerged as alternatives to the preservatives based upon heavy metals \cite{24}.

The main objective of the present research was mainly focused on preparing inorganic Al–B–P amphiprotic surfactant solutions. Then we used it to improve wood properties, and to study the effect of their interaction on white-rot fungi. Therefore, after the characterization of the impregnation on wood, accelerated biological tests against the white and brown-rot fungi (\textit{Coriolus versicolor} and \textit{Poria}}
two of the most aggressive fungi against the wood, were run to determine the efficacy of the solution.

To clarify these issues, the processing parameters of wood, an experimental design of the response surface methodology (RSM) model, was used to analyze the problems and get exact results by various independent variables.

Additionally, treated and untreated wood sample surfaces, along with the microstructures, chemical structures, mechanical performance and thermal stability of Al–B–P amphiprotic surfactant is also discussed in this study.

2. Materials and Methods

2.1. Wood Materials

Concerning Pinus (Pinus massoniana) and Sitka spruce (Picea sitchensis), both species have been chosen according to their availability in the region of Fujian, for each species having a relatively straight stem with the age of 15-yrs-old. The Pinus and Spruce density was 0.48 and 0.45 g·cm⁻³, respectively. The samples prepared from sapwood portions with the dimensions of 50 × 20 × 5 mm³ (longitudinal; tangential; radial) for a wood sample were placed in Petri dishes. We made other dimensions for a sand test (19 × 19 × 19 mm³) and soil contact test (457 × 19 × 19 mm³). Before treatment, we dried wood samples at 103 °C for 24 h. All wood blocks were: having no defects, as knots, and being without visible evidence of fungus infection. All specimens’ size, respectively, was obtained from Fujian Minhou.

2.2. Chemical Products and Fungi

99% aluminum sulfate (Al₂(SO₄)₃), 99% boric acid (H₃BO₃), 85% phosphoric acid (H₃PO₄), 99% cupric salt (CuSO₄) and amphiprotic surfactant (C₅H₁₁NO₂HCl) were purchased from Tianjin Fuchen Chemical Co. Ltd. (Tianjin, China), and Sino Pharm Chemical Reagent Co. Ltd. (Shanghai, China). 99.5% sodium tetraborate (Na₂B₄O₇·10H₂O) was bought Sigma-Aldrich in Shanghai (China). The fungi used in this study were Poria placenta (brown-rot fungi) and Coriolus versicolor (white-rot fungi) obtained from the collections of the laboratory Beijing Zhongke Quality Inspection Biotechnology Co., Ltd (Beijing, China) and kept at 26–28 °C, and placed in the incubator at 85% of relative humidity.

2.3. Preparation of Al–B–P Amphiprotic Surfactant Solution

In a beaker of 1000 mL, containing 25 mL of Al₂(SO₄)₃, 25 mL of H₃BO₃, 1.2 g of CuSO₄ and 15 g of 85% H₃PO₄, were dissolved in distilled water at 70 °C and quickly added to a solution of 4.8 mL of amphiprotic surfactant (C₅H₁₁NO₂HCl), and the entire solution was stirred for 15 min until the solution became blue. The pH of the solution measured was around 2.5 and 3. The optimum parameters for antifungal agents were: the mass ratio of Na₂B₄O₇·10H₂O, CuSO₄ and Al₂(SO₄)₃ are 1.40%, 2% and 3%, respectively.

2.4. Field Testing Methods

For this study, soil contact analyzed the data collected from Fujian Minhou (26°4’45’’ N119°15’30’’E). Fujian climate is hot and humid, with a subtropical monsoon climate, with moderate winters, which is suitable for the growth of decaying bacteria and termites, causing severe damage to wood. The field tests aim to visualize the fungal decomposition of wood to test the durability of the treated wood, and then compare it to the untreated wood. Similarly, the method was described by Råberg (2013) [25].

The data average is 15 for each specimen of the mechanical properties of a wood sample with a moisture content at 12%. The size of all samples for MOE and MOR was 457 ×19 × 19 mm³ (L × W × H), and they were tested according to the British Standard BS EN 252:2014 [26]. Reported results are the average of six replications. Wood treatment with Al–B–P and amphiprotic surfactant sol-gel influences the static strength (MOR) and elastic modulus (MOE) of the treated wood.
2.5. Preparation Method of Culture of Fungi

75 g of sand, 75 g of pine sawdust, 7.5 g (25 mesh) of cornflour and 4.3 g of brown sugar were added in a flask of 250 mL and mixed. 50 mL of maltose was slowly added to the mixture and sterilized for 1 h at 120 °C. After cooling, before the Potato Dextrose Agar was inoculated with fungi, 90 Petri dishes of (120 by 20 mm) were sterilized by autoclaving at 120 °C for 15 min. After that, we inoculated each petri dish in the center with P. placenta or C. versicolor. We placed the inoculated culture in a growth chamber at 28 °C with 85% relative humidity for 20 days. For Potato Dextrose Agar (PDA), we boiled 200 g of sliced potatoes in 1 liter of water for 30 min into the flask, added 20 g of glucose and 15–20 g of agar. It was then sterilized for 20 min. The medium was prepared according to the methods described by the American Society for Testing and Materials (ASTM) D4445,2015 [27]. Treated and untreated wood was placed in a petri dish (120 mL) containing 25% PDA and introduced into the soil block, then exposed for 16 weeks [28].

