Properties of Poplar Veneer Modified by Acid Red 3R Dye in Combination with Ammonium Dihydrogen Phosphate

Xin Shi,[a,#] Hao Shen,[a,#] Shenglei Qin,[a] Yangguang Liu,[a] Xiaoshuang Shen,[a,b] Demiao Chu,[a,b] and Shengquan Liu [a,b,]*

Ammonium dihydrogen phosphate (ADP) is a nitrogen-phosphorus-based inorganic flame retardant that is environmentally friendly and non-toxic. Wood treated with ADP has enhanced thermal stability and flame retardancy. Compounding ADP with Acid Red 3R dye further improves the decorative effect of the wood on the basis of excellent flame retardancy, resulting in a kind of dyeing and flame retardant multifunctionalized wood. Single-factor tests were designed to investigate the effects of flame retardant concentration, dye concentration, temperature, and time on three evaluation indexes: dye-uptake, color difference, and oxygen index, respectively. Through SEM and FTIR analysis, it was found that after the wood was simultaneously treated with flame retardant and dye, the two additives were aggregated in the grain pores of the cell wall by a simple physical combination. They did not undergo a chemical reaction. TG analysis showed that fire-retardant dyed wood had good thermal stability, which can delay the thermal degradation of wood and increase the residual charcoal rate of wood. XRD showed that the crystallinity of fire-retardant dyed wood increased compared to untreated wood. Through cone calorimetric test, it is found that flame retardant dyed veneer had excellent flame retardancy.

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Keywords: Poplar wood; Ammonium dihydrogen phosphate; Acid dyes; Dyed and flame retardant wood; Dye-uptake; Color difference; Oxygen index

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INTRODUCTION

Fast-growing poplar is the preferred species for short-cycle industrial timber forests in China. It has become an important industrial timber in China due to its fast growth rate, wide cultivation area, and convenient harvesting and transport (Lv *et al.* 2014). However, the monotonous color of poplar wood, as a diffuse porous wood and its annual structure or three-dimensional pattern is not clear enough and lacking in decorative character. These defects greatly limit the scope of its application. Wood is affected by the external environment and self-structuring. It often has uneven color, easily changing color, and other problems. The wood color is an important indicator for determining the commercial value of wood, as are wood strength, density, other appearance attributes, and wood properties. Among them, in order to improve the decorative role and product value of poplar wood, often it is necessary to color it (Chen *et al.* 1999; Li and Yu 2005; Javaid and Qazi 2019; Guo *et al.* 2020; Zhang *et al.* 2023).

Wood dyeing can increase the value of low-grade wood by endowing it with the color and texture of high-grade wood to meet the ornamental demand for high-grade wood products (Wang 2020a). However, as the main component of dyed wood is wood, the high content of carbon and hydrogen in the wood component is easy to burn (He *et al.* 2022; Hansen and Richard 2023; Mensah *et al.* 2023), which limits the development of the application of dyed wood. Although the decorative effect of wood after dyeing can be greatly improved, the inherent flammability of wood itself on the safety of people's lives and property is still a hidden danger. The need for fire prevention greatly restricts the development of the application of dyed wood. In order to improve the flame retardancy of wood, flame retardants can be added.

Flame retardant treatment of wood refers to the introduction of flame retardants into wood cell walls, cell cavities, or surfaces by various methods such as impregnation, dipping, or painting to achieve flame retardancy (Dasari *et al*. 2013). Impregnation allows the flame retardant to contact the interior of the wood and provides a larger surface area for flame retardant modification (Fu *et al*. 2017). Impregnation can involve physical filling (Guo *et al*. 2020) or chemical grafting (Zhang *et al*. 2020). Wood flame retardants include halogens, phosphorus (Salamova *et al*. 2014), or nanofillers (Fu *et al*. 2017). Halogenated flame retardants have high flame retardant efficacy, but halogens produce toxic and harmful smoke when burned, causing environmental safety issues (Fu *et al*. 2020; Wang *et al.* 2023). Nanofillers have limited flame retardancy enhancement. In contrast, nitrogen-phosphorus-based flame retardants have the advantages of being environmentally friendly, having lower toxicity, and producing less smoke. They can produce refractory gases after being heated, which can effectively reduce the concentration of oxygen and combustible gases in the vicinity of the wood.

The combined use of dyes and flame retardants can give excellent flame retardant properties to dyed wood without affecting the ornamental demand of dyed wood, which can broaden its application scope.

Zhang used an orthogonal experimental method to treat woolly poplar (*Populus tomentosa*) veneer with dye and flame retardant. In a study of hot press gluing of veneer laminates, the optimum parameters for veneer dyeing, flame retardant treatment, and hot press process were determined (Zhang *et al.* 2005). Li (2011) selected four different types of dyes and BL-flame retardants to jointly treat poplar veneer with a thickness of 1.5 mm. They carried out research on the modified wood veneer in terms of resistance to water washing and sunlight fastness, and they determined that the preferred mating dyes with flame retardants were acid dyes (Li 2011). Wang (2020b) utilized the method of joint modification of wood by flame retardants and dyes, using environmentally friendly and efficient nitrogen-phosphorus flame retardants and acid dyes with good compatibility to carry out simultaneous treatment of dye and flame retardant on poplar wood. The effects of different factors on dye-uptake and oxygen index were analyzed.

The family of acid dyes represents a complete range of chromatography, including bright colours and a wide range of applications (Chen 1999; Wang *et al.* 2016a; Rahat *et al.* 2019). It has good compatibility with nitrogen-phosphorus flame retardants. Among them, Acid Red 3R is a typical azo acid dye that is widely used in the printing and dyeing industries. Ammonium dihydrogen phosphate is a nitrogen-phosphorus type inorganic flame retardant. It is environmentally friendly and non-toxic, and the ADP-treated wood can enhance its thermal stability and flame retardancy (Cui and Yan 2018; Kong *et al.* 2018; Haji *et al.* 2021). Ammonium dihydrogen phosphate (ADP) has been used to improve the flame retardancy of carbon-enriched/non-carbon-enriched polymers (Kong *et al*. 2018) and in the preparation of intumescent coatings (Zhang *et al*. 2018). Its decomposition can catalyse the formation of char, which is an insulating barrier to inhibit heat and gas transfer (Carosio *et al*. 2018; Qutab *et al.* 2021).

