Review Article

Preparation and characterization of sodium silicate impregnated Chinese fir wood with high strength, water resistance, flame retardant and smoke suppression

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\textbf{Abstract}

To improve the properties and added value of Chinese fir wood, sodium silicate-modified Chinese fir wood (SSMCF) was prepared by respiratory impregnation method. Phenol formaldehyde oligomer-modified Chinese fir wood (PFOMCF) as control sample, the impregnation and reinforcement effects, water resistance of PFOMCF and SSMCF were compared. The results showed that the weight percentage gain, density growth rate, bending strength, compressive strength, and dimensional stability of SSMCF were clearly higher than those of PFOMCF, and the SSMCF showed a lower water absorption rate within 60 h. The impregnation and reinforcement effects, for SSMCF were better than those for PFOMCF. FT-IR, XRD, CONE, and TGA examinations were used to analyze the chemical structure, crystalline structure, flame retardancy, and heat resistance of these modified woods. The results indicated that Si—O—Si chemical bonding with high bond energy was formed in SSMCF, and there are possessed more hydrogen bonds in SSMCF than PFOMCF and that Si—O—Si chemical bonding with high bond energy was formed. Meanwhile, the weakened degree of the diffraction peak of SSMCF was much less than that of PFOMCF. These results explained the better mechanical properties and water resistance of SSMCF. Compared with PFOMCF, SSMCF had lower heat release rate (HRR), peak-HRR, mean-HRR, total heat release, smoke production rate, and total smoke production, and showed higher thermal decomposition temperature and residual rate. Inorganic sodium silicate was shown to be a better flame retardant, while SSMCF had good smoke suppression effects, thermal stability, and safety performance in the case of fire.

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1. Introduction

Chinese fir (Cunninghamia lanceolata) is one of the most important plantation tree species in China [1]. Its planting area accounts for ~25% of the total Chinese plantation area because of its rapid growth, straight texture, few pests and diseases, and easy processing [2,3]. However, Chinese fir wood natural biological macromolecule has some shortcomings, such as low density, short fibers, high pH value, severe cracking and deformation, high moisture content, low strength, poor stiffness, and large chord-radial shrinkage ratio. These shortcomings can easily cause the deformation and cracking of Chinese fir products in use, as well as greatly limit its applications in furniture, floors, wood structures, and other building materials [4]. Therefore, it is increasingly important to strengthen and dimensionally stabilize this wood. Injecting organic resin or inorganic material into Chinese fir wood and curing it can improve its strength, corrosion resistance, wear resistance, water resistance, weather resistance, dimensional stability, and subsequent processing [5,6]. Impregnating reinforced wood is a method of immersing modifier into wood cells by using wood as matrix and infiltration method. On one hand, sediments are formed in the lumen or even the cell walls of wood cell, and subsequently play a filling role. On the other hand, chemical bonds can be formed between the modifiers and cell wall substances, thus endow the wood with new properties. After impregnation modification, the physical and mechanical properties of the wood have been significantly improved [7], such that it can replace high-quality natural forest trees and be used as structural materials, such as in brackets, trusses, carriage floors, and container boards, which significantly improve the wood’s applications and value.

Previous studies have focused on impregnation modification of Chinese fir wood with organic resin, especially the aldehyde resin. Qian et al. [8] impregnated fast-growing Chinese fir wood with urea-formaldehyde resin and Huang et al. [9] impregnated Chinese fir wood with water-soluble low molecular weight phenolic resin, which effectively improved the strength and dimensional stability of Chinese fir wood. Aldehyde resins not only play a filling role in wood modification but also react with the wood’s active functional groups to form a new stable structure, improving the wood’s corrosion resistance, water resistance, dimensional stability, and physical and mechanical properties [10,11]. However, impregnation of organic resin has a negative impact on wood finishing and bonding properties and the price of these organic chemicals is high. More unacceptable in this impregnation process is the release of some toxic gases, which has threats to the environment and human safety [12]. In contrast, impregnation with inorganic substances has no adverse effect on wood finishing and gluing, and it is inexpensive, natural, and nontoxic [13], meanwhile the visual environmental characteristics of wood are retained to a great extent. Moreover, inorganic modifiers have the advantages of low cost and being environmentally-friendly, and inorganic-modified Chinese fir wood showed improved mechanical strength, anti-corrosion, and flame retardancy [14,15]. Inorganic modified Chinese fir wood has wide application prospects in furniture manufacturing and interior decoration, which are in direct contact with people. Therefore, inorganic-reinforced Chinese fir wood has gradually become a focus of current research.

