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Article

Preparation and Characterization of Phenolic Prepolymer Impregnated Chinese Fir by Cyclic Increasing-Pressure Method with Green and Efficient

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Abstract: The Chinese fir wood was impregnated using a cyclic increasing-pressure method (CIPM) with phenolic prepolymers as the impregnating modifier. Unmodified Chinese fir and progressive increasing-pressure method (PIPM) impregnated Chinese fir were used as reference samples and were compared and analyzed. The product's chemical structure, internal morphology, crystal structure, and heat resistance were characterized. The transversal and longitudinal sections showed better filling effects, so that it bore greater external loading and reduced the water storage space. CIPM infused more phenolic prepolymer into the Chinese fir. Not only producing more physical filling but also forming more hydrogen bond associations and chemical bond combinations. Compared with PIPM and unmodified Chinese fir, the CIPM impregnated Chinese fir had better mechanical strength and water resistance. The cellulose chains in CIPM impregnated Chinese fir were more closely linked and their crystallinity were clearly improved. Changes in internal morphology and crystal structure explained the reason why the mechanical properties and water resistance of CIPM impregnated Chinese fir were improved significantly. This Chinese fir had lower thermal decomposition rates, higher decomposition residual rates, and smaller combustion flames, which confirmed that it possessed improved heat and fire resistance.

Keywords: Chinese fir; phenolic prepolymer; cyclic increasing pressure method; chemical structure; crystalline structure; heat resistance

1 Introduction

As a kind of natural renewable resource, wood is a nontoxic, accessible and low-cost biological material. Since ancient times, humans have used wood for its intrinsic properties, with specific species or portions of trees used for optimal performance [1,2]. Chinese fir, as an important coniferous timber species peculiar to China, plays an important role in Chinese national economy and in ecological and environmental construction [3]. Chinese fir is largely distributed in south China, with a wide field distribution and strong adaptability, and it occupies an extremely important position in China's wood production and forest stock volume. In addition, dry Chinese fir wood is perfectly straight, large diameter, not deformed, light in density, beautiful texture, easily processed, pleasant in fragrance, and has a short maturity period and good processing performance. It is widely used for housing, furniture, and shipbuilding construction [4,5]. However, there are also a series of disadvantages related to construction applications of Chinese fir, mainly including its soft material, low strength, low impact toughness, easy decay, easy combustion, and drying shrinkage as well as being subject to wet-swelling, and the latter which can lead to unstable size and moth damage that restricts its application range and utilization efficiency [6,7]. Thus, there is an urgent need to improve Chinese fir properties with the goal of expanding its utilization [8]. The purpose of chemical modification is to make full use of the characteristics of Chinese fir, to reduce and eliminate its disadvantages, and to increase the product's value as well as safety for the use of Chinese fir as a kind of building material [9,10].

In recent years, plenty of researchers have entered into the field of Chinese fir modification and achieved much advancement. Song et al. [11] reduced the hydrophilicity of wood by water heat treatment, so that the wood surface formed a dense protective layer of carbon-rich additives after low load (5% wt%) water vacuum impregnation. The results showed that the total heat release rate of wood obtained by this method was reduced by 32%, the flame spread rate was reduced, the average carbon dioxide production and the total mass loss were reduced by 12% and 10% respectively, which significantly slowed down the pyrolysis reaction of wood. This research was of great significance for the development of value-added wood products with high fire safety, especially fast-growing wood with relatively low cost. Okon et al. [12] studied the effect of metal bath heat treatment (MBHT) on corrosion resistance and dimensional stability of Chinese fir. Anti-shrink efficiency (ASE) results showed that MBHT promoted the dimensional stability of both kinds of wood, indicating that the samples after MBHT had strong corrosion resistance. Wang et al. [13] modified Chinese fir with low molecular weight phenol melamine urea formaldehyde (PMUF) resin, boron compounds (BB), and PMUF/BB mixtures (PMUF-BB), and then carried out fire resistance test. The results showed that PMUF resin reduced the altered wood's heat release rate while increasing its total heat release and PMUF resin improved the wood's thermal stability. Yue et al. [14] impregnated Chinese fir with BPF resin, and the result of high frequency heating have shown that high frequency heating was an efficient hot-pressing process with higher heating rate than ordinary hot pressing. Compared with the unmodified samples, the BPF modified samples were obviously improved in the mechanical properties and fire performance. The higher the resin retention is, the better the performance of BPF modified samples is. From this conclusion, in addition to the need for good drugs, efficient methods are also important.

According to the research of other investigators, impregnation effects are key factors of improving Chinese fir's performance [15]. However, most of the research rarely mentioned the research of impregnation method. Only by adopting a good impregnation process can fully combine various agents with Chinese fir to produce improved effects. In this study, a new impregnation process, with a cyclic increasing-pressure method (CIPM) was adopted, which was compared with progressive increasing-pressure method (PIPM) to examine and demonstrate the advantages of CIPM. By analogy, it has been observed that, when the human body breathe, oxygen is delivered evenly to the whole lung and that the porous structure of the lung is similar to the structure of wood, thus suggesting the use of biomimetic wood impregnation, via cyclic pressure changes (Fig. 1). Specifically, liquid is used to replace gas and wood is used to replace lungs so that the process of human respiration is simulated alternately by negative and positive pressures.

2 Materials and Methods

2.1 Materials

Chinese fir was purchased in Chenzhou, Hunan Province, China. The size of samples to be tested were produced in accordance with GB/T 1929-2009, GB/T 1931-2009, GB/T 1936.1-2009, and GB/T 1941-2009. Ten test specimens for weight percentage gain and density measurement were used with a size of 20 × 20 ×

20 mm (tangential × radial × longitudinal dimensions). Ten test specimens for bending strength evaluation were 20 × 20 × 300 mm, respectively. Ten hardness test specimens were 50 × 50 × 70 mm, respectively. Samples are not allowed to contain seams, cracks, corrosion, twill, or other defects. Formaldehyde (37% aqueous solution, AR) was purchased from Cologne chemicals Co., Ltd. Phenol (AR) was purchased from Xilong Scientific Co., Ltd. Sodium hydroxide (AR) was obtained from Sinopharm Group Chemical Reagent Co., Ltd., Shanghai, China. A ZWL-PA1-20 ultrapure water system was used to prepare ultrapure water.