Therefore, in this paper, it was chosen to use acid red 3R as the dye and ammonium dihydrogen phosphate as the flame retardant to carry out the flame retardant dyeing combined modification treatment on poplar wood by the atmospheric pressure impregnation method. A one factor at a time test strategy was employed to explore the change rule of the influence of each factor on the dyeing rate, color difference, and oxygen index respectively. In addition, in order to further study the mechanism of combined treatment of poplar veneer with flame retardant dyeing, scanning electron microscope (SEM), Fourier Transform Infrared Spectrometer (FTIR), Thermogravimetric Analysis (TGA), X-ray Diffractometer (XRD), and Cone Calorimeter (CONE) were used to analyze the microscopic morphology and structure, chemical structure, thermal stability, crystalline properties, and combustion characteristics of the flame retardant dyed material. On the basis of improving the decorative effect of poplar wood and further endowing it with excellent flame retardancy, a dyeing-cum-flame-retardant multifunctionalized poplar wood was prepared.

EXPERIMENTAL

Materials

In accordance with the test requirements to collect the corresponding test material, fast-growing poplar veneer was obtained from Taihe County, Fuyang City, Anhui Province. The air-dried poplar wood was sawn into 50 mm (T) × 30 mm (L) × 2 mm (R) veneer specimens. The untreated veneer had a luminance index (L^*) measured by colourimeter of 85.91 ± 1.43, a red-green index (a^*) of 4.73 ± 0.54, and a yellow-blue index (b^*) of 14.13 ± 0.87. The specimens then were subjected to room temperature drying to 8 to 12% moisture content, and then kept at that condition pending further tests. Acid Red 3R (*C.I. Acid Red 18*) was purchased from Wuhan Rongcan Biotechnology Co. Ltd. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was purchased from Sinopharm Group Chemical Reagent Co., Ltd. All of the above reagents, other than the dye, were analytically pure. Distilled water was homemade in the laboratory.

The molecular structure formulae of Acid Red 3R and ammonium dihydrogen phosphate are shown in Fig. 1.

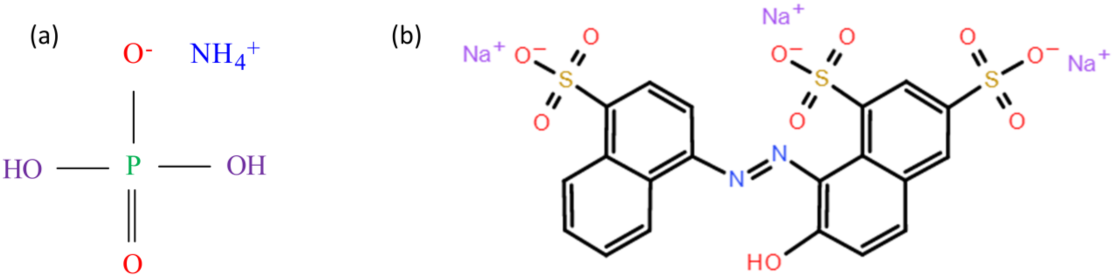

Fig. 1. Molecular structure formula of ammonium dihydrogen phosphate (a) and acidic red 3R (b)

Methods

Preparation process of poplar veneer treated with dye and flame retardant

In this test, the atmospheric pressure impregnation method was adopted to simultaneously carry out the flame retardant dyeing of poplar wood veneer. The solid-liquid ratio was fixed, and the flame retardant dyeing mixture solution with a total mass of 120 g was prepared. A single-factor test was designed to investigate the effects of flame retardant concentration (X_1), dye concentration (X_2), temperature (X_3), and time (X_4) on dye-uptake, color difference and oxygen index. Among them, the veneer should be vertically inserted into the slot in the dyeing cylinder, and there should be a certain interval of space between the veneer and the veneer to ensure that the veneer and the modification mixture are fully impregnated. After the impregnation, the modified veneer was rinsed with distilled water several times to replace the surface residual liquid. The specimens were placed in a constant temperature of 80 °C in the drying oven for 4 h. Then the veneer was equilibrated in air to the moisture content of 8 to 12%, followed by storage in a sealed bag to be kept in reserve (Fig. 2).

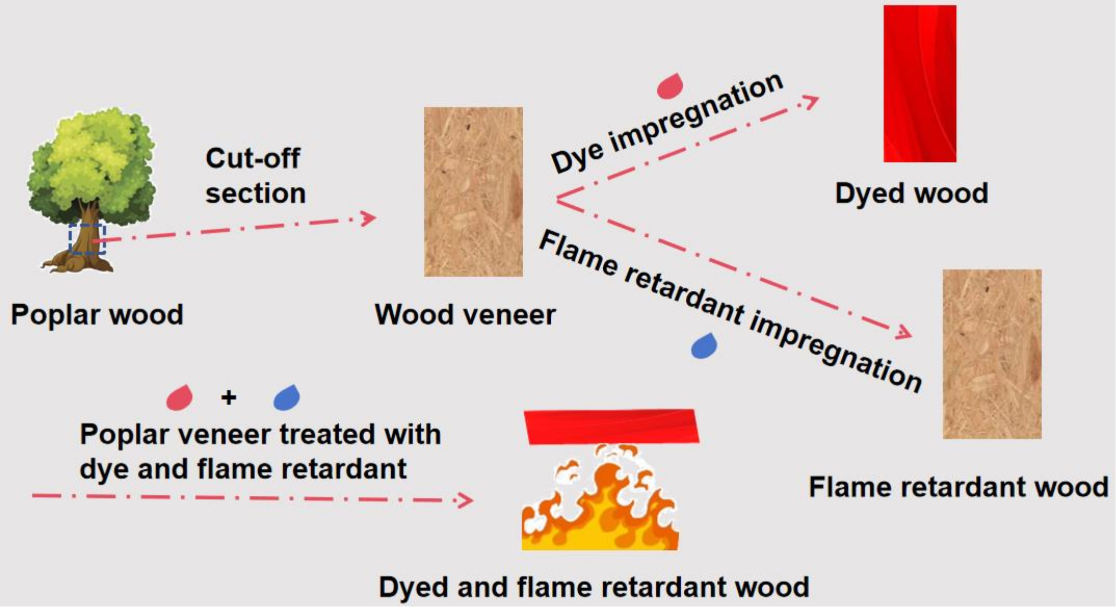

Fig. 2. Preparation of dyed and flame retardant veneer

With the other conditions remaining unchanged, one of the factors was varied as the independent variable to explore its impact on a single or multiple indicators of the change rule. To ensure that other conditions remained unchanged, default values were assigned as follows: The flame retardant concentration was fixed at 20%, the dye concentration was 1%, the temperature was 80 ℃, and the time was 2 h. The specific design factor levels are shown in Table 1.