2.6. Treatment Procedure of Wood Sample

Wood samples were weighed, and the moisture content of the wood was collected. All wood was first soaked in Al–B–P and amphiprotic surfactant solution by dipping according to the normal pressure for 6 h. Three replicates were used for this experiment. Following impregnation, we dried wood in an oven for 6 h at 80 °C. Following impregnation, we cleaned each wood with cotton and absolute ethanol. The impregnated wood was then kept for the evaluation of the durability. Response surface methodology (RSM) was used to optimize the parameters of the Na2B4O7·10H2O, CuSO4, and Al2(SO4)3, solution concentration, for the effective treatment process. Design-Expert software trial version 8.0.5 was used to draw the analysis diagram based on the regression equation. The Box–Behnken design method was adopted to carry out the test at the level of three factors m(Na2B4O7·10H2O), m(CuSO4) and mAl2(SO4)3, with respective values of 1.4%, 2% and 3%. The test designs were coded as X1, X2 and X3. Table 1, and Table S1 show the results of the response surface (ML (mass loss) of two types of fungi, Poria placenta and Coriolus versicolor).

| Factors | Code and Levels * |
|---------|------------------|
| X1      | -1 0 1           |
| X2      | 0 1 2            |
| X3      | 0 1.5 3          |

* Combinations at two levels (-1, 0) low (0, 1) high levels

2.7. Retention Rate of Chemical Effectiveness

The retention of wood preservatives depends upon treatment time, temperature and pH of the solution. All these factors influence the fixation of chemicals on wood [29,30].

Wood was weighed before and after the impregnation of the solution. The chemical retention of the anti-fungi agents was determined using the following Equation (1) [31].

\[
\text{WPG} = \frac{W_1 - W_2}{W_2} \times 100
\]

Where: WPG—Weight Percent Gains
W1 = the oven dried weight before treatment
W2 = the oven dried weight after treatment respectively.

2.8. Evaluation of Fungicide and Testing Procedure

After the characterization of the treated wood sample, their resistance against decay by C. versicolor and P. placenta was assessed following the American standard ASTM D2017-05 [28].
The mass loss of the wood after characterization was evaluated after 16 weeks of exposure to fungi. The mycelium on the surface of the test specimens was a softness removed with care, and the wood blocks were oven-dried for 24 h at 103 °C, weighed, and we saved the final mass loss. The average mass loss rate (AML%) of treated and untreated wood samples was determined by following Equation (2):

\[
AML\% = \frac{W_{\text{initial}} - W_{\text{final}}}{W_{\text{initial}}} \times 100
\]

Where \(W_{\text{initial}}\) is initial dried mass of wood before treatment and \(W_{\text{final}}\) is the dry mass after fungi attack. Table 2 below gave the resistance grade of wood after fungi attacks.

### Table 2. Specific standards evaluation of wood-decay fungi.

| (AMLR%) * of Wood Sample | Level Class Resistance to Test Fungus | Average Residual Weight (%) |
|--------------------------|--------------------------------------|----------------------------|
| 0%–10%                   | Strong rot Resistant                  | 90–100                     |
| 11%–24%                  | rot resistant                         | 76–89                      |
| 25%–44%                  | slightly rot resistant                | 56–75                      |
| <45%                     | not resistant to rot                  | <55                        |