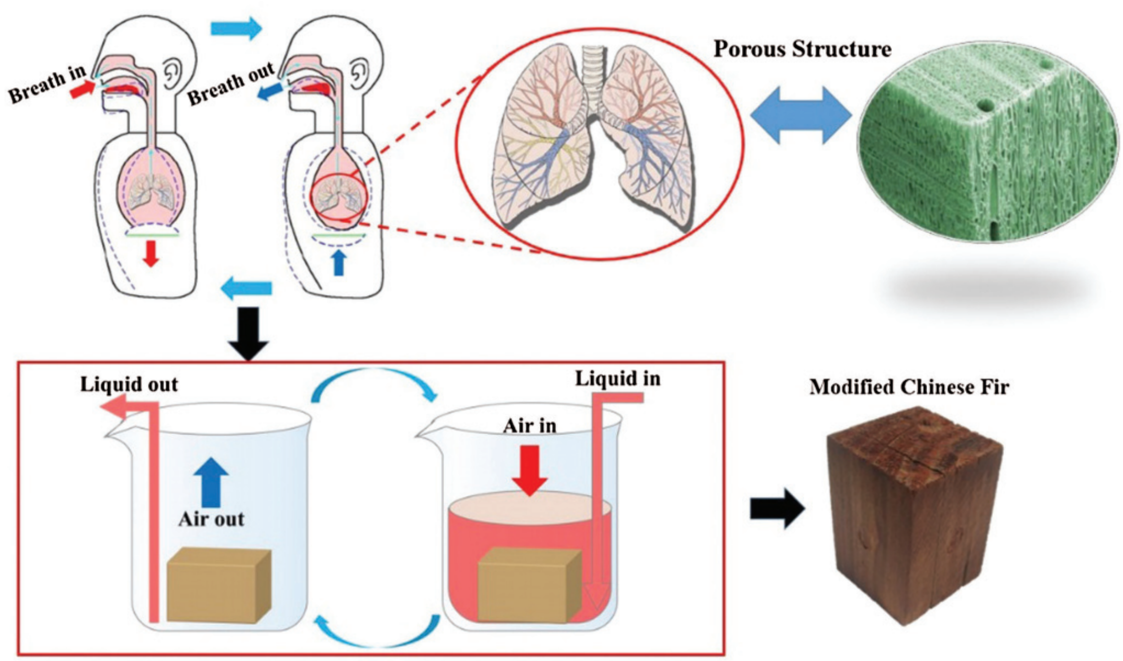

Figure 1: Schematic diagram of cyclic increasing pressure method

2.2 Preparation of Phenolic Prepolymer

During synthesis of the phenolic prepolymer, the raw material molar ratio was phenol/formaldehyde/sodium hydroxide, 1/3.5/1. The phenol/formaldehyde solution was reacted at 30°C for 40 h under sodium hydroxide catalysis [16]. The solid content of the product was 40.5%, and the viscosity was 52.2 mPa.s.

2.3 Preparation of Impregnated Chinese Fir

Three groups of Chinese fir materials were prepared with each group containing 20 × 20 × 20 mm, 20 × 20 × 30 mm, 50 × 50 × 70 mm wood blocks, and 20 × 20 × 300 mm wood strips for gain weight rate, density measurement, hardness measurement, and strength measurement, respectively. These samples were immersed in pure water for 24 h, placed into a drying box at 60°C for 24 h, and then removed for experiment. As shown in the Fig. 2, the modified Chinese fir specimens were impregnated by using CIPM or PIPM.

There were two main steps in CIPM. In the first step, the Chinese fir was subjected to −0.1 MPa for 10 min and then phenolic prepolymer at 20% solid content was introduced into the jar to release the pressure. In the second step, the jar was pressurized to 0.5 MPa, held for 20 min, and then the pressure relieved to drain the solution. This operation was repeated 4 times for a total processing time of 2 h.

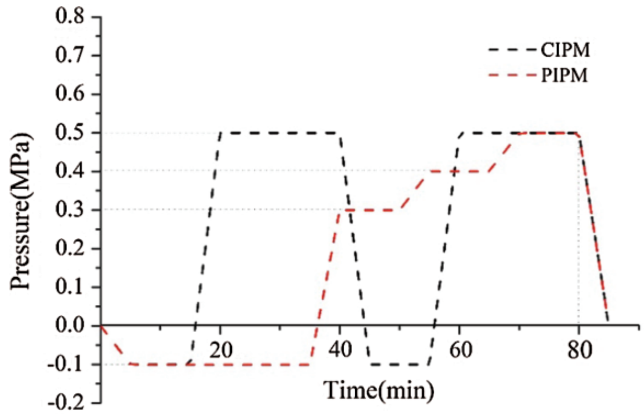

Figure 2: The flow diagram of CIPM and PIPM

PIPM was divided into two steps. In the first step, phenolic prepolymer at 20% solid content was added to the jar, a negative pressure of −0.1 MPa applied for 30 min, and then the pressure released. In the second step, the jar was pressurized to 0.3 MPa for 10 min, pressurized to 0.4 MPa for 10 min, pressurized to 0.5 MPa for 10 min, and then the pressure released. This operation was repeated twice for a total immersion time of 2 h.

After impregnation was complete, samples were retrieved, wiped dry of agent, set aside for 6 h for aging, placed in an air-blast dryer, and dried them at 60°C for 24 h to control the moisture content to 9–15%.

2.4 Properties and Characterization

2.4.1 Weight Percentage Gain Test

Weight percentage gain (WPG) is an important index for testing the effect of wood impregnation. Because wood is a kind of natural porous, limited expansion, capillary material, it can be used to measure the weight of modified agents in the wood impregnation process and general permeability, as it directly affects wood density as well as related wood mechanical properties. The calculation method was shown in Eq. (1). Where M_0 is the absolute dry mass before modification and M_1 the absolute dry mass after modification.

$$WPG\ (\%) = \frac{M_1 - M_0}{M_0} \times 100\% \tag{1}$$

2.4.2 Scanning Electron Microscopic Analysis

Specimens were cut open, after dipping treatment, to size less than a 10 × 10 × 5 mm block and affixed after drying with a conductive adhesive to the metal base. Sample surfaces were sputtered with gold, for electron beam bombardment of sample surfaces through the interaction between electrons and secondary electrons, back scattered electrons, allowing fracture morphology observation and analysis on sample surfaces.

2.4.3 Fourier Transforms Infrared Spectroscopic Analysis

Dried Chinese fir samples were ground up and particles of <80 micron diameter selected using a 200 mesh. The wood particles were evaluated using a Bruker Vertex 70 FTIR spectrophotometer (FTIR, Bruker Corp., Billerica, MA, USA). Samples were ground into powder with a weight ratio of 1/100, with KBr as the raw material, and then pressed into tablets. The infrared spectrum of the samples ranged from 400 to 4000 cm^{-1}.