The respiratory impregnation is a method that simulates the biological respiratory process, alternating positive and negative pressure circulation. Through negative pressure treatment of the wood, the internal pores and cell cavities are fully compressed. When the negative pressure is converted to positive pressure, the pores and cavities are fully opened, forming channels for the entry of modifiers and significantly improving impregnation. Hence, in this work, the modification of Chinese fir wood was carried out by respiratory impregnation method. Phenol formaldehyde oligomer is the most commonly used and widely studied organic modifier, and sodium silicate is an inorganic modifier with environmental protection, flame retardancy, and low cost. The phenol formaldehyde oligomer and sodium silicate were therefore used to compare the differences between inorganic and organic impregnation. The differences of the impregnation and reinforcement effects and water resistance between phenol formaldehyde oligomer-modifier Chinese fir wood (PFOMCF) and sodium silicate-modified Chinese fir wood (SSMCF) were analyzed by comparing its weight percentage gain, density growth ratio, blending strength, compressive strength, hardness (end face, diameter, and chord face), and water absorption rate. Fourier-transform-infrared and X-ray diffraction, cone calorimetric analysis, and thermogravimetric analysis (FT-IR, XRD, CONE, and TGA, respectively) were used to test and analyze the chemical structure, crystalline structure, flame retardancy, and heat resistance of modified wood. The purpose was to improve the wood properties and resulting product, providing added value to Chinese fir plantations and expanding their scope of application.
2. Materials and methods

2.1. Materials

Chinese fir wood used in this experiment was cut from Yongzhou, Hunan Province, China. The air-dry density of Chinese fir wood was 0.38 g/cm³ at 12% moisture content. Test specimens were prepared according to the Chinese standard GB/T1929-2009. Six samples of 20 × 20 × 20 mm (tangential × radial × longitudinal) were prepared for weight percentage gain and density tests. Twelve samples of 300 × 20 × 20 mm were produced for bending strength testing and 12 samples of 50 × 50 × 70 mm produced for compressive strength testing. Specimens used had no knots, cracks, decay, oblique texture, or other defects. Sodium silicate (44.5%, 3.4 modulus) was purchased from Hunan Hetang Chemical Co., Ltd. (Changsha, Hunan, China). Formaldehyde (37.0% aqueous solution, AR), phenol (AR), and sodium hydroxide (AR) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Ultrapure water was prepared using a ZWL-PA1-20 ultrapure water system (Hunan Zhongwo Water Environmental Protection Technology Co., Ltd., Hunan, China).

2.2. Preparation of phenol formaldehyde oligomer [16]

Phenol formaldehyde oligomer (PFO) was prepared with a molar ratio of phenol/formaldehyde/sodium hydroxide as 1/3.5/1. Formaldehyde and phenol were accurately weighed and poured into four bottles with an agitator and placed in a water bath adjusted to 30 °C. The sodium hydroxide was mixed with ultrapure water to form a 50 wt-% sodium hydroxide aqueous solution, which was then slowly added into four bottles within 30 min. After 40 h of reaction, the PFO was discharged. The main components of the PFO were 2,4-dihydroxymethyl phenol, 2,6-dihydroxyphenol, and 2,4,6-trihydroxyphenol (Fig. 1), with the solid content at 43.5% and viscosity of 52.2 mPa/s.