* Average mass loss rate%

#### 2.9. Materials Characterization

The morphological aspects of treated and untreated wood samples were characterized using a Scanning Electron Microscopy (SEM, Hitachi UHR FE-SEM SU8010, Tokyo, Japan). The cross-sectional of the wood samples had been cut with a microtome and sprayed with carbon to 15 nm before image acquisition and operating at 50 µm 15 kV and variable pressure (5–10 Pa). EDS (Supra 55 Zeiss, Oberkochen, Germany) was carried out using an acceleration voltage of 15 kV and variable pressure (5–10 Pa). We performed the mapping of the wood sample with a distance of 10 mm, and the time of capture was 600 s. We performed the pore size distribution analysis of wood realized by nitrogen absorption desorption on (JW-BK132F, Beijing, China). The sample size of 50 \( \times \) 20 \( \times \) 5 mm\(^3\) weighing as a 0.5–1 g powder specimen was determined using a blast dryer, under the conditions of 103 ± 3 °C. The pore size of the wood was calculated according to the Barrett–Joyner–Halenda (B–J–H) formula. The surface porosity of the wood was calculated according to the Brunauer, Emmett and Teller (BET) equation. FTIR spectra were obtained with the MIR-FIR spectrum (VERTEX 70, Bruker Instrument, Billerica, MA, USA). The KBr pellet method was employed in each sample by grinding 2 mg of dried wood powder (200 mesh) and potassium bromide powder (1:100) to produce thin sheet disks. The diffraction analysis was performed using an X-ray diffractometer (XRD) (X’Pert PRO Malvern Panalytical Ltd, Almelo, The Netherlands). The wood powder (200 mesh) was pressed into 10 \( \times \) 10 \( \times \) 1 mm\(^3\) size on a slide. The test of cellulose crystallinity and chemical bond combinations between wood and chemical compound with Cu Ka radiation at a wavelength \( \lambda = 1.790 \) nm were examined. Nuclear magnetic resonance (NMR) analysis. The \( ^{31} \)P and \( ^{27} \)A1 MAS NMR spectra of Al–B–P compounds specimens were recorded on a Bruker ADVANCE III 500 spectrometer (Billerica, MA, USA), using a 7 mm zirconia oxide rotor with a spinning speed of 4.5 kHz. We recorded all spectra at room temperature, using dry air as driving gas. The \( ^{27} \)A1 MAS NMR spectra were recorded at a frequency of 105 MHz with a pulse length of 1 \( \mu \)s.

The wettability of the treated wood and untreated wood was measured using the contact angle by placing a droplet of water in contact with the wood surface using a micrometer syringe, and the Contact Angle was measured by scanning the droplet profile 0, 30 and 60 s after placing water drops on the wood surface, using an analyzer (Harke-spcaxd contact angle measuring instrument, Beijing, China). The curves of the thermal gravimetric analyser (TGA) were obtained using a thermogravimetric analyser (NETZSCHSTA449F3, Selb, Germany). Under high-purity nitrogen atmosphere, approximately 10 ± 0.5 mg of the sample was heated in air at room temperature to 800 °C. The experiments started with a different heating rate of 10 and 20 °C/min. The reported results are
the average of eight specimens. The measurement of the MOR and MOE values of the wood samples after exposure to the ground was performed on the MTS Exceed Series 40 Electromechanical Test system (Eden Prairie, MN, USA) at a constant speed of 100 mm/min. The reported results are the average of 120 samples. The sample preparation was according to TS 2474. Loading was done at the tangential directions of samples. For this purpose, the size of samples was 457 × 19 × 19 mm³ (L × W × H), and the dimension between the centers of the two supports was 240 mm. X-ray photoelectron spectroscopy (XPS) was performed on the ESCALAB 250Xi (Thermo Fisher Scientific Company, Waltham, MA, USA). Experiments were carried out at an ambient temperature in an ultrahigh-vacuum system with Al Kα (λ = 1486.6 eV) a power of 300 W radiation with high sensitivity spectroscopy 500 µm.

3. Results and Discussion

3.1. Inhibition Efficiency

For the anti-fungal effectiveness of Al–B–P and the amphiprotic surfactant, the evaluation was determined by 16 weeks exposure of specimens with different treatments concentration to the different white and brown-rot fungi *C. versicolor* and *P. placenta*, as well as under sterile control conditions, according to our previous report [28]. Our results show that Al–B–P and the amphiprotic surfactant were significantly higher than those reported by Lesar 2018 [32]. Of boron–ethanolamine-treated specimens exposed to *C. versicolor*, the incubation time was thirteen weeks. There were minor differences in mass loss between CuSO₄- and Al₂(SO₄)₃-treated specimens in Figure 1. When exposed to fungi, we observed lower mass loss in treating wood samples compared to the control sample. Also, minor differences in mass loss between the Agar block test and the soil block test treated samples in Figure 1b. However, the test has shown that were found to be more effective against brown-rot fungi (*P. placenta*) than white-rot fungus (*C. versicolor*). Untreated *Pinus* shows a higher weight loss after exposing (*C. versicolor*) Figure 1a, which is also confirmed through the morphological difference of microstructures between natural wood and Al–B–P and amphiprotic surfactant-treated wood, as shown in Figure 1c. We obtained the average percentage difference for each combination of chemical compounds, where the mass loss of treated specimens exposed to *C. versicolor* was more than 5%, while in *P. placenta* it was below 4%. Figure 1b. The higher mass losses observed for *C. versicolor* compared to the *P. placenta* mass loss of the control blank sample wood specimens exposed to *C. versicolor* was above 45%, and it was 40% for *P. placenta*.