2.4.4 Mechanical Properties Test

As shown in the Fig. 3, a universal mechanical testing machine was used to test mechanical properties. The bending strength test was carried out according to the Chinese national standard GB/T 1936-2009. The bending strength test specimen size is 20 × 20 × 300 mm. The loading direction was the tangential direction of the sample, and the distance between the two fulcrums was 240 mm. Twelve modified and control samples were tested under the specified experimental conditions. The compressive strength was tested according to the Chinese national standard GB/T 1935-2009. The size of the compressive strength test specimen was 20 × 20 × 300 mm, and the specimen was loaded at a constant loading rate until it collapsed. The maximum compression strength recorded was that the specimen maintained over 90 s without collapse. The hardness values of end face, radial face and bastard face were tested according to the Chinese national standard GB/T 1941-2009. Each sample size was 50 × 50 × 70 mm, and it was tested once on two end faces, two radial faces and two rough faces. The hemispherical steel head was pressed into the test surface at a uniform speed of 3 to 6 mm /min until the depth was 5.64 mm, and the measured load reading with an accuracy of 10 N.

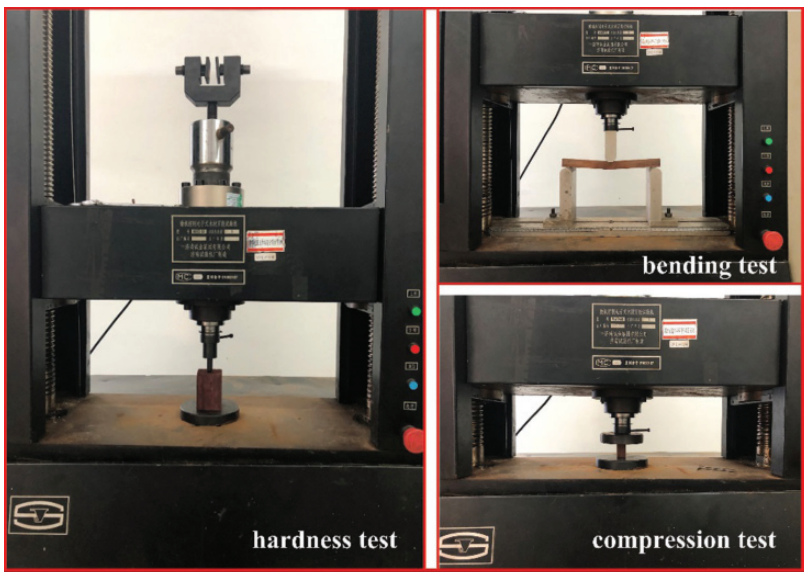

Figure 3: Mechanical properties testing

2.4.5 Water Resistance Rate Test

Wood is a loose and porous organic material, which has a good ability to absorb surrounding water. Calculation of wood water absorption is expressed by the ratio of the wood water absorption to the water quantity that is not absorbed within a specified period of time and the water quantity when the wood is absolutely dry. The measured bending strength specimens were sawn to a cube of 20 × 20 × 20 mm and the block soaked in pure water for 12 h intervals, at which time the surface water was removed and the weight recorded. After absorbing water for 96 h, the soaking was stopped and the final water absorption rate of the wood calculated at 96 h. The calculation method was shown in Eq. (2).. Where G_a is the mass after water absorption and G_0 the absolute dry mass.

$$W(\%) = \frac{G_a - G_0}{G_0} \times 100\% \tag{2}$$

2.4.6 X-ray Diffraction Analysis

X-ray diffraction phase analysis is a technique for analyzing a substance's structure by the diffraction effects of X-rays in a crystalline substance. Each crystalline material has its specific crystal structure, including lattice type, crystal surface spacing, and other parameters. The sample is illuminated by X-rays with sufficient energy. When the sample material is excited, it will generate secondary fluorescent X-rays (marking X-rays). By determining the diffraction angle position (peak position), a compound can be qualitatively analyzed, its integral strength (peak strength) of the determination line quantitatively analyzed, and the size and shape of the grain detected by the determination line strength changing with the angle. The empirical method of was used for these calculations and the calculation method was shown in Eq. (3) [17]. Where I_{002} is the maximum strength of the lattice diffraction angle of (002) and I_{am} the scattering intensity of amorphous background diffraction at 2θ, approaching 18°.

$$CrI(\%) = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \tag{3}$$

2.4.7 X-ray Photoelectron Spectroscopy Analysis

The XPS spectra of natural and modified wood were obtained on a K-Alpha XPS apparatus (supplied by Thermo Fisher Scientific Co., Ltd.) at room temperature using monochromatic Al Kα radiation (1486.6 eV). The X-ray beam was a 100 W, 200 mm-diameter beam raster over a 2 mm by 0.4 mm area on the sample. A high-energy photoemission spectrum was collected using pass energy of 50 eV and resolution of 0.1 eV. For the Ag3d5/2 line, these conditions produced an FWHM of 0.80 eV.

2.4.8 Thermogravimetric Analysis

The thermal stability of samples of impregnated modified Chinese fir was analyzed. A Netzsch STA 2500 synchronous thermal analyzer system (Netzsch Instruments, Inc., Burlington, MA, USA) was employed with a temperature rise rate of 10 °C/min, ranging from 30°C to 790°C, nitrogen flow rate of 30 mL/min, and 5 mg samples.

2.4.9 Fire Tests

Butane gun combustion tests were carried out on Chinese fir samples in a calm environment. The upper end of the sample was clamped on the bracket, and the vertical axis of the sample was perpendicular to the ground. The Angle between the sample direction and the butane gun flame with a flame temperature of 1300°C was 45°, and the butane gun was 50 mm from the lower end of the sample. After the sample was burned for 60 s, the butane gun flame was removed, and the combustion condition of the samples were observed and photographed.

2.4.10 Statistical Analysis

The data in this research was statistically evaluated using the Minitab Version 15 statistical software package. It reported with the mean and standard deviation of the number of replicates. A single-factor analysis of variance was used to determine the significance difference between the mean value according to the minimum significance difference criterion of 95% confidence level ($p < 0.05$).

3 Results and Discussion

3.1 Comparative Analysis of Impregnation Effects

The distribution uniformity of the modifier in wood is the most intuitive performance of impregnation effects. At the same time, the weight percentage gain (WPG) is also an important index for evaluating the impregnation effects of wood. Therefore, the impregnation effects on CIPM and PPIM were compared, and the results are shown in Fig. 4.