2.3. Preparation of modified Chinese fir wood

Chinese fir wood specimens for density, hardness, bending, and compression testing were selected and dried in an electric heat blast-drying chamber at 60 °C until the moisture content ranged from 10 to 12%. The specimens were impregnated into an impregnation tank by the respiratory impregnation method, the principle is illustrated in Fig. 2. First, the impregnating tank was evacuated to −0.1 MPa and pressure was held for 10 min. Organic sodium silicate or inorganic PFO modifiers solution (20 wt%) was sucked into the impregnating tank by negative pressure, followed by the release of the pressure. Second, the impregnation system was pressurized by an air compressor to 0.5 MPa for 20 min. Afterward, the organic or inorganic modifiers was unloaded and discharged from the impregnating tank. Four cycles with alternating positive-negative pressure were performed and the total immersion time was 2 h. After immersion, the pressure was relieved, the impregnated wood was removed, and the surfaces were carefully washed. Finally, the samples were dried at 120 °C for 6 h to obtain the sodium silicate-modified (SSMCF) or phenol formaldehyde oligomer-modified Chinese fir wood (PFOMCF).

2.4. Properties and characterization

2.4.1. Weight percentage gain

The oven-dried weight of Chinese fir specimens before and after impregnation was recorded as \( m_0 \) and \( m_1 \), respectively. The weight percentage gain (WPG) was assessed using Eq. (1).

\[
WPG = \frac{(m_1 - m_0)}{m_0} \times 100\%
\]  

(1)

2.4.2. Density growth ratio

Referring to GB/T 1933–2009, Wood density measurement method, for testing, the wood was dried to absolute dryness in a blast oven at 103 ± 1 °C and recorded as \( m_0 \). The longitudinal \( L_0 \), the radial \( R_0 \), and the tangential \( T_0 \) were assessed using a vernier caliper. The density of the specimen before impregnation was calculated as \( \rho_0 = \frac{m_0}{V_{\text{total}}} = \frac{m_0}{L_0 \times R_0 \times T_0} \). The immersion modification of Chinese fir specimens was assessed as \( m_f \) and the longitudinal \( L_1 \), radial \( R_1 \), and tangential \( T_1 \) measured. In addition, the density of the specimens after immersion was calculated as \( \rho_1 = \frac{m_f}{V_{\text{total}}} = \frac{m_f}{L_1 \times R_1 \times T_1} \). The density growth ratio (\( \Delta \rho \)) was assessed using Eq. (2).

\[
\Delta \rho = \frac{(\rho_1 - \rho_0)}{\rho_0}
\]  

(2)

2.4.3. Mechanical properties test

Wood bending strength was tested in accordance with the Chinese national standard GB/T 1936–2009. The dimensions during the bending strength test were 300 × 20 × 20 mm. The load was applied in the tangential direction of the samples, with a distance of 240 mm between two fulcrums. Twelve samples were tested in each experimental condition for both treated and control samples.

Compressive strength was tested according to the Chinese national standard GB/T 1935–2009. Specimens with a size of 20 × 20 × 30 mm were loaded at a constant loading rate and the maximum compressive load under which the sample stood for more than 90 s without collapse recorded.

The hardness values of the end face, radial face, and bastard face were measured with reference to Chinese national standard GB/T 1941–2009. Each specimen with the size of 70 × 50 × 50 mm was tested once at two end faces, two radial faces, and two bastard faces. The hemispherical steel indenter was pressed into the test surface at a uniform rate of 3–6 mm/min until an indent depth of 5.64 mm, with the load reading accurate to 10 N.

2.4.4. Water absorption rate

The water absorption coefficient (WAR) was tested according to the Chinese national standard GB/T 1934.1–2009. Dry specimens were immersed in water at 20 ± 5 °C. Specimens were taken out every 24 h and weighed after surface water was removed using a filter paper. The detection period was 60 h, with the WAR calculated using Eq. (3).

\[
WAR = \frac{(W_2 - W_1)}{W_1} \times 100\%
\]  

(3)
where $W_1$ is the mass of oven-dried wood sample before impregnation and $W_2$ the mass of oven-dried wood sample after impregnation.

2.4.5. Fourier transform infrared spectroscopy analysis
Chinese fir wood samples were ground and crushed into small particles in a mortar with a diameter of $<0.074$ mm (200-mesh). An IRAffinity-1 Fourier transform infrared (FTIR) spectrometer (Shimadzu Corp., Kyoto, Japan.) was used to test the particles. Samples were ground to powders with KBr in a weight ratio of 1/100. FTIR curves of samples were obtained in the range of 400–4000 cm$^{-1}$.