The change in the appearance of the wood samples after exposure to *C. versicolor* and *P. placenta* is shown in Figure 1c. Evidently, the control blank sample is severely damaged, while the inorganic Al–B–P and amphiprotic surfactant-treated (optimized) sample Figure 1c had minimal damage for specimens exposed to the *C. versicolor* and *P. placenta*. Thus, the inorganic Al–B–P and amphiprotic surfactant protected the wood samples from extensive white-rot fungi deterioration. While though the treated sample exposed to *C. versicolor* and *P. placenta* does not show cracks on their surfaces, that is, no visible damage, compared to the control blank samples, which have shrunk considerably because of lignin degradation. These results have shown that the Al–B–P gel provides efficiency, and the protection of wood against fungi. The results obtained from the soil block test were like those reported in the literature [33,34]. When raw wood and soil block test samples were exposed to fungus mass loss, it was observed that the mass loss of untreated wood specimens exposed to *C. versicolor* was above 35% and it was 31% for *Poria placenta* after 16 weeks of incubation.
3.2. Optimize Preparation Parameter of Wood

The parameters chosen for the study code and levels are shown in Table 1. The statistical analyses were performed by using the response surface methodology (RSM) to the analysis of preservatives in wood samples. The ordering of three independent and dependent variables of mass loss (ML%) is illustrated in (Tables 3, 4, S2 and S3). The final coded factors are given by Equation (3).

\[
ML(\%) = 6.76 + 1.83 \times X_1 - 3.09 \times X_2 + 1.00 \times X_3 + 4.56 \times X_1X_2 - 4.08 \times X_1X_3 + 2.86 \times X_2X_3 + 4.26 \times X_1^2 + 6.60 \times X_2^2 + 10.40 \times X_3^2
\]  

(3)

Where: ML: mass loss, \(X_1\): (Na\(_2\)B\(_4\)O\(_7\)·10H\(_2\)O), \(X_2\): Al\(_2\)(SO\(_4\))\(_3\), and \(X_3\): (CuSO\(_4\)) respectively.

To test the validity of mass loss, the regression equation and the analysis of Variance (ANOVA) was used, and the model coefficients are presented in Table 3. The Na\(_2\)B\(_4\)O\(_7\) ratio (\(X_1\)) has the largest influence on the \(p\)-value. The model was 0.0013, which shows that the model was significant. In the quadratic’s prediction term, the Na\(_2\)B\(_4\)O\(_7\)-10H\(_2\)O ratio (\(X_1\)), reaction Al\(_2\)(SO\(_4\))\(_3\) (\(X_2\)) and reaction CuSO\(_4\) (\(X_3\)) have an extremely interactive effect between them, and the model of the quadratic polynomial model has a significant influence because of the \(F\)-value 13.19 and the Prob > \(F\) is 0.0013. This indicates that the model was significant. As shown in Table S4, the model summary statistics of both \(R^2 = 0.9443\) and 0.4740 of each response demonstrates appropriate correlation [8]. This shows an excellent correlation between the experiment and the predicted value for each of the responses between the preparation variables and the polynomial model. The response surface graph is a three-dimensional (3D) response surface plot and 2D contour plots showing the optimal levels composed of specific response value ML\(\%\) and corresponding factors \(X_1\), \(X_2\), and \(X_3\), which can intuitively reflect the influence of various factors on response value [35].
The response surface analysis results of the various factors on the interaction between Al\(\text{2(SO}_4\text{)}_3\), CuSO\(_4\) and Na\(\text{2B}_4\text{O}_7\cdot10\text{H}_2\text{O}\) are shown in Figures 2a–f. As shown in Figure 2e, the Al\(\text{2(SO}_4\text{)}_3\) ratio ranged from 0 to 1.4%. Response values present a tendency to increase. When the Al\(\text{2(SO}_4\text{)}_3\) ratio exceeds 1.4%, the ML tends to decrease. The effect of CuSO\(_4\) on the response value of ML is like the Al\(\text{2(SO}_4\text{)}_3\) ratio, indicating that the interaction effect between the Al\(\text{2(SO}_4\text{)}_3\) ratio and CuSO\(_4\) provide significantly better resistance to fungi activities. Although there are no significant differences, these results are the same as those observed with the ANOVA in Figure 2c, when the reaction of CuSO\(_4\) is fixed with the temperature at 70 °C, the reaction of CuSO\(_4\) ranges from 0 to 2%, and the response value ML decreases. In summary, when examining the concentration effects of \(X_1, X_2\) and \(X_3\), the interaction of \(X_1X_2\) is significantly greater than that of \(X_1X_3\) and \(X_2X_3\). This is the significance of opting for 3% of concentration, which has an excellent anti-fungal effect.