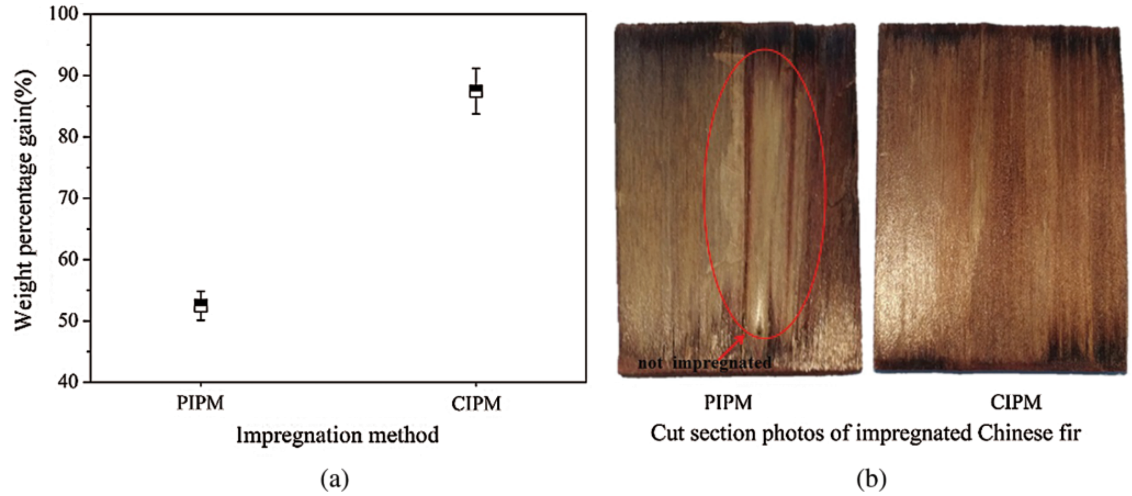

Figure 4: Impregnation effects of Chinese fir modified by PIPM and CIPM

In Fig. 4a, both CIPM and PIPM impregnated Chinese fir showed weight percentage gain of >50%, indicating good impregnation effects. However, the WPG of CIPM impregnated Chinese fir was better than that of PIPM impregnated Chinese fir, which showed that CIPM more effectively infused phenolic prepolymer into the Chinese fir. It can effectively improve the properties of Chinese fir by immersing phenolic prepolymer into the pores of Chinese fir, the principle is shown in Fig. 5. We obtained the interior of the modified wood by splitting the 50 × 50 × 70 mm specimens. The color distribution of CIPM impregnated Chinese fir was also more uniform than that of PIPM impregnated Chinese fir (Fig. 4b), which further indicated that impregnation by CIPM was better than by PIPM. This was attributed to CIPM effectively opening the aspirated pits of the wood under the repeated action of negative and positive pressures, so that paths for modifier penetration and migration into the wood were opened (Fig. 6). This also showed that modifier penetrated into every corner of the samples. The results of electron microscopic observations of Chinese fir treated with CIPM clearly showed that the pit membranes treated by CIPM were broken, which effectively explained why CIPM exhibited the better impregnation effects.

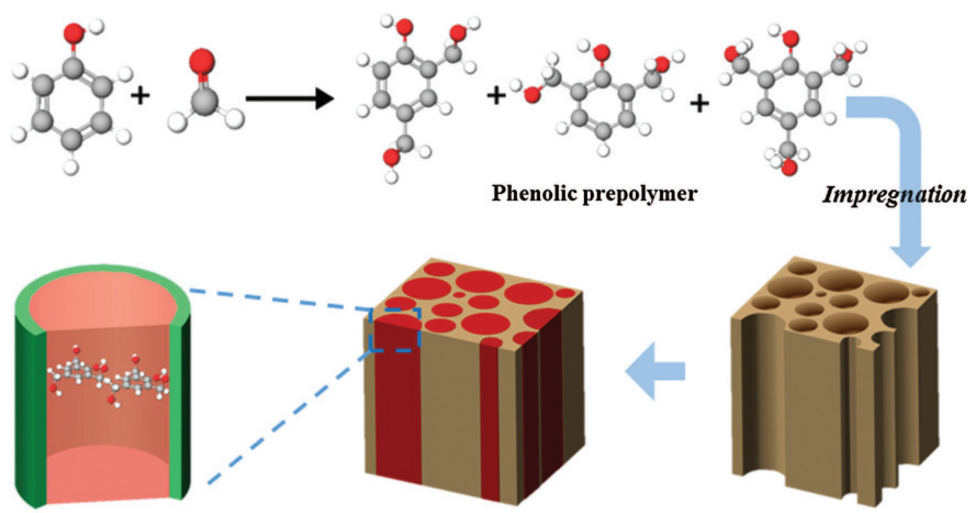

Figure 5: Principle of phenolic prepolymer immersed in Chinese fir

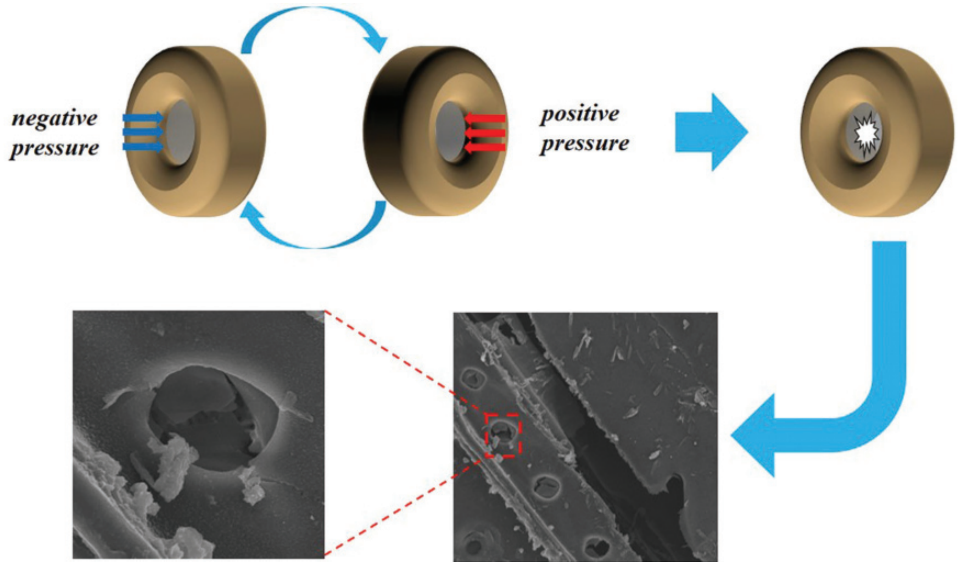

Figure 6: Fracture principle and effect of aspirated pits

3.2 Comparative Analysis of Internal Morphology

There are a lot of longitudinal tracheids, pits, cell cavities, and other pores in Chinese fir, which leads to low density defects and loose material in this fast-growing tree. These defects directly lead to poor strength and dimensional stability of the Chinese fir. Therefore, to compare the filling effects of PIPM and CIPM on the pores of this Chinese fir was vital. SEM was used to observe its transverse and longitudinal structure, and the result was shown in Fig. 7. In which a and b represent the transverse and longitudinal morphologies of unmodified Chinese fir, c and d represent the transverse and longitudinal morphologies of PIPM impregnated Chinese fir, and e and f represent the transverse and longitudinal morphologies of CIPM impregnated Chinese fir, respectively.