2.4.6. Scanning electron microscope analysis
The end and diametral morphology of Chinese fir wood were determined using a QUANTA 200 (FEI) scanning electron microscope (SEM) operated at 20 kV. The samples were mounted on circular aluminum stubs with a double-sided adhesive tape and sputtered with a thin layer of gold before the analysis.

2.4.7. X-ray diffraction analysis
Samples were completely dried in a vacuum oven at 50 $^\circ$C for 48 h to remove remaining moisture. The crystallinity index of the samples was measured using an X-ray diffractometer (XD-2, Purkinje General Instrument Co., Ltd., Beijing, China) with a Cu target at 36 kV and 20 mA. The samples were tested in the angular range of $2\theta = 5–40^\circ$ with a scanning rate of 4/$^\circ$/min. The empirical crystallization index Crl, proposed by Segal et al. [17],

The calculation used to determine this parameter expressed as Eq. (4).

$$Crl = \frac{I_{002} - I_{amorph}}{I_{002}} \times 100\%$$ (4)

where $I_{002}$ is the maximum diffraction peak intensity of the main crystallization peak 002 and $I_{amorph}$ the diffraction intensity of 2$\theta$ angles to 18$^\circ$.

2.4.8. Cone calorimetric
CONE tests of the Chinese fir wood were performed on a cone calorimeter (FTT; Stanton Redcroft Inc., East Grinstead, UK) following ISO5660-1. For each test, 100 x 10 x 100 mm (T x R x L) specimens were covered with aluminum foil, except the upper surface, which was placed into a specific steel frame, the steel frame mounted horizontally on the loader, and then exposed to heat radiation of 50 kW/m$^2$. This heat radiation corresponded to a temperature of 780 $^\circ$C on the upper test sample surface.

2.4.9. Thermo gravimetric analysis
TGA measurements of the impregnating modifiers and Chinese fir wood samples were conducted with 209 F3 TGA (Netzsch Instruments, Inc., Burlington, MA, USA). Removal of moisture content from phenol formaldehyde oligomer and sodium silicate solution by freeze-drying, and grind the dry modifiers into powder for testing. Approximately 5 mg of dried sample were placed in a platinum crucible and heated from 25 to 600 $^\circ$C at the rate of 10 $^\circ$C/min, with a nitrogen gas flow rate

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**Fig. 1** – Reaction principle of phenol formaldehyde oligomer.

**Fig. 2** – Respiratory impregnation modification process of Chinese fir wood.
at 30 mL/min. TGA and derivative thermogravimetric analysis (DTG) data of each sample were obtained.

2.4.10. Statistical analysis
Data were statistically evaluated using the statistical software package Minitab Version 15 and reported as the mean value ± standard deviation of replicates. A single-factor analysis of variance was conducted to identify significant differences among mean values according to least significant difference criteria with a 95% confidence level (p < 0.05).

3. Results and discussion

3.1. Comparison of impregnation effects

The weight percentage gain and density growth ratio of impregnated Chinese fir wood directly reflected the impregnation effects on the wood. Therefore, the effects of organic and inorganic modifiers on the impregnation of the wood were evaluated by comparing the weight percentage gain and density growth ratios of PFOMCF and SSMCF. The results are shown in Fig. 3.

The weight percentage gain and density growth ratio of SSMCF were 52.20 ± 1.88 and 53.44 ± 1.59% while those of PFOMCF were 44.45 ± 1.31 and 45.14 ± 1.28%, respectively. The weight percentage gain and density growth ratio of SSMCF were clearly higher than those of PFOMCF, which indicated that the impregnation effect of SSMCF was better than that of PFOMCF. The experimental results showed that the densities of 3.4 M sodium silicate solution and phenol formaldehyde oligomer were 1.42 and 1.20 g/cm³, respectively. The solid content of the two modifiers was 44.5 and 43.5%, indicating that the concentrations of the two modifiers were basically the same. This also indicated that the density of inorganic sodium silicate-soaked in Chinese fir wood was higher than that with organic phenol formaldehyde oligomer, which resulted in the higher weight percentage gain and density increase growth ratio of SSMCF. In addition, the molecular weight of sodium silicate was 122, while that of hydroxymethyl, dihydroxymethyl, and trihydroxymethyl phenols in phenol formaldehyde oligomers were 124, 154, and 184, respectively. The lower molecular weight of sodium silicate made it more easily be penetrated into the wood's pores than the phenol formaldehyde oligomer.