**Table 3.** Box–Behnken design and response values.

| Test | \(X_1\)% | \(X_2\)% | \(X_3\)% | * Mass Loss% |
|------|----------|----------|----------|-------------|
| 1    | 3.00     | 2.80     | 0.00     | 18.8        |
| 2    | 3.00     | 1.40     | 2.00     | 11          |
| 3    | 6.00     | 1.40     | 0.00     | 26          |
| 4    | 3.00     | 0.00     | 4.00     | 23          |
| 5    | 3.00     | 1.40     | 2.00     | 5           |
| 6    | 3.00     | 2.80     | 4.00     | 23.3        |
| 7    | 3.00     | 1.40     | 2.00     | 4           |
| 8    | 3.00     | 0.00     | 2.00     | 29.93       |
| 9    | 0.00     | 0.00     | 2.00     | 25.1        |
| 10   | 6.00     | 2.80     | 2.00     | 20.36       |
| 11   | 0.00     | 1.40     | 4.00     | 25          |
| 12   | 6.00     | 0.00     | 2.00     | 17.08       |
| 13   | 3.00     | 1.40     | 2.00     | 7.2         |
| 14   | 0.00     | 2.80     | 2.00     | 9.02        |
| 15   | 3.00     | 1.40     | 2.00     | 6.58        |
| 16   | 6.00     | 1.40     | 4.00     | 23.04       |
| 17   | 0.00     | 1.40     | 0.00     | 11.63       |

* ML: Mass loss of white and brown-rot fungi (Poria placenta; and Coriolus versicolor)

**Table 4.** Analysis of variance (ANOVA).

| Source     | Squares | df | Mean Square | \(F\)-Value | \(p\)-Value |
|------------|---------|----|-------------|-------------|-------------|
| Model      | 1079.80 | 9  | 119.98      | 13.19       | 0.0013      |
| \(X_1\) (Na\(\text{2B}_4\text{O}_7\)) | 26.75   | 1  | 26.75       | 2.94        | 0.1301      |
| \(X_2\) Al\(\text{2(SO}_4\text{)}_3\) | 76.45   | 1  | 76.45       | 8.40        | 0.0230      |
| \(X_3\) (CuSO\(_4\)) | 7.96    | 1  | 7.96        | 0.87        | 0.3807      |
| \(X_1X_2\) | 83.36   | 1  | 83.36       | 9.16        | 0.0192      |
| \(X_1X_3\) | 66.67   | 1  | 66.67       | 7.33        | 0.0303      |
| \(X_2X_3\) | 32.66   | 1  | 32.66       | 3.59        | 0.1000      |
| \(X_1^2\) | 76.39   | 1  | 76.39       | 8.40        | 0.0231      |
| \(X_2^2\) | 183.38  | 1  | 183.38      | 20.16       | 0.0028      |
| \(X_3^2\) | 455.59  | 1  | 455.59      | 50.08       | 0.0002      |
| Residual   | 63.68   | 7  | 9.10        | –           | –           |
| Lack of Fit| 34.77   | 3  | 11.59       | 1.60        | 0.3219      |
| Pure Error | 28.92   | 4  | 7.23        | –           | –           |
| Cor Total  | 1143.48 | 16 | –           | –           | –           |
| Model      | 1079.80 | 9  | 119.98      | 13.19       | 0.0013      |
Figure 2. Three dimensional (3D) Response surface plots and contour plots for the maximum ML% and two dimensional (2D) contour lines: (a,b) effects of mass rate of Na$_2$B$_4$O$_7$·10H$_2$O and Al$_2$(SO$_4$)$_3$; (c,d) effects of mass rate of Na$_2$B$_4$O$_7$·10H$_2$O and CuSO$_4$; (e,f) effects of mass rate of CuSO$_4$ and Al$_2$(SO$_4$)$_3$.