In Fig. 7a, the tracheids were seen clearly in transverse sections of unmodified Chinese fir, with adjacent rows of tracheids staggered in front and back, and most of them were square and hollow, without any filling substance. In Fig. 7b, the tracheid surfaces on longitudinal sections of unmodified Chinese fir were smooth, with unopened aspirated pits clearly seen on the inner wall, and there was also no filling material. After phenolic prepolymer infusion, infilled phenolic resin was seen in the transverse and longitudinal sections of modified Chinese fir, which showed that phenolic prepolymer was infused into Chinese fir pores. However, the filling effects of resin impregnation with PIPM and CIPM were different. Although the tracheids of PIPM impregnated Chinese fir were filled with phenolic resin, there were still some unfilled tracheid cavities (Fig. 7c). In Fig. 7d, the open and unfilled aspirated pits were also seen in longitudinal sections of PIPM impregnated Chinese fir, which suggested that the impregnation effects of PIPM in this Chinese fir was not the best and it was incomplete and uneven. In Fig. 7e, the transverse sections of CIPM impregnated Chinese fir were better filled with phenolic resin and the unfilled tracheids were basically seen. Longitudinal sections of CIPM impregnated Chinese fir were also completely devoid of unfilled spaces, being completely filled with phenolic resin and no pits observed (Fig. 7f). This further confirmed that CIPM produced better infusion results than PIPM. At the same time, analytical results of mechanical strength and water resistance were verified. The filling effects of CIPM impregnated Chinese fir were better than PIPM, so its mechanical strength and water resistance were also better [18].

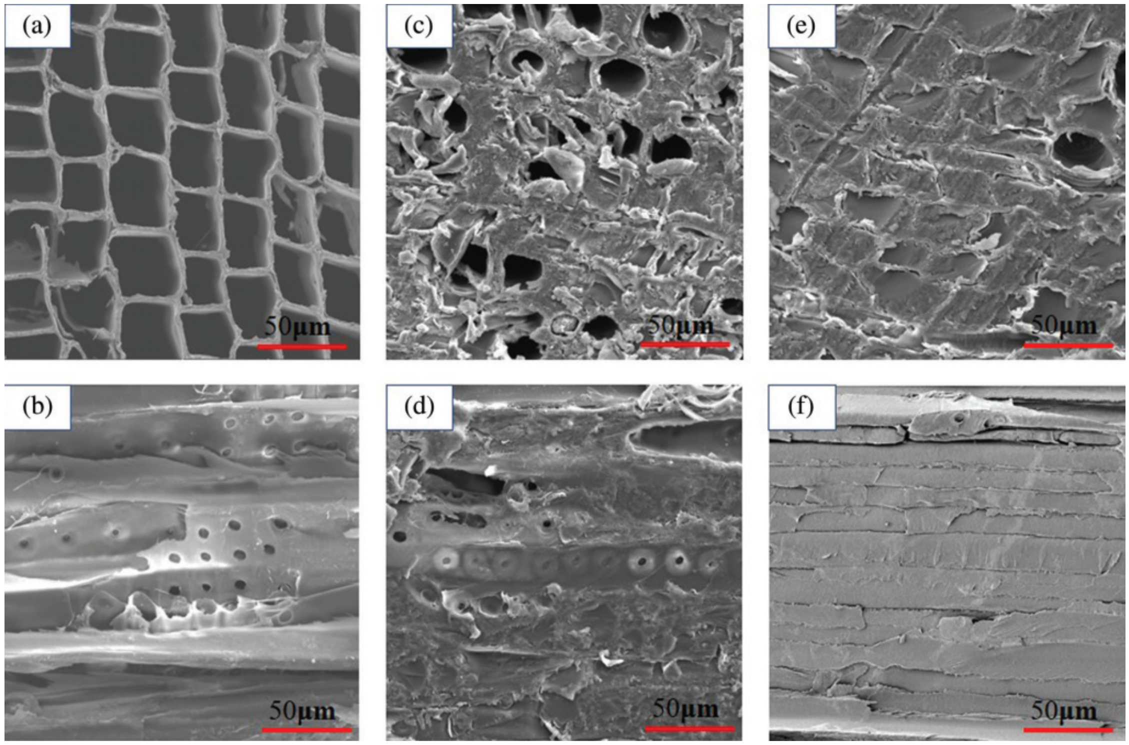

Figure 7: SEM of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

3.3 Comparative Analysis of Chemical Structure

The chemical structure of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir were compared using FT-IR to detect chemical groups. The results are shown in Fig. 8. In the range of 3000–3700 cm$^{-1,}$ the vibration peak bands of hydroxyl group absorption of PIPM and CIPM impregnated Chinese fir were widened and enhanced compared with unmodified Chinese fir. This demonstrated that the free hydroxyl group content descended and the associated hydroxyl group context ascended in impregnated Chinese fir. The stretching vibration peak of C–O within 1030–1060 cm^{-1} was dramatically improved, from which it was concluded that phenolic prepolymer was better infiltrated into the wood and formed certain ether bonds with hydroxyl groups in the wood. This indicated that phenolic prepolymer had formed chemical bonds with hydroxyl groups in the wood rather than being a simple physical filling [19]. Modification was observed as phenolic resin was formed by curing the phenolic prepolymer, which played a beneficial role in filling the Chinese fir pores. More importantly, the chemical reaction between phenolic prepolymer and Chinese fir chemical groups formed more hydrogen and chemical bonds. Compared with PIPM impregnated Chinese fir, the intensity of infrared absorption peak of CIPM impregnated Chinese fir clearly increased, with the latter having a hydrogen bond association peak range of 3200–3500 cm^{-1}, the C=O stretching vibration peak of at 1735 cm^{-1}, vibration peak of benzene ring at 1606 cm^{-1}, and the stretching vibration peak of C–O from 1030–1060 cm^{-1}. This also showed that CIPM infused more phenolic prepolymer into the Chinese fir, not only producing more physical filling but also forming more hydrogen bond associations and chemical bond combinations. This demonstrated that the CIPM impregnated Chinese fir was superior to PIPM impregnated Chinese fir in mechanical strength and water resistance.