3.2. Comparison of strengthen effects

There are some defects in Chinese fir wood, including loose material and low strength [18]. Impregnating wood with a filler is an effective method of improving its mechanical properties. Therefore, the bending and compressive strengths and hardness are the most significant parameters for the utilization of Chinese fir wood. To compare the strengthening effects of this wood modified by inorganic sodium silicate and organic phenol formaldehyde oligomer, the bending strength, compressive strength, and hardness of SSMCF and PFOMCF were tested (Figs. 4 and 5).

The bending and compressive strengths of unmodified Chinese fir wood were 46.50 ± 2.58 and 22.54 ± 1.97 MPa,
respectively (Fig. 4). After impregnation modification, the bending and compressive strengths of SSMCF and PFOMCF were significantly improved. These results showed that impregnation modification effectively improved the wood strength. This was attributed to the introduction of sodium silicate and phenol formaldehyde oligomer into the wood, which solidified in the wood cell cavities and cell wall spaces to form a hard, solid structure [19]. However, there were some differences in the strengthening effects between SSMCF and PFOMCF. The bending and compressive strengths of SSMCF were higher than those of PFOMCF, which was directly related to the impregnation effect of the two modifiers. The better the impregnation effect, the more significant the strength improvement. At the same time, it was indicated that the inorganic impregnation modification of sodium silicate had a better strengthening effect than modification with phenol formaldehyde oligomer.

Comparison with unmodified Chinese fir wood showed that the end, radial, and bastard face hardness of SSMCF and PFOMCF were significantly improved (Fig. 5). The three-surface hardness of SSMCF was higher than that of PFOMCF, which showed that inorganic impregnation with sodium silicate was better than organic impregnation with phenol formaldehyde oligomer for reinforcement of this wood.

3.3. Comparison of water resistance

There are many pores in the wood structure, which include a large number of hydrophilic groups. Therefore, wood hygroscopicity occurs in a wet environment, which leads to deformation, cracking, and other defects. The effects of inorganic and organic impregnation modification on the water resistance of this wood were verified by examining the water absorption rate of unmodified Chinese fir wood, PFOMCF, and SSMCF over 60 h.

As can be seen from Fig. 6, the water absorption rate of PFOMCF and SSMCF was lower than that of unmodified wood within the 60 h test time. The results showed that impregnation with silicate and phenol formaldehyde oligomer effectively improved the water resistance of wood, thus improving its dimensional stability. This can be owed to number reasons: (i) most of the wood voids were filled by sodium silicate and phenol formaldehyde oligomer after the impregnation, which reduced the water storage area; (ii) the modifier immersed in the wood could react with hydroxyl groups in the wood components to form stable chemical bonds that effectively reduced the number of hydrophilic groups. In addition, the water absorption rate of SSMCF was lower than that of PFOMCF within 60 h, which was attributed to the fact that the weight percentage gain and density growth ratio of SSMCF was greater than that of PFOMCF. This meant that more sodium silicate was introduced into the wood interior, resulting in more pores being filled and more chemical bonds being formed. This not only reduced the water storage space in the wood, but also reduced the amount of water absorbent groups. These two effects led to a better water resistance and higher dimensional stability of SSMCF.

3.4. Comparison of chemical structure

Wood is a natural complex composed mainly of cellulose, hemicellulose, and lignin, which contain a large number of reactive groups, such as hydroxyl groups [20]. Also, silicate ions, SiO\textsuperscript{2-}, and the molecular chains of phenol formaldehyde oligomer have greater numbers of reactive hydroxymethyl phenol groups. Therefore, sodium silicate and phenol formaldehyde oligomer can form hydrogen bonds and some chemical bonds with hydroxyl groups in wood. To verify the chemical bonding between impregnating modifiers and this wood, FT-IR was used to compare unmodified wood with PFOMCF and SSMCF (Fig. 7).