3.3. Microstructure Analysis of the Inoculated Wood

The morphological features of inorganic Al–B–P and the amphiprotic surfactant examined by SEM, as well as the microstructures and morphologies of untreated and treated wood with the solution Al–B–P, can be viewed from the cross-section, and this is displayed in Figure 3. It was observed that the impregnation of wood with Al–B–P revealed the differences between the fungi decay, which can be visible to the naked eye (Figure 3b). Under the higher magnification of 50 µm, it can be seen that the unmodified surface samples showed signs of colonization after 16 weeks of incubation with C. versicolor and P. placenta. Presented in Figures 3 d,f, the penetration of the hyphae inside the wood has caused the weakness in the S2 layer because the C. versicolor can the degrade lignin ultimately [36]. It can be noted that the appearance of wood changed following exposure to fungi; the untreated wood was seriously broken-down, compared to the treated wood (Figures 3b,d,f). The Al–B–P-treated samples have minimum damage for the samples exposed to P. placenta and C. versicolor. In Figure 3e, the inorganic film around the wood cell was because of the presence of the amphiprotic surfactant in the aluminosilicate network; the toxic threshold values of the wood treated with a solution of Al–B–P in the cell walls was more effective in enhancing the properties of the wood, and this wood would become effective in enhancing the functionality against H$_2$O$_2$ and Fe [37]. Consequently, we could reasonably conclude that Al–B–P and the coupling agent amphiprotic surfactant both play a vital role to enhance the interfacial interaction between the fungi colonization and wood.
Using Energy-dispersive X-ray (EDX) maps confirms the distribution of chemical composition of inoculated wood. In Figure 3g, it can be seen that the treated sample contains large amounts of Al, P, B, Cu and O elements inside the wood cells, respectively. The inoculated woods with white-rot fungi results showed that in the presence of carbon and oxygen, the obtained elements were Fe, Mg, K, Ca, C and O. White-rot fungi-produced Fe elements have a function to mechanism to decompose wood cellulose or render it more susceptible to attack by conventional cellulases [38]. The absorption and desorption isotherm results of the treated sample with inorganic Al–B–P and amphiprotic surfactant, shown in Figures 3i and S1. The absorption surface capacity progressively increases by the addition of Al–P–B with an augment of relative pressure $N = 2$ of the EO unit, especially when the relative pressure of $N_2$ is more than 0.9. The hysteresis curve indicates the presence of a porous structure in the Al–B–P compound [39]. The pore diameter and the total pore volume of Al–B–P and the amphiprotic surfactant material are 0–12 nm, while the specific surface area of Al–B–P and the amphiprotic surfactant material was $1.78 \times 10^{-2} \text{ cm}^2/\text{g}$, and the pore diameter is 5.02 nm, respectively. The average surface area was $9.11 \text{ m}^2/\text{g}$. The total BET surface areas and micropore surface areas are 282.7 and $156.2 \text{ m}^2/\text{g}$, for Pinus and Spruce, respectively. Results show that the integrated mesoporous Al–B–P and amphiprotic surfactant material with hierarchical porosity exhibit unique structure mechanical properties, which provide the improved mechanical properties of a treated sample over that of the untreated sample [39].

**Figure 3.** Scanning electron microscopy (SEM) morphology of natural, untreated wood after exposure to Poria placenta for 16 weeks (b,d,f); SEM morphology of inorganic Al–B–P and amphiprotic surfactant treated wood after exposure to the white rot fungus (a,c,e); 100, 50, 10, 5 µm respectively. Energy-dispersive X-ray spectroscopy (EDX) profile map energy dispersive solutions compounds inside sample-treated wood specimens (g) natural wood after exposure to P. placenta EDX profile (h); nitrogen adsorption-desorption isotherm and mesopore distribution of inorganic Al–B–P and amphiprotic surfactant material (I).
3.4. Reaction Mechanism Analysis

To further investigate the probable chemical bonds and interaction between the presences of the functional groups among inorganic Al–B–P amphiprotic surfactant components and wood samples, we present the corresponding FTIR spectra in Figure 4b. The intensity range used for this test was ranged from 410–3740 cm\(^{-1}\). In Figure 4b, we observe differences between Pinus and Spruce wood before and after treatment. The spectra can be separated into two regions; the first region exhibits a strong O–H stretching peak vibration range between 2800–3740 cm\(^{-1}\) [40]. The absorption intensities of treated and untreated samples have shown strong O–H stretching, and the second is the vibration bands between 2900–3540 cm\(^{-1}\). Similarly, the same spectra were observed in treated and untreated spruce at the same frequencies. The intensities of the absorption peaks at 1300–1594 cm\(^{-1}\) can be assigned to the aromatic ring [41,42]. Moreover, the peak at 800 cm\(^{-1}\) that can be attributed to C–H deformation in cellulose and hemicellulose was shifted to 1000 cm\(^{-1}\) for modified spruce. The bands at 1010–1079 cm\(^{-1}\) in the untreated wood were more intense than in the treated wood [43]. The absorption peaks at 1508–1735 cm\(^{-1}\) can be attributed to C=C of hemicelluloses. The impregnation of Al–B–P and amphiprotic surfactant into raw wood could be proven through THE group C–Br band position, stretch at 507–647 cm\(^{-1}\) and C–N stretch of C–H in wood at 1600–2900 cm\(^{-1}\).