To study the influence of flame retardant concentration on the process parameters of composite modified veneer, for example, fixed test conditions were as follows: total mass of the mixed solution was 120 g, the water bath temperature was 80 ℃, and the impregnation time was 2 h. For each condition, there was a group of six specimens, and these were compared with six untreated specimens. Weighing was done with an electronic balance. Mass amounts were prepared with 0, 5, 10, 15, 20, 25% or 30% of ammonium dihydrogen phosphate powder and 1% of the acidic red 3R dye. These were dissolved in a certain amount of distilled water. They were constantly stirred with a glass rod until the Acid Red 3R dye and ammonium dihydrogen phosphate completely dissolved.

Table 1. Single Factor Design of Experiments Level

Level	Factors			
	X_1/wt%	X_2/wt%	X_3/℃	X_4/h
1	0	0.5	40	0.5
2	5	1.0	50	1.0
3	10	1.5	60	1.5
4	15	2.0	70	2.0
5	20	2.5	80	3.0
6	25	3.0	90	4.0
7	30			

Measurements of dye-uptake

Keeping the quality of the dye solution the same before and after dyeing, 2 mL of the original dye solution and residual solution were pipetted into a 250 mL volumetric flask with a pipette gun. The absorbance value of the staining solution was measured at the maximum absorption wavelength (λ_{max}= 510 nm) using a UV-5200 UV-visible spectrophotometer. Each dye solution was pipetted twice, and the absorbance values were measured three times each time. The results were averaged over six times with the following formula,

$$C_t = (A_0 - A_1)/A_0 \times 100\% \tag{1}$$

where C_t is the value of dye-uptake (%); A_0 is the absorbance value of the dye solution before dyeing; and A_1 is the absorbance value of the residual solution after dyeing.

Among them, the UV absorption spectra of flame retardant solution, dyeing solution, and flame retardant dye-modified solution are shown in Fig. 3.

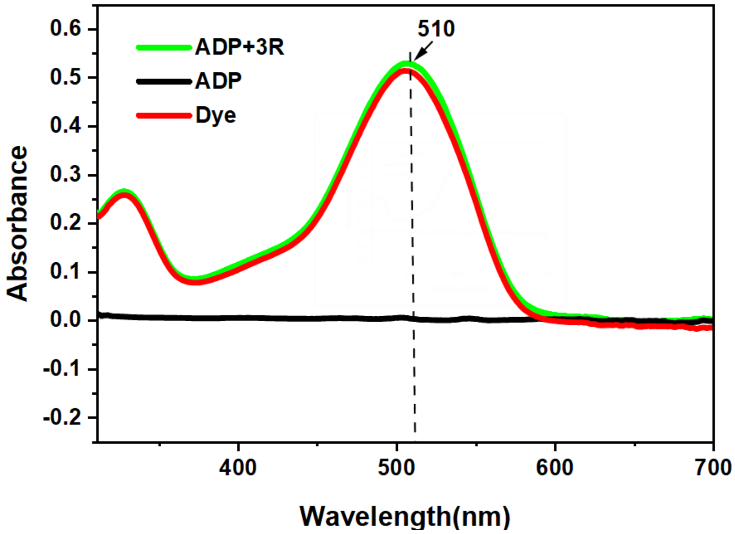

Fig. 3. UV absorbance spectrogram of dyeing solution, flame retardant solution and flame-retardant dyeing solution

The flame retardant line did not exhibit the maximum absorbance wavelength, while the number, position, and intensity of the absorbance peaks of the dye solution and the flame retardant dyeing mixture solution did not change. The result shows that the addition of flame retardant did not have an effect on the absorbance spectrum of acid red dyeing solution, so the maximum absorbance wavelength of the flame retardant dyeing modified solution was consistent with the dyeing solution, which was 510 nm.

Measurements of surface color difference

An HP-200 type precision colorimeter was used to determine the lightness index L^*, red-green index a^*, and yellow-blue index b^* of wood before and after treatment. The overall color difference was expressed as $\triangle E$,

$$\triangle E=\sqrt{(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2} \tag{2}$$

where,

$$\Delta L^* = L_1^* - L_0^* \tag{3}$$

$$\Delta a^* = a_1^* - a_0^* \tag{4}$$

$$\Delta b^* = b_1^* - b_0^* \tag{5}$$

and where L_0^*, a_0^*, b_0^* and L_1^*, a_1^*, b_1^* denote the brightness index, red-green index, yellow-blue index of the wood before and after the treatment, respectively.

Measurements of oxygen index

The oxygen index of the wood specimens was determined at room temperature using a JL-JF-5 fully automatic oxygen index tester. The wood specimens were cut into sizes of 50 mm (*T*) × 10 mm (*L*) × 2 mm (*R*), and 15 specimens were prepared for each group. The test was carried out using the tip ignition method, where the wood specimens were fixed vertically in the centre of the burning cylinder. When the test reached a predetermined oxygen concentration, the ignition test was started on the top of the specimens. The oxygen index was calculated using the following equation,

$$\mathrm{LOI} = V_\mathrm{O}/(V_\mathrm{O}+V_\mathrm{N})\times 100\% \tag{6}$$

where LOI is the value of limiting oxygen index (%); V_O is the lowest volume percentage of oxygen in the gas mixture at room temperature supporting a flame, and V_N is the volume percentage of nitrogen in the gas mixture at room temperature.

Measurement of microstructure

The microstructure of poplar veneer before and after modification was observed and analysed using a VEGA 3 SBH field emission scanning electron microscope. The chordal cuts of untreated, stained, flame-retarded, and flame-retarded stained lumber after drying treatment were glued to the carrier stage with conductive adhesive, vacuum ion-sprayed with a gold film, and the test voltage was 10 kV, respectively.