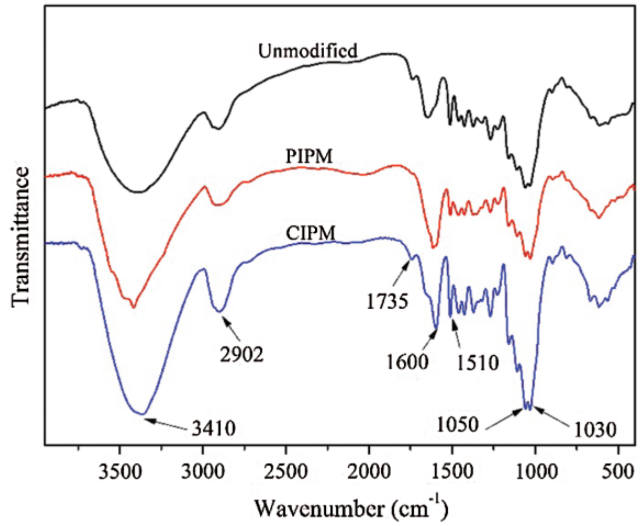

Figure 8: Infrared Spectra of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

Figs. 9a–9c are the survey XPS spectra of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir, and it can be seen that the three specimens all have two peaks in 286 eV and 533 eV, which are respectively absorption peaks of C and O. Combined with the Tab. 1, it can be seen that the main elements of the three materials are C and O. Compared with the unmodified wood, the O elements of modified woods increased from 18.98% to 24.51% and 26.61%, further indicating that the oxygen-containing functional groups in wood increased after phenolic prepolymer modification. Fig. 9d is the O1s XPS spectra of the three specimens, and the O element content of CIPM remains the highest among the three samples, consistent with the former. In addition, CIPM is superior to PIPM, which combined with the 1600 cm^{-1} peak enhancement shown in Fig. 8, and it can confirm the superiority of CIPM.

3.4 Comparative Analysis of Mechanical Properties

As a kind of fast-growing wood, Chinese fir has the disadvantages of being a loosely-structured material with poor mechanical properties, so that it is not widely used in structural applications. Therefore, an effective means for improving Chinese fir mechanical properties is impregnation with a stiffening modifier, introducing desirable properties into cell cavities and walls. The bending strength, compressive strength, and hardness of impregnated Chinese fir are the reference standards to estimate whether a kind of modified wood can be widely applied. The mechanical properties of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir are shown in Fig. 10.

In Fig. 10a, compared with unmodified Chinese fir, the bending strength and compressive strength of both PIPM and CIPM impregnated Chinese fir were improved. This is because that the phenolic prepolymer had been infused into the fir interior and became a hard and brittle phenolic resin after curing, effectively filling the Chinese fir pores. Under the action of external force, these phenolic resins shared external loads, which improved the fir mechanical strength [20]. However, there were differences in the enhancement effects from CIPM and PIPM on mechanical strength, with CIPM enhancement significantly better than that of PIPM. This was attributed to CIPM having better polymer infusion into the Chinese fir and more phenolic resin solids filling Chinese fir pores. While the density increase ratio of CIPM impregnated Chinese fir was more obvious and the resulting material was finer and closer, the phenolic resin solids in CIPM impregnated Chinese fir shared more external loading.

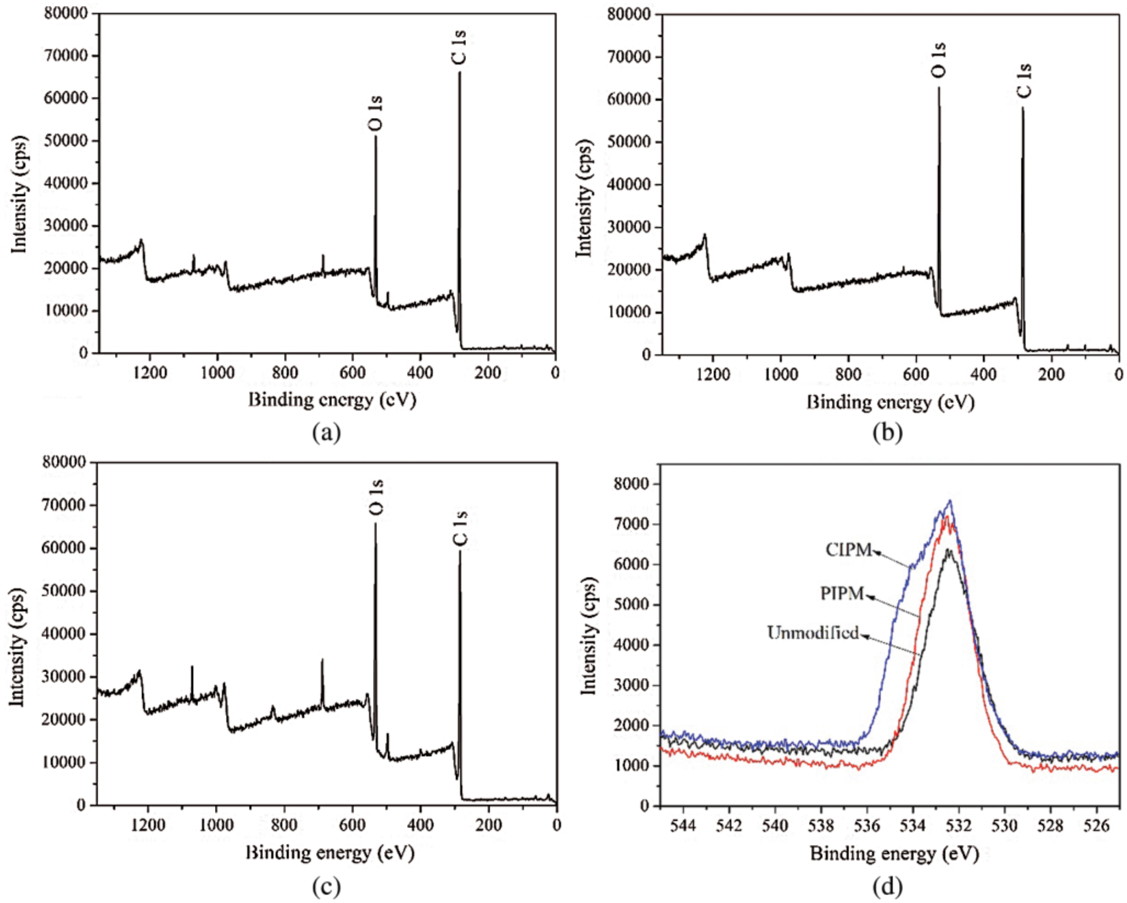

Figure 9: Survey and O1s XPS spectra of unmodified, PIPM and CIPM impregnated Chinese fir

Table 1: Elemental composition and content of unmodified and modified wood

Group	C/%	O/%
Unmodified	81.02	18.98
PIPM	75.49	24.51
CIPM	73.29	26.61

Fig. 10b shows the hardness measurements of the transverse, radial and tangential surfaces of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir. It was showed that the hardness of three sections of impregnated Chinese fir were greater than those of unmodified Chinese fir, with CIPM hardness improvement being higher than PIPM [21], which was due to the better impregnation effects of CIPM. The improvement effects from CIPM impregnation with more phenolic resin solid materials on the hardness of Chinese fir were the most significant, such that the hardness could contribute to the application of Chinese fir as solid wood flooring.