The X-ray diffraction method which was employed to test the crystallinity of samples is one of the essential methods to have the characteristics of physical, chemical and other properties of samples [44,45]. To further analyze the formation of Al–B–P and amphiprotic surfactant, the XRD patterns showed the crystalline and non-crystalline regions of the wood sample. It can be seen from Figure 4a that the three major diffraction peaks at the 2\(\theta\) value of the untreated and treated wood appears around 16\(°\), 20\(°\), 22, and 33\(°\), respectively, corresponding to the (110), (200) and (300) diffraction plane of crystalline cellulose I\(\beta\) [46]. The diffraction peaks show a higher increase due to the deposited particles (Al and B), which have not destroyed the crystalline structure of the cellulose on treating wood [47]. Compared to untreated samples, curve 1 and curve 3 exposes after exposure to (Poria placenta) and (Coriolus versicolor), they flatten between 30\(°–35°\), samples showing a decrease in the intensity of diffraction plane (300) plane, caused by exposure to white-rot fungi substantially degrading the lignin and decrease the thickness of crystalline cells [48]. In addition, NMR MAS provides the structural knowledge about \(^{31}\)P MAS NMR and \(^{27}\)Al MAS NMR spectra of Al–B–P presented in Figures 4c,d, according to the experimental protocol standard of \(^{31}\)P (100) = 1/2 and \(^{27}\)Al (100) = 5/2 MAS NMR spectra. Resonances are shifted by about 150 ppm. Inorganic Al–B–P structure remains unaltered at the processing temperature below 100 °C with a pH of around 9 [49]. \(^{31}\)P MAS NMR and \(^{27}\)Al MAS NMR spectra indicate a significant quadrupole shift and exhibit one small peak around 115.59 ppm with another sharp peak at ~18.20 ppm. These suggest that the degree of aluminum polymerization could have increased. We can assign this \(Q_0^0\) (0Al), \(Q_1^0\) (1Al), \(Q_2^0\) (2Al), \(Q_3^0\) (3Al) and \(Q_4^0\) (4Al) of the structural Octahedral network, Figure 4e. Furthermore, this observation was confirmed by the \(^{31}\)P NMR, which shows that the increasing interaction of phosphorus connectivity at these spectra could provide the formation of the Al–P linkages. The \(^{31}\)P characteristic chemical signal presence of peaks near ~13 ppm, which was due to the double resonance [50]. Therefore, the schematic reaction between the Al–P compounds and the wood could be described as Figure 4e.
3.5. Mechanical and Physical Properties Analysis

The contact angle was measured on rectangles 20 × 20 × 5 mm³ (T × R × L), distilled water droplets of a 5 µL microsyringe of deionized water were placed onto the tangential, radial and longitudinal surfaces. As shown in Figure 5d, a water droplet was resting on the Al–B–P amphiprotic surfactant wood surface. Contrary to untreated or unmodified wood, a typical wetting behavior is observed immediate absorption and spreading of water inside the untreated wood sample after 4s, and images were taken at a specific frequency. As shown in Figure 5d.

The drop angle was measured 0, 30 and 60 s after the contact of the drop with the wood samples, and the average angles were calculated to determine the wettability. There was a significant difference between the contact angle of the untreated wood and the Al–B–P treated samples. The hydrophobicity of Al–B–P and the surface roughness of the wood is about 98°. Enhancement of the hydrophobicity of the sample CuSO₄ and the C₅H₁₁NO₂HCl was used as the indicator to characterize the wetting property of the treated, exhibiting the property of excellent super-hydrophobicity [51].

Figure 5a,b presents the results of the TG and differential thermogravimetric (DTG) curves of Al–B–P amphiprotic surfactant wood specimens subjected to heat in the range 50−800 °C are shown in Figures 5a,b. There is a total weight loss of 57.21% for the Al–B–P amphiprotic surfactant. Three distinct weight loss stages have accounted for 52.55%, 58.83% and 60.26%, respectively, which are assigned to the loss of free and moisture, cross-linked, and the process of thermal dehydrogenation [39].

The first region starts around 100 °C and corresponds to the dehydration of material leading to 4.16% of mass loss. The second region starts around 240 °C and corresponds to the degradation of cellulose and hemicellulose. Hemicellulose starts its decomposition around 200 °C and ends around 300 °C, while cellulose decomposed between 300 and 350 °C. The third region corresponds to the degradation of lignin and is between 350–800 °C. The entire bonds are broken, a large part of the material is pyrolyzed, and only the ashes remained [52],[53]. Nevertheless, we found the many factors that influence the DTG area of the composition of inorganic constituent distribution of the chains within a constituent, the number of inorganic compounds (boric phosphoric cupric content) in the DTG curves Figure 5b. The mass wood reduction was higher in the untreated specimens as compared to the Al–B–P treated specimens with thermal decomposition peak temperatures of 331 and 336 °C. The exposure time of wood exposed to field test makes it susceptible to the attack of decay fungi, resulting in the degradation of cell wall constituents, which consequently causes a loss of mechanical strength [52]. The MOR and MOE of wood changing trends found on the Fujian site are inconsistent,
which may be related to factors such as heat treatment temperature and climate [54], after impregnated wood specimens with inorganic Al–B–P mechanism performance can affect, the origin mechanical properties change. The H3PO4 phosphoric acid remaining in the Al–B–P amphiprotic surfactant may react with other wood constituent or deteriorate the wood constituent, which decreases the bonding strength of the wood specimens. In Figure 5c the results show that treated specimens MOR gradually increase by 110, 115 and 120 MPA. Figure 5c compared to untreated specimens gradually decrease by 90 and 80 MPA. Besides, the laboratory test provided a better durability value of the wood treated with Al–B–P amphiprotic surfactant than the soil contact test.