Measurement of chemical structure

A Tensor 11 Fourier Transform Infrared Spectrometer (FTIR) was used to analyse and characterise the changes in chemical structure of the veneer before and after modification. The specimens needed to be dried sufficiently before milling, and the specimens were baked until absolutely dry. A pulveriser was used to pulverise the wood specimens into a powder form that could pass a 120 mesh standard sieve. The FTIR tests were done under the following conditions: a scanning range of 4000 to 400 cm^{-1}, a scanning number of 32, and a resolution of 4 cm^{-1}.

Measurement of crystalline properties

The crystalline properties of the flame-retardant dyeing wood veneer were analysed using an XD6 polycrystalline X-ray diffractometer. The specimen was crushed with a pulveriser, passed through a 120 mesh sieve, and the wood powder was pressed into a thin slice at room temperature. Then the diffraction intensity curve of 2θ was made, with the scanning range of the sample of 2θ=10 to 50°, the scanning speed of 2°/min, and the scanning step size of 0.02°. The crystallinity of cellulose was calculated according to Segal’s method,

$$\mathrm{CrI} = (I_{002}-I_{\mathrm{am}})/I_{002}\times 100\% \tag{7}$$

where CrI is the value of oxygen index (%); I_{002} is the (002) crystal plane diffraction intensity, representing the crystalline region of cellulose; and I_{am} is the diffraction intensity of the amorphous region.

Measurement of thermal stability

The thermal stability of untreated and flame-retarded dyed materials was analysed using a thermogravimetric analyser type TG 209 F3 Tarsus. The specimens were crushed with a pulveriser, passed through a 120 mesh sieve, weighed 5 to 10 mg of powder, and put into the thermogravimetric analyser for testing, and the temperature was increased from room temperature to 700 °C under nitrogen atmosphere at an increase rate of 10 °C/min.

Cone calorimetry test

With reference to the ISO5660 standard, the flame retardant properties of untreated poplar plywood, dyed poplar plywood, flame retardant poplar plywood, and flame retardant dyed poplar plywood were tested using a cone calorimeter with a radiation intensity of 50 kW/m^2. Prior to testing, the bottom and sides of the samples were wrapped in an aluminium box. Two samples were tested in the horizontal direction and the average of the two replicate samples was taken. In this case, four different types of poplar plywood were prepared as follows: After drying at room temperature, the poplar wood was sawn into veneer specimens of 100 mm (*T*) × 100 mm (*L*) × 2 mm (*R*), and the veneer was impregnated with 0.5% acid red dye solution for 3 h under the condition of 80 °C. At the end of the test, the veneer was removed and the residue on the surface was continuously washed with pure water. The stained veneer was obtained by naturally drying the veneer to a moisture content of 8 to 10% at room temperature. Same as for the above dyeing veneer preparation process, flame-retardant veneer was prepared under set conditions: water bath temperature 80 °C, flame-retardant concentration of 30%, and time 3 hours. Preparation of flame retardant dyeing veneer was done under the following set conditions: water bath temperature 80 °C, flame retardant concentration of 30%, the dye concentration of 0.5%, and time 3 h. Four types of veneer were prepared: untreated veneer, dyeing veneer, flame retardant veneer, and flame retardant.

Following the preparation method of Hu (2013), the prepared adhesive was evenly applied to the surface of various poplar veneers at a coating level of 200 g/m^2 (one side) and bonded to the common plywood substrate. The untreated poplar plywood, stained plywood, flame-retardant plywood, and flame-retardant stained plywood were obtained after the hot-pressing treatment and were recorded as U-Pl, D-Pl, FR/Pl, and D/FR-Pl, respectively, where the parameters of the plywood hot-pressing process were set as follows: unit pressure of 1.5 MPa, pressing temperature of 120 °C, and hot-pressing time of 10 min.

RESULTS AND DISCUSSION

Effect of Various Factors on Dye-uptake, Color Difference, and Oxygen Index

Flame retardant concentration

Under the condition of dye concentration of 1%, temperature of 80 °C, and treatment time of 2 h, the effects of flame retardant concentration on dye-uptake, color difference, and limiting oxygen index of poplar veneer are shown in Fig. 4. From the figure, it can be seen that the addition of flame retardant played a certain role in promoting dye-uptake, colour difference, and limiting oxygen index. Among them, with the increasing concentration of flame retardant (ADP), the dye-uptake, and colour difference of poplar veneer showed a trend of increasing and then decreasing. When the concentration of ADP was 15%, dye-uptake reached the maximum value of 15.3%. This is mainly attributed to the fact that ADP is a nitrogen-phosphorus inorganic flame retardant that is soluble in water. (Duan *et al.* 2003; Gu *et al.* 2007; Zheng *et al.* 2016; Yu 2017; Wang 2020b). However, when the concentration of the flame retardant is increased, the dye-uptake gradually decreases. This is attributed to a larger number of flame retardant molecules occupying the pores of the wood, such as conduits and grain holes, which is not favorable to the diffusion of dye molecules (Wang *et al.* 2016).

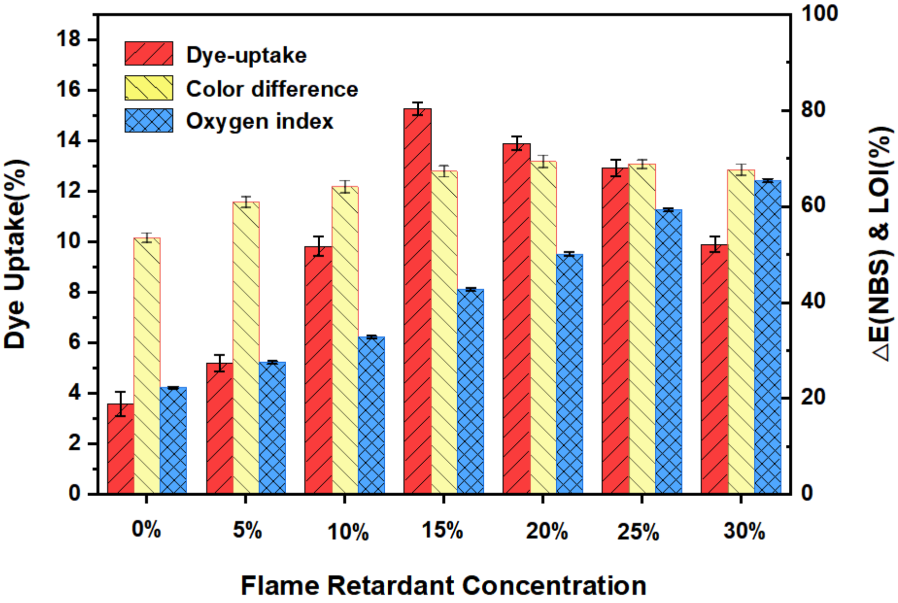

Fig. 4. The effect of flame retardant concentration on dye-uptake, color difference and oxygen index