3.5 Comparative Analysis of Water Resistance

Wood is a kind of porous material, which can absorb the moisture from the environment. This action can lead to wood mildewing and deformation and affect its applications in furniture, floor, interior decoration, and wood structures. Therefore, wood water resistance becomes the reference standard of whether it can be put into various practical uses and has become a reference standard for its production and application. The water absorption rates of PIPM and CIPM impregnated Chinese fir in 84 h were almost the same after they were soaked for 6 h, but they were far lower than of unmodified Chinese fir (Fig. 11). This indicated that the water absorption rate of impregnated Chinese fir was greatly reduced by prepolymer impregnation, but the advantage of CIPM was not clear compared with PIPM. After 6 h, the water absorption rate of CIPM impregnated Chinese fir was lower than that of PIPM impregnated Chinese fir, such that, at 60 h, the water absorption rate of CIPM impregnated Chinese fir was nearly 10% lower than that of PIPM impregnated Chinese fir. In addition, the water absorption rate of CIPM impregnated Chinese fir was reduced by 50% compared to unmodified Chinese fir. Therefore, prepolymer impregnation significantly improved the Chinese fir water resistance and the CIPM effects on Chinese fir were better than that of PIPM. On the one hand, the phenolic prepolymer reacted with the hydrophilic hydroxyl group in Chinese fir to form a chemical bond, which effectively reduced the number of hydrophilic groups and thus reduced the absorption of water. On the other hand, the pores of PIPM impregnated Chinese fir were filled with phenolic resin and the water storage volume decreased.

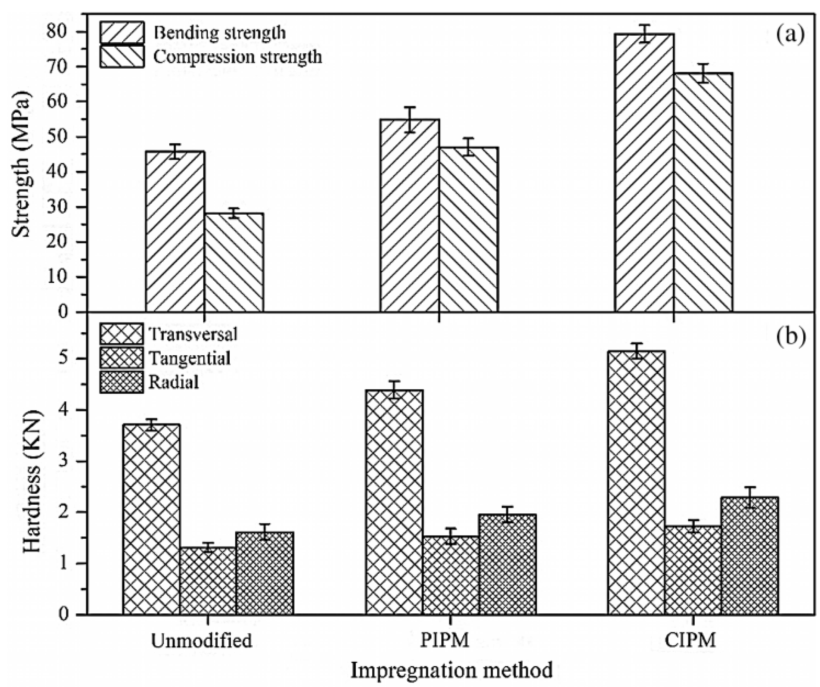

Figure 10: Bending strength, compressive strength and hardness of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

3.6 Changes in Crystal Structure of Modified Chinese Fir

The crystallinity of a material directly affects impregnation effects and indirectly reflects the material's mechanical strength. To compare unmodified Chinese fir with the influence of these modification methods on crystal structure, XRD was used to test unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir. In Fig. 12, the diffraction peaks of wood cellulose at (101) and (002) crystalline planes occurred in unmodified Chinese fir when the 2θ were 16° and 22.5°, separately [22]. The diffraction peak positions of Chinese fir before and after modification were not changed, which indicated that the infusion of phenolic prepolymer did not change the Chinese fir's crystal type. However, the crystal diffraction intensities of PIPM and CIPM impregnated Chinese fir were different. Compared with unmodified Chinese fir, the crystal diffraction peak intensity of modified Chinese fir was clearly enhanced, being improved by phenolic prepolymer infusion, which infiltrated into noncrystalline areas in the wood and made noncrystalline cellulose stick together, to improve the regular arrangement of cellulose molecular chains. As the diffraction peak of the 002 crystalline planes was directly related to wood fiber crystallinity, the crystallinities of unmodified and impregnated Chinese fir were calculated. The crystallinity of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir were 62.83%, 65.40% and 70.84%, respectively, which showed that the crystallinity of CIPM impregnated Chinese fir was higher than that of PIPM impregnated Chinese fir. The reason for this phenomenon was that CIPM had better infusion effects on Chinese fir and more modifiers injected and the cellulose chains in the noncrystalline area of CIPM impregnated Chinese fir more closely linked. XRD analysis results demonstrated that the CIPM impregnated Chinese fir was more significantly improved than the PIPM impregnated Chinese fir in mechanical properties and water resistance.

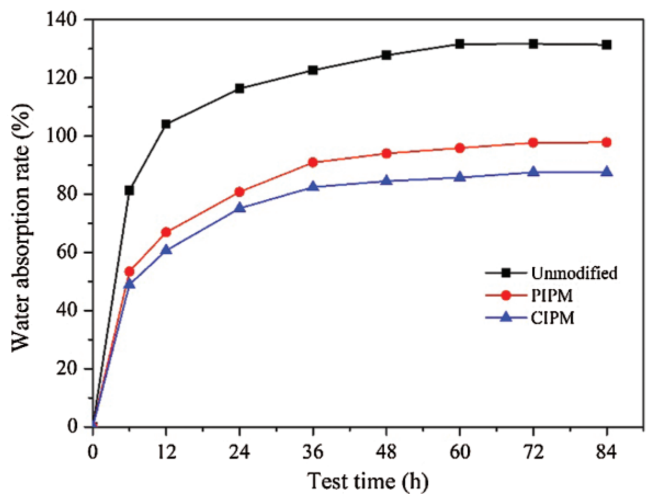

Figure 11: Water absorption rate of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