3.6. XPS Surface Chemical Analysis

To clarify the specific chemical bond between Al–B–P amphiprotic surfactant and wood specimens, the surface chemistry of Al–B–P and wood was performed by XPS. The results of the experiment have shown that carbon and oxygen are the main elements of a scan of the survey spectrum, as presented in Figure 6b. The survey spectrum provides the elemental surface composition of wood [55]. The carbon C 1s and oxygen O 1s binding energy spectra ranges of 286.4–565 eV and 286.6–573 eV for the treating specimen, indicating the four components were designated C1, C2, C3 and C4, based on their binding energy the C 1s peak corresponds to C–C and C=C aromatic stretch attributed to lignin. The characteristic Al 2p of the Al–B–P amphiprotic surfactant is present at 75.10 ev and B 2p peaks with the binding energy of 191.70 ev (Figure 6a,c). This value is because of the electronegativity of O 1s, C 1s and the presence of the amphiprotic surfactant in the Al–B–P network. Table S5 shows the division peak percentage content for wood modified and unmodified.
4. Conclusions

In this study, new preservative materials based on inorganic chemical combinations based on boron compounds (B), aluminum sulfate compounds (Al), phosphoric acid (P) and amphiprotic surfactant materials have been obtained and impregnated on wood.

The parameters result obtained from the RSM had demonstrated the excellent anti-corrosion properties of Al–B–P amphiprotic surfactant preservatives.

The investigation of mass loss demonstrated the fact that the weight loss of the treated samples with Al–B–P compounds was 4% greater than without Al–B–P compounds wood sample more than 45%.

The decay fungi resistance was tested by exposure to *Poria placenta*, *Coriolus versicolor* and monitored using the XRD, FTIR and SEM-EDX methods.

The fixation has a significant effect on the antifungal with more remarkable durability properties in an outdoor application or usage. The test showed that Al–B–P and amphiprotic surfactants have excellent hydrophobicity.

Further research is under progress and very promising for wood conservation based on inorganic compounds for all kinds of fungus organisms’ infections in the global wood trade.

Supplementary Materials: The following are available online at www.mdpi.com/2079-6412/10/2/108/s1, Table S1: Mass loss of control and impregnated sample exposed to wood *Poria. Placenta* and *Coriolus versicolor* fungi for 3 months according to ASTM D4445-10(2015) [1] procedure. (Al2(SO4)3—aluminum sulfate, Na2B4O7·10H2O—sodium tetraborate; CuSO4–cupric sulfate), Table S2: Lacks of fit tests, Table S3: Sequential model sum of squares, Table S4: Model summary statistics of $R^2$, Figure S1: Nitrogen adsorption-desorption isotherm and mesopore distribution of inorganic Al–B–P and amphiprotic surfactant material, Table S5: Peak, intensity, and atom percent of different element.

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**Abbreviations**

- RSM: response surface methodology
- \(\text{Al}_2(\text{SO}_4)_3\): aluminum sulphate
- \(\text{CuSO}_4\): copper sulphate
- \(\text{Na}_2\text{B}_4\text{O}_7\): sodium tetraborate
- \(\text{H}_3\text{PO}_4\): phosphoric acid
- \(\text{H}_3\text{BO}_3\): boric acid
- CAA: copper azole alkaline
- CQC: copper quaternary creosote
- ACQ: alkaline copper quaternary
- \(\text{C}_9\text{H}_{11}\text{NO}_2\text{HCl}\): amphiprotic surfactant
- FTIR: Fourier Transform infrared spectroscopy
- XRD: X-ray diffraction
- MOE: modulus of elasticity
- MOR: modulus of rupture
- SEM: scanning electron microscopy
- EDS: energy-dispersive spectroscopy
- TGA: Thermogravimetric analysis
- DTG: differential thermogravimetric
- XPS: X-ray photoelectron spectroscopy
- NMR: nuclear magnetic resonance
- BET: Brunauer–Emmett–Teller equation
- ANOVA: analysis of variance
- MLR: Loss mass rate

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