When ADP was not added to the dye solution, the minimum value of colour difference was 53.5 NBS, at which time the surface colour of the veneer was light and the dyeing was not uniform. When ADP was added to the dye solution, the surface colour of the veneer gradually became uniform and vivid, and when the ADP concentration was 20%, the veneer colour difference reached a maximum value of 69.4 NBS. However, by continuing to increase the concentration of ADP, the veneer colour difference value decreased slightly and the surface colour appeared slightly darker.

However, unlike the dye-uptake and colour difference, the flame retardant (ADP) was positively correlated with the oxygen index change law, and the oxygen index increased as the ADP concentration continued to increase. The oxygen index reached a maximum value of 65.4% when the ADP concentration was 30%. By increasing the concentration of the flame retardant, the opportunity for the flame retardant to penetrate the interior of the wood increases. In addition, more flame retardant molecules occupy cell cavities, wood vessels, and pores in preference to dye molecules, thus impeding penetration of dye molecules.

Dye concentration

Under the condition of flame retardant concentration of 20%, temperature of 80 °C and treatment time of 2 h, the effects of dye concentration on dye-uptake, color difference and oxygen index of poplar veneer were shown in Fig. 5.

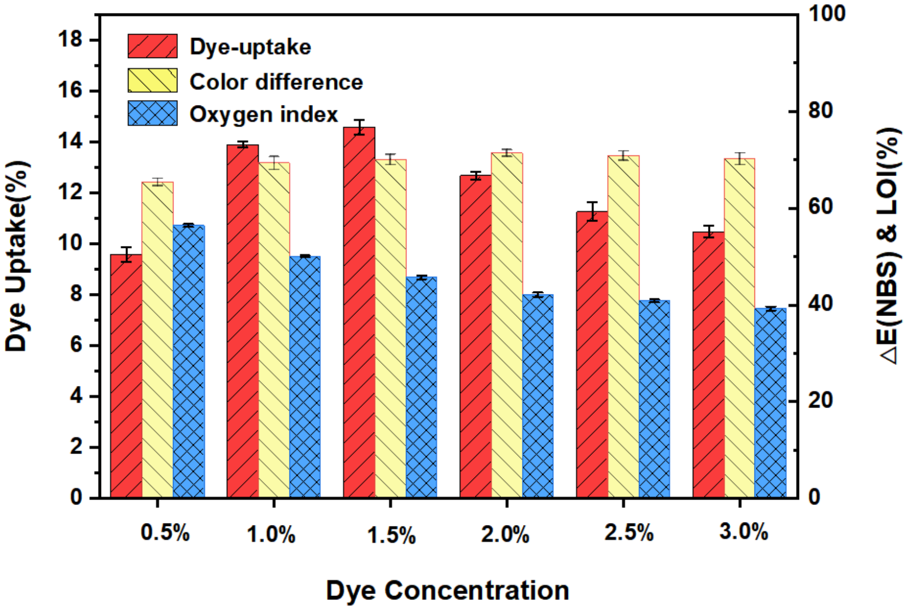

Fig. 5. The effect of dye concentration on dye-uptake, color difference and oxygen index

With the increase of the dye concentration, dye-uptake showed a trend of first increasing and then decreasing. When the dye concentration grew from 0.5% to 1.5%, the dye-uptake increased all the time and reached a maximum value of 14.58% at a dye concentration of 1.5%. However, by continuing to increase dye concentration, the dye-uptake started to decrease. When the dye concentration was low, increasing the dye concentration allowed more dye molecules to enter the wood, resulting in an increase in the dye-uptake. However, high concentration of dye is not conducive to the penetration of dye molecules inside the wood, and too many dye molecules were prone to agglomeration, resulting in poor mobility, which hindered the diffusion of dye molecules (Wang *et al.* 2018). The colour difference showed a similar trend with the dye-uptake, when the dye concentration was increased from 0.5% to 2%, the colour difference also increased from 65.45 NBS at the beginning to the maximum value of 71.46 NBS, which was an increase of 9.18%, and when the dye concentration was continued to be increased, the colour difference was slightly decreased, and basically reached the saturation state. Unlike the dye-uptake and color difference, the oxygen index decreased and then leveled off as the dye concentration increased, with a maximum of 56.4% at a dye concentration of 0.5%. When the dye concentration was increased to 3%, the oxygen index decreased by 30.5% to a minimum of 39.2%.

Temperature

Under the condition that the concentration of flame retardant was 20%, the concentration of dye was 1%, and the treatment time was 2 h, the influences of temperature on the dye-uptake, color difference and oxygen index of poplar veneer were shown in Fig. 6. As the temperature rose, the dye-uptake, color difference and oxygen index generally had a similar law of change, showing a trend of first increase and then decrease. At the temperature of 80 °C, all three reached their maximum value, which at this time, the dye-uptake was 13.89%, the maximum value of color difference was 69.38 NBS, and the maximum oxygen index was 50.1%. However, when the temperature continued to increase to 90 °C, all three began to decline. This is mainly because when the temperature was too high, the movement of dye molecules and flame retardant molecules were intense, resulting in decomposition of a portion of the dyes and flame retardants, and there was also a phenomenon of color bloom, which led to the dye-uptake, color difference, and oxygen index, showing a decreasing trend (Gu *et al.* 2007; Wang *et al.* 2016b).