In comparison with unmodified Chinese fir wood, the vibration peak bands of hydroxyl absorption of PFOMCF and SSMCF were widened and substantially strengthened in the range of 3000–3600 cm\textsuperscript{-1} (Fig. 7). The results indicated that
the content of free hydroxyl groups decreased and the associative hydroxyl groups increased in the wood. In addition, the absorption peak strengths of PFOMCF and SSMCF at other locations also increased. For SSMCF, vibration peaks of Si—O—Si appeared at 1042 and 464 cm\(^{-1}\) and the vibration absorption peak of —OH stretching near 3300 and 1635 cm\(^{-1}\) increased [21]. This indicated that silicate was immersed in the wood and chemical bonds was formed with wood hydroxyl groups, resulting in an increase in the number of associated hydroxyls. Silicates were reactive fillers rather than simple physical fillers, this caused the sealing or bonding of hydroxyl groups in the wood, and greatly improved the mechanical properties and water resistance of SSMCF. For PFOMCF, the strength of —C=C— stretching vibration peak on benzene ring was near 1615 cm\(^{-1}\), the methylene bending vibration peak near 1390 cm\(^{-1}\), and C—O stretching vibration peak on —CH\(_2\)OH within 1080–1140 cm\(^{-1}\) were significantly enhanced. It was concluded that phenol formaldehyde oligomer was better infiltrated into the wood and formed certain ether bonds with hydroxyl groups in the wood. However, the bond energy of ether bonds was much lower than that of Si—O—Si bonds, leading to the impregnation effect of PFOMCF was not as good as SSMCF. Therefore, the mechanical properties and water resistance of PFOMCF were less improved compared with the SSMCF, i.e., the silicates were more effective in strengthening the wood and enhance the water resistance of wood.

### 3.5. Comparison of microscopic morphology

In order to compare the effects of inorganic and organic impregnation modification on the internal microscopic morphology of Chinese fir wood, SEM were used to test the unmodified wood, PFOMCF, and SSMCF. The results are shown in Fig. 8A and B represent the longitudinal and transverse morphologies of unmodified Chinese fir wood, C and D represent the longitudinal and transverse morphologies of PFOMCF, and E and F represent the longitudinal and transverse morphologies of SSMCF, respectively.

In Fig. 8, the transverse section of unreinforced Chinese fir wood rough, and the cell wall was broken. The longitudinal tracheid surface of the unreinforced Chinese fir wood was smooth, and the pits on the inner wall of tracheid could be clearly seen. After impregnation modification, the solid filler could be seen in the longitudinal of PFOMCF and SSMCF, and the surface roughness was weakened because of the filler in the transverse. It was due to that the alternate infiltration of impregnating modifiers into the pore of Chinese fir wood dur-

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**Fig. 8** – Internal microscopic morphology of unmodified Chinese fir wood, PFOMCF and SSMCF.

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**Fig. 9** – XRD diffraction patterns of unmodified Chinese fir wood, PFOMCF and SSMCF.
ing the impregnation process of negative–positive pressure cycle. After drying, modifiers were immobilized in tracheid and intercellular spaces of Chinese fir wood. Although the attached phenolic resin solid can be seen longitudinally in the PFOMCF, the content of the phenolic resin solid was less, resulting in uncovered pits. There were also some phenolic resin solid fillings on the transverse, but the surface was still rough. The SSMCF was longitudinally attached to a large number of sodium silicate solid, and pits were hardly observed. The transverse was also filled with sodium silicate solid, and the rough pores of Chinese fir wood were filled. SEM analysis results further proved that the impregnation effect of inorganic sodium silicate on Chinese fir wood was better than that of organic phenol formaldehyde oligomer. It was also explained that the mechanical strength and water resistance of SSMCF were better than those of PFOMCF.

3.6. Comparison of crystal structure

Cellulose is a very important component in wood chemical composition and cellulose molecular chains are aligned and ordered to produce crystalline regions [22]. The crystallinity of cellulose is closely related to the physical, mechanical, and chemical properties of wood. Therefore, to study the effects of inorganic and organic impregnation modification on the crystalline structure of Chinese fir wood, XRD recuts were used to test the unmodified wood, PFOMCF, and SSMCF. The results are presented in Fig. 9.