3.7 Comparative Analysis of Heat Resistance

The infusion of phenolic resin and the change of crystallinity inevitably affected the heat resistance of these impregnated Chinese fir. TGA tests of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir were performed, and the results were shown in Fig. 13a. Compared with unmodified Chinese fir, the thermal decomposition rates of PIPM and CIPM impregnated Chinese fir were significantly decreased after 200°C. The thermal decomposition residues of these two kinds of wood increased to 33.31% and 43.51%, respectively. Relative to unmodified Chinese fir, which indicated that the heat resistance of modified Chinese fir was significantly improved after phenolic prepolymer infusion. This was attributed to the phenolic resin, having excellent heat resistance, being infused into the Chinese fir and impregnation improving Chinese fir crystallinity. These two effects improved the heat resistance of Chinese fir, in the range of 200–350°C, the weight loss rate of impregnated Chinese fir was slightly lower than that of unmodified Chinese fir. In addition, the maximum rate of decomposition temperature in DTG curves of PIPM and CIPM impregnated Chinese fir decreased to 286.5°C and 299.4°C, respectively, compared with unmodified Chinese fir. The reason of this change was that the infiltration of prepolymer into Chinese fir crystal zones, which had a swelling effect on the crystal zone cellulose. This weakened the forces between cellulose chains and made them easier to decompose when heated. Compared with PIPM impregnated Chinese fir, CIPM impregnated Chinese fir had higher initial decomposition temperatures, maximum decomposition rate temperatures, and decomposition residual rates. Thus, CIPM had better impregnation effects and more prepolymer infused into the Chinese fir. Also, the crystallinity of CIPM impregnated Chinese fir was the largest after curing and the adhesion between cellulose chains stronger, which then possessed better heat-resistant effects. With improving heat resistance, the safety in case of fire of such impregnated Chinese fir products was significantly improved.

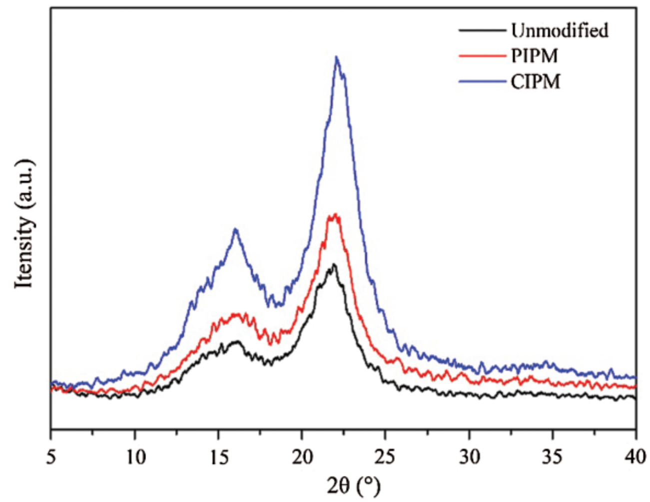

Figure 12: XRD diffraction patterns of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

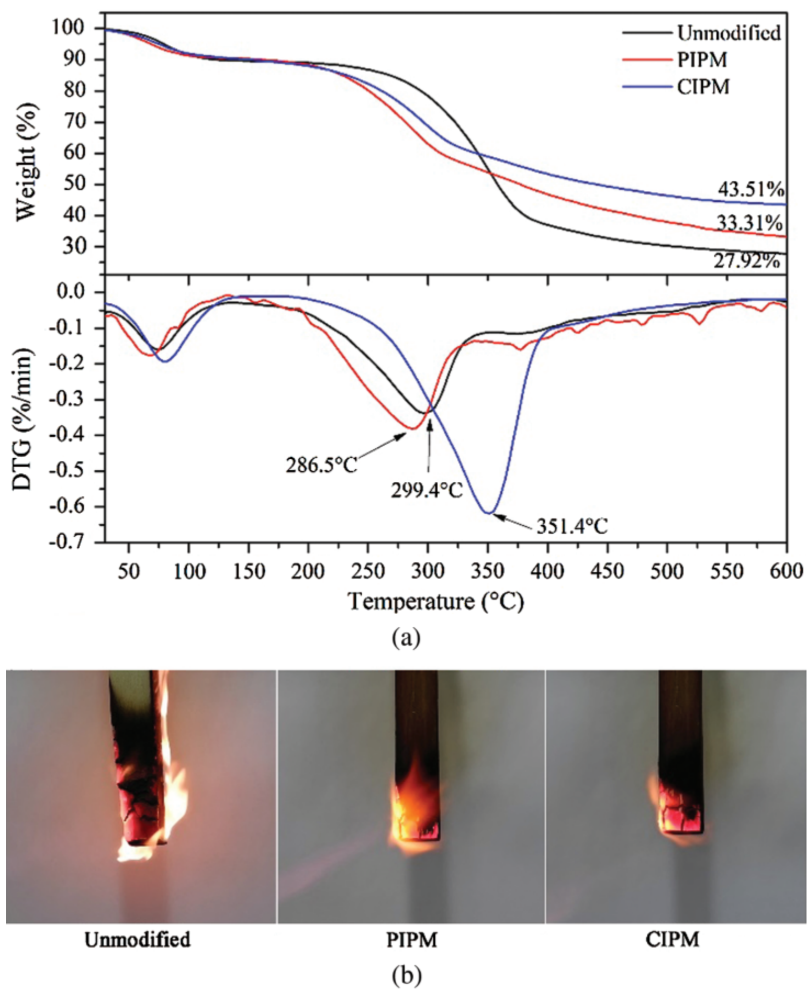

Figure 13: TG-DTG curves (a) and combustion test (b) of unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir

Fire resistance is an important index for the application of wood products as building materials. Unmodified Chinese fir, PIPM and CIPM impregnated Chinese fir were burned continuously for 60 s under butane flame at 1300°C respectively; combustion conditions are shown in Fig. 13b. After removal of the butane gun flame, unmodified Chinese fir wood continued to burn with a well-defined flame and sample surfaces severely carbonized. However, the flames from wood modified by PIPM and CIPM were smaller than that of unmodified wood, which showed that phenolic prepolymer modification can improve the wood's fire resistance. However, the yellow flame of CIPM impregnated Chinese fir was significantly smaller than that of PIPM impregnated Chinese fir when the flame source was removed. This was a clear indication that CIPM impregnated Chinese fir possessed better fire resistance.

4 Conclusions

To improve the added value of Chinese fir, phenolic prepolymer was infused into Chinese fir by CIPM. The aspirated pits of Chinese fir were successfully opened by the negative pressure/positive pressure cycle treatment of CIPM, resulting in increased weight percentage rate and density increase ratio in CIPM impregnated Chinese fir, which was larger than in PIPM impregnated Chinese fir. More phenolic prepolymers were infused into Chinese fir to form more physical filling and chemical bounding, which significantly improved the mechanical properties and water resistance of CIPM impregnated Chinese fir. SEM analysis showed that phenolic resin had better filling effects on transverse and longitudinal sections of CIPM impregnated Chinese fir. XRD analysis indicated that phenolic prepolymer made the cellulose chains in Chinese fir more closely bound, which further explained the reason for its better mechanical properties. TGA analysis and combustion experiments confirmed that the heat resistance of CIPM impregnated Chinese fir was significantly improved and it was more difficult to burn. The above analysis demonstrated that CIPM impregnated Chinese fir had the characteristics of high strength, water resistance, and combustion resistance, which are required in building materials. Therefore, phenolic prepolymer CIPM impregnated Chinese fir expanded this wood's application potential in the field of building materials.

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