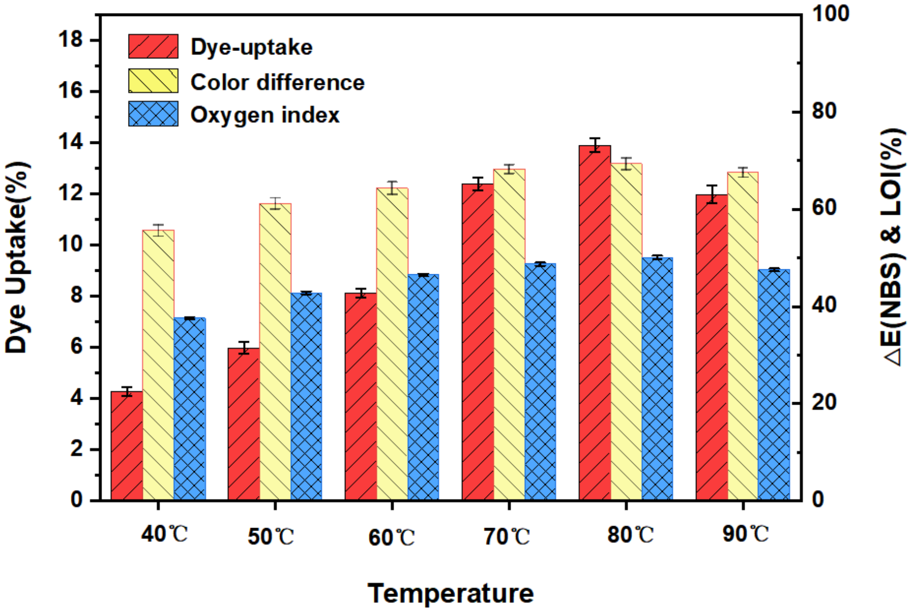

Fig. 6. The effect of temperature on dye-uptake, color difference and oxygen index

Time

Under the condition that the concentration of flame retardant was 20%, the concentration of dye was 1%, and the temperature was 80 °C, the effects of time on the dye-uptake, color difference and oxygen index of the veneer are shown in Fig. 7. With the prolongation of impregnation time, the dye-uptake and color difference of the veneer showed the trend of increasing and then decreasing, while the oxygen index had been increasing. At the impregnation time of 0.5 h, the dye-uptake, color difference and oxygen index reached the minimum values of 5.13%, 56.51 NBS, and 34.5%, respectively. At an impregnation time of 2 h, the dye-uptake reached a maximum value of 13.89%, which was 170.8% higher than the impregnation time of 0.5 h. However, with further extension of time, the dye-uptake slightly decreased, which could be caused by the evaporation of water from the solution. When the impregnation time was 3 h, the color difference reached the maximum value of 69.56 NBS, an increase of 22.9% compared with the impregnation time of 0.5 h. When the impregnation time was 4 h, the color difference was slightly decreased, indicating that at this time the dye dyeing to the inside of the veneer had reached a saturated state in the dynamic equilibrium of adsorption and desorption. When the impregnation time was extended from 0.5 to 2 h, the oxygen index increased; however, when the impregnation time was extended, the oxygen index leveled off and increased slightly.

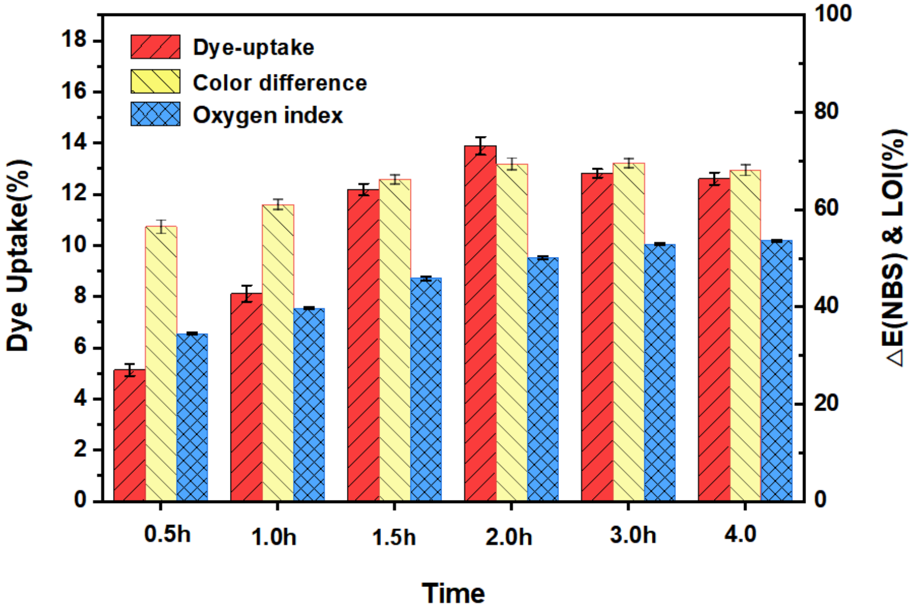

Fig. 7. The effect of time on dye-uptake, color difference and oxygen index

Analysis of Micromorphology

In order to observe the microscopic morphology and distribution of the flame retardant and dye molecules in the wood, scanning electron microscopy (SEM) was carried out on the untreated, dyed, flame retardant, and flame retardant-dyed wood, respectively. Wood is a porous material and there are many voids between the wood fibers, as can be seen from the untreated, smooth veneer conduit inner wall surface, in which grain holes are clearly visible and there is no particles filler (Fig. 8a and e). The dyed wood veneer has some small particles aggregated near the catheter, and the perforations are surrounded by aggregated small molecules of dye, however, the inner wall of the catheter is still relatively smooth at this point (Fig. 8b and f). Unlike the dyed veneer, the aggregated particles of the flame retardant molecules were larger and the surface of the conduit also appeared to be rough, and the pores of the cell wall became smaller, which could be attributed to the fact that the concentration of the added flame retardant (30%) was much larger than that of the dye (0.5%), and the aggregation was higher, and a large number of flame retardant molecules adhered to the vicinity of the conduit and filled the striated pores in the cell wall (Fig. 8c and g). The above phenomena appear to be more prominent in the specimens after the simultaneous treatment with dye and flame retardant, in which the grain holes were densely filled with flame retardant and dye molecules, the aggregated particles were larger, and the roughness of the inner wall of the conduit was increased (Fig. 8d and h).