It can be seen from Fig. 9 that the diffraction peaks of wood cellulose at (101), (002), and (040) crystalline planes occurred in unmodified Chinese fir wood when 2θ was 16, 22.5, and 35°, respectively [23]. XRD peaks of wood modified by silicate and phenol formaldehyde oligomer did not shift, indicating that the unit cell types of modified Chinese fir wood did not change. However, it was clearly observed that the intensity of crystallization diffraction peaks of these two kinds of wood decreased to various degrees. The reasons for this change were because, on the one hand, impregnating modifiers were immersed into the noncrystalline zone of the wood, which produced a certain swelling effect in the process of infiltration, wetting, diffusion, adsorption, and curing of wood cellulose. This series of processes disturbed the well-ordered microfibrils in the crystallization zone and reduced the relative crystallinity. On the other hand, the impregnating modifiers infiltrated into the cellulose molecular chain and reacted with the wood hydroxyl groups, which destroyed cellulose hydrogen bonds and weakened intermolecular interactions between cellulose molecular chains. However, the reduction of the diffraction peak of SSMCF was much less than that of PFOMCF, which showed that phenol formaldehyde oligomer decreased wood crystallinity to a greater extent. The mechanical strength of the wood was seriously affected by decreased crystallinity, which confirmed that the blending strength, compressive strength, and hardness of PFOMCF were lower than those of SSMCF. Meanwhile, the decreased crystallinity made the molecular chains of cellulose looser and water entrance easier, which also led to a higher water absorption for PFOMCF compared with SSMCF.

3.7. Comparisons of flame retardant and smoke suppression

Flame retardancy and smoke suppression are important characteristics in ensuring the safe use of wood products. Especially in the case of fire, wood products with flame retardancy and smoke suppression characteristics provide more time for rescue and effectively ensure personal and property safety [24]. The effects of organic and inorganic impregnation modification on the flame retardancy and smoke suppression properties of Chinese fir wood were evaluated in unmodified wood, PFOMCF, and SSMCF by cone calorimetry. The curves of heat release rate (HRR), total heat release (THR), smoke production rate (SPR), and total smoke production (TSP) are presented in Fig. 10.

Fig. 10(a) shows that there were two heat release peaks in unmodified wood, PFOMCF, and SSMCF. The first peak corresponded to the rapid exothermic reaction of wood during decomposition combustion under thermal radiation. At the same time, a carbonized layer formed on the wood surface, which acted as a heat and oxygen insulator. This led to a gentle trough in the HRR curves after the first heat release peak. However, with prolonged combustion time, the wood in the carbonized layer continued to decompose under thermal radiation and high temperature and produced gas products, which burst and cracked the carbonized layer, resulting in rapid decomposition and flammable gas release from the internal wood, thus forming the second combustion heat release peak [25]. Fig. 10(a) and (b) and Table 1 show that the peak heat release rate (peak-HRR), mean heat release rate (mean-HRR), and THR of PFOMCF and SSMCF were lower than those of unmodified wood. This indicated that sodium silicate and phenol formaldehyde oligomer immersion into this wood effectively reduced the wood’s HRR and THR. This change was due to impregnating modifiers attached to the wood interior, which helped isolate oxygen and decreased heat transfer, thus the modifiers acted as a flame-retardant role to protect the wood. Compared with PFOMCF, SSMCF had a lower HRR, peak-HRR, mean-HRR, and THR. On one hand, the flame retardant and smoke suppression performance of inorganic sodium silicate was better than that of organic resin [26]. On the other hand, the weight percentage gain of SSMCF was greater than that of PFOMCF and more flame retardant modifier was thus immersed into the wood.

Smoke and toxic gases in fires were more harmful to human life than fire and heat. Smoke poisoning reduces people’s vision and hinders the evacuation and escape of people in a fire, eventually leading to increased suffocation probability. In Fig. 10(c), (d) and Table 1, the mean-SRP and TSP during the whole combustion time of PFOMCF and SSMCF were significantly lower than those of the unmodified wood. This was because the inorganic sodium silicate and organic phenol formaldehyde oligomer effectively prevented wood from burning, thus reducing the smoke release rate and total smoke production. In addition, the mean-SRP and TSP of SSMCF was lower than those of PFOMCF, which was due to the better flame retardancy and smoke suppression of inorganic sodium silicate, as well as the larger weight percentage gain of SSMCF.
3.8. Comparisons of heat resistance

Under normal conditions, the heat resistance of the inorganic modifier was better than that of the organic modifier. To investigate the effects of the two modifiers on the heat resistance of modified wood, thermogravimetric (TGA) tests were performed on the PFOMCF and SSMCF.