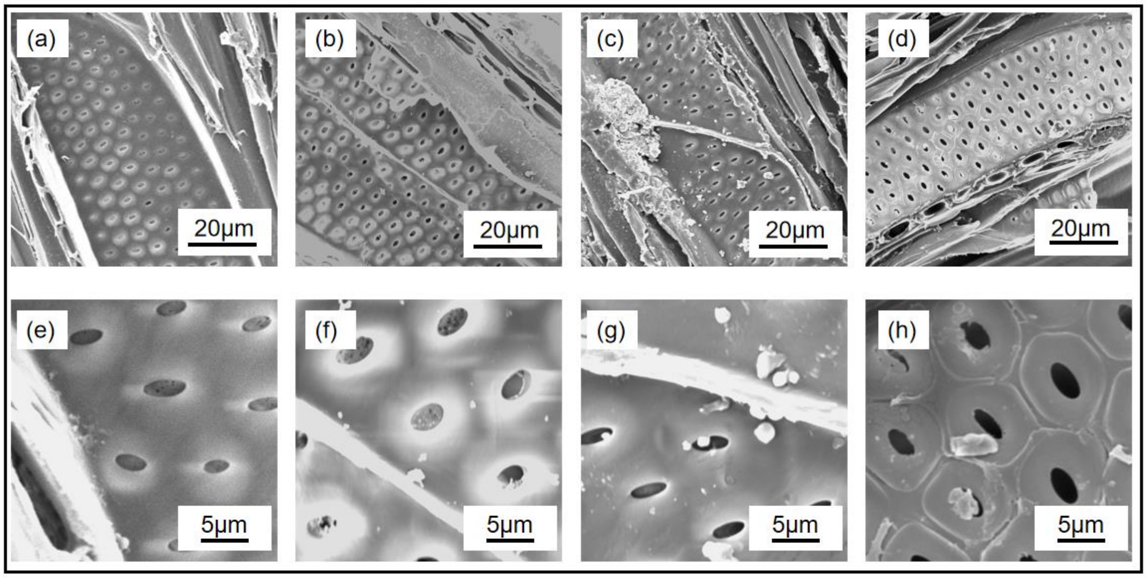

Fig. 8. The SEM image of wood. a & e: control wood; b & f: dyed wood; c &g: flame retardant wood; d & h: dyed and flame retardant wood

Analysis of FTIR

To study the modification mechanism of flame-retardant dye-modified solutions on wood, they are analyzed by FTIR spectroscopy, in which the FTIR spectra of untreated, dyed, flame-retardant and flame-retardant dye-modified wood are shown in Fig. 9. The absorption peaks generated at 3341 cm^{-1} were from O-H stretching vibrations in cellulose, hemicellulose, and lignin (Carmen *et al.* 2007). After the veneer was treated with ADP, the band of hydroxyl absorption peaks was significantly broadened and reduced in intensity, indicating that the number of hydroxyl groups was reduced. This is due to the presence of N and P elements in ammonium dihydrogen phosphate, which have a synergistic effect, the decomposition of ammonium dihydrogen phosphate to produce phosphoric acid that will graft with free hydroxyl groups, and the heat treatment during the test process, which also leads to a weakening of the intensity of the hydroxyl absorption peaks (Haji *et al.* 2021). The absorption peak at 2867 cm^{-1} is a C-H stretching vibration, and ADP treatment caused the C-H bond to be broken, and the intensity of the absorption peak was weakened, which indicates that the hydrolysis of polysaccharides such as cellulose and hemicellulose occurs under the catalytic action of high-temperature acid. The absorption peak located at 1713 cm^{-1} is the C=O stretching vibration in the non-conjugated carbonyl group of hemicellulose/lignin, and the intensity of the absorption peak was weakened by ADP treatment, which indicates that the wood leads to the shedding of the acetyl group under acidic conditions. The absorption peak at 1443 cm^{-1} of the untreated veneer is attributed to C-H bending vibration, which is enhanced by ADP treatment, which is likely to be due to the substitution of C atoms by N atoms in the flame retardant, resulting in N-H bending vibration peaks. The weaker absorption peaks at 887 cm^{-1} were the C-H in-plane deformation vibration, as well as the C-O stretching vibration in cellulose, which became weaker after ADP treatment, which was mainly attributed to the P-O asymmetric stretching vibration of the flame retardant P-O-P. Compared to the untreated veneer, a new absorption peak was generated at 538 cm^{-1} and was the P=O stretching vibration, suggesting that ADP had a condensation reaction with lignin (Wang *et al.* 2016b). As can be seen from Fig. 9. the absorption spectra of the veneer specimens treated with ADP only and the veneer specimens treated with ADP/acidic Big Red composite modification were roughly similar, and no new absorption peaks were generated, suggesting that there was no chemical reaction between ADP and the acidic red dye.