The TGA curves in Fig. 11(b) showed that the thermal decomposition rates of PFOMCF and SSMCF were significantly lower than those of unmodified wood at 300 °C. The thermal decomposition residues of PFOMCF and SSMCF increased to 48.82 and 43.51%, respectively. The results showed that the heat resistance of modified wood was significantly improved after impregnation. However, the initial decomposition temperature and decomposition rates of PFOMCF and SSMCF were slightly lower than those of unmodified wood below 300 °C. At the same time, the DTG curves showed that the maximum decomposition rate temperature of unmodified fir was higher than that of PFOMCF and SSMCF. This was attributed to the observation that the crystalline structure of modified wood was damaged to a certain extent after silicate was introduced into the wood, leading to the decomposition of the wood more easily with increased heating [27,28]. Comparing the two kinds of impregnated wood in TG and DTG curves, the initial decomposition temperature, maximum decomposition rate temperature, and decomposition residual rate of SSMCF were higher than those of PFOMCF. The results demonstrated that the thermal resistance of wood modified by silicate inorganic impregnation was better than that of phenol formaldehyde oligomer impregnation. The reason for this difference was that sodium silicate had a better thermal stability than phenol formaldehyde oligomer. From Fig. 11(a), the decomposition residues of sodium silicate and phenolic oligomers were 72.69 and 50.12%, respectively. When a modifier with good heat resistance was immersed in this wood, the heat resistance was improved. Therefore, silicates play an important role in improving the safety of Chinese fir products in case of fire.

Table 1 – Heat parameter date of unmodified Chinese fir wood, PFOMCF and SSMCF.

<table>
<thead>
<tr>
<th>Name</th>
<th>Peak-HRR (kW/m²)</th>
<th>Mean-HRR (kW/m²)</th>
<th>THR (MJ/m²)</th>
<th>Mean-SPR (m²/s)</th>
<th>TSP (m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unmodified</td>
<td>230.0187</td>
<td>32.1838</td>
<td>60.2961</td>
<td>0.006313</td>
<td>3.7821</td>
</tr>
<tr>
<td>PFOMCF</td>
<td>131.2311</td>
<td>19.0316</td>
<td>39.1132</td>
<td>0.003285</td>
<td>1.5916</td>
</tr>
<tr>
<td>SSMCF</td>
<td>96.1476</td>
<td>14.2745</td>
<td>30.4448</td>
<td>0.001173</td>
<td>0.7873</td>
</tr>
</tbody>
</table>

Fig. 10 – Heat release and smoke formation curves of unmodified Chinese fir wood, PFOMCF and SSMCF.
4. Conclusions

The effects of organic and inorganic impregnation on the properties of Chinese fir wood were compared by modifying the wood with phenol formaldehyde oligomer and sodium silicate using the respiratory impregnation method, forming PFOMCF and SSMCF, respectively. The weight percentage gain, density growth ratio, blending strength, compressive strength, hardness (end face, diameter, and chord face), water absorption rate, chemical structure, crystalline structure, flame retardancy, and heat resistance of PFOMCF and SSMCF were analyzed. The results showed that the impregnation and reinforcement effects and dimensional stability of SSMCF were better than those of PFOMCF. The results of FT-IR and XRD analyses indicated that SSMCF had more hydrogen bonds than PFOMCF and that high bond energy Si—O—Si bonds were formed. Meanwhile, the weaker degree of the diffraction peak of SSMCF was much less than that of PFOMCF. These two observations explained that the mechanical properties and water resistance of SSMCF were better than PFOMCF. CONE and TGA results showed that HRR, peak-HRR, mean-HRR, THR, SPR, and TSP of SSMCF were lower than those of PFOMCF, but the thermal decomposition temperature and residual rate were higher. This illustrated that inorganic sodium silicate was a better flame retardant and that SSMCF had a smoke suppression effect as well as better thermal stability and safety performance in case of fire.

Conflicts of interest

The authors declare no conflicts of interest.

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REFERENCES