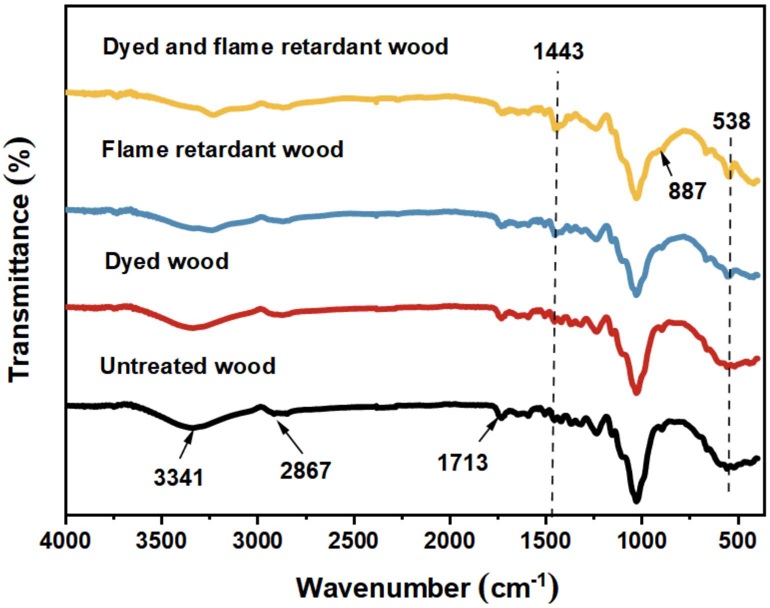

Fig. 9. The FTIR spectrogram of wood veneer after different treatments

Analysis of Crystalline Properties

The XRD spectra of untreated, dyed, flame-retarded, and flame-retarded dye-modified veneer are shown in Fig. 10. Three main XRD diffraction peaks appeared in the untreated wood, at the positions of 15.6°, 22.3°, and 33.5°, which corresponded to the wood cellulose crystallographic surfaces (101), (002), and (040), respectively (Chen and Chen 2014). Three new peaks (1), (2), and (3) appeared in the ADP-treated wood, which were mainly caused by the crystallization region of the flame retardant ADP (Xu *et al.* 2023). It is not difficult to find that the shape of the diffraction peaks of the stained veneer is roughly similar to that of the untreated veneer, and the position of the peaks has not changed, and that there is no significant difference compared with the untreated veneer.

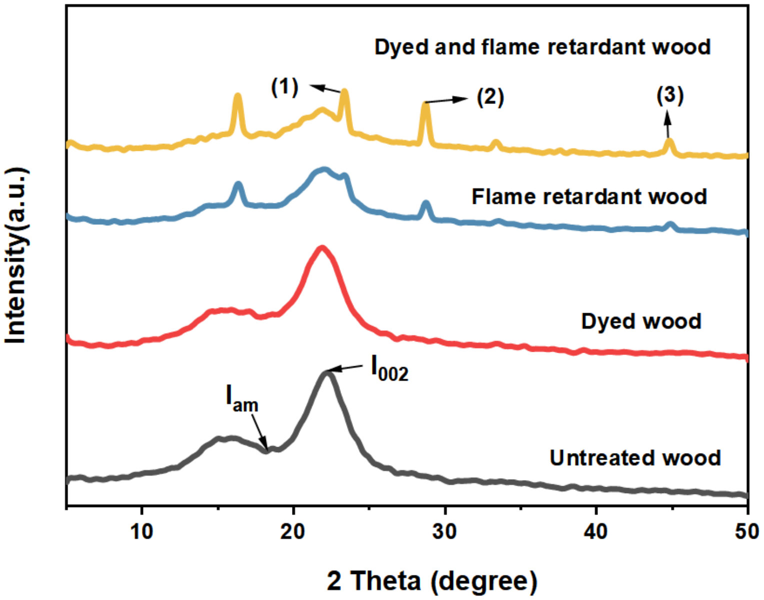

Fig. 10. The XRD spectrogram of wood veneer after different treatments

In addition, in order to more intuitively describe the changes that occur in the cellulose crystalline zone before and after poplar veneer modification, the crystallinity can also be calculated by the Segal method, and the crystallinity of different wood specimens is shown in Table 2. The crystallinity of the untreated veneer was 59.73%, which was slightly increased after either flame retardant or dyeing treatment. Due to the combined effect of hydrothermal treatment and ammonium dihydrogen phosphate, the crystallinity of the veneer was higher than that of both dyed and flame-retarded veneer after combined flame-retarded and dyed treatment.

Table 2. Crystallinity of Different Wood Specimens

Samples	CrI/%
Control Wood	59.73
Dyed Wood	60.31
Flame Retardant Wood	60.70
Dyed and Flame Retardant Wood	62.65

Analysis of Thermal Stability

To study the effect of simultaneous treatment of flame retardant dyeing on the thermal stability of wood, TG and DTG analyses were carried out on the four kinds of wood. The mass loss curve (TG) and the rate of weight loss curve (DTG) of wood specimens heated continuously from room temperature to 700 °C are shown in Fig. 11.

For untreated wood, thermal degradation is mainly divided into the following stages: firstly, heating from room temperature to about 120 °C, mainly the evaporation of water within the wood, dehydration and drying stage. Secondly, continuously heating to about 250 °C, the wood began to sharply thermal decomposition, into the wood pre-charring stage, in which the wood within the hemicellulose and cellulose mainly in this stage of thermal decomposition, and part of the lignin was also decomposed in this temperature range, this stage had been continued to about 400 ℃. Finally, the heating was continued to 700 °C, the weight loss started to slow down, some charring residues were formed, and the wood specimen entered the final charring stage. Combined with Table 3, the residual charcoal rate of dyed wood is higher than that of untreated wood, which is mainly due to the fact that acid scarlet 3R is an azo acid dye with a more stable molecular structure. It is not difficult to find that the initial decomposition temperature of flame-retardant treated wood is reduced, and the thermal decomposition temperature range is increased. It can be seen that there are two maximal peaks in the thermal decomposition mass loss rate curve of flame-retardant treated wood, whereas there is only one maximal peak in the thermal decomposition mass loss rate curves of untreated wood and dyed wood, and the initial decomposition temperature of flame-retardant treated wood is reduced by about 40 ℃ compared with that of untreated wood. In addition, the residual charcoal rate of the flame retardant treated wood is much higher than that of the untreated wood, and the mass loss rate is significantly reduced. The residual charcoal rates of the flame retardant wood and the flame retardant dyed synchronous treated wood are 2.67 and 2.96 times higher than those of untreated wood, which indicated that wood has a good thermal stability after the flame retardant treatment, and it can delay the thermal degradation of wood, and promote wood carbonization, thus improving the residual charcoal rate. The analysis of ADP wood flame retardant mechanism, which is mainly because ADP thermal decomposition releases water and non-combustible gases, dilute the volatile combustibles of wood pyrolysis, and produce a layer of non-combustible coating on the surface of wood, nitrogen-phosphorus flame retardant mainly catalytic pyrolysis reaction of wood, and produce a coating that conducts heat fast, which reduces pyrolysis reaction activation energy, so that wood pyrolysis reaction occurs at a lower temperature. In addition, ADP will absorb a large amount of heat in the combustion process, reducing the wood decomposition temperature, resulting in residual charcoal rate that will be significantly increased (Yan *et al.* 2015; Cui and Yan 2018; Kong *et al.* 2018; Haji *et al.* 2021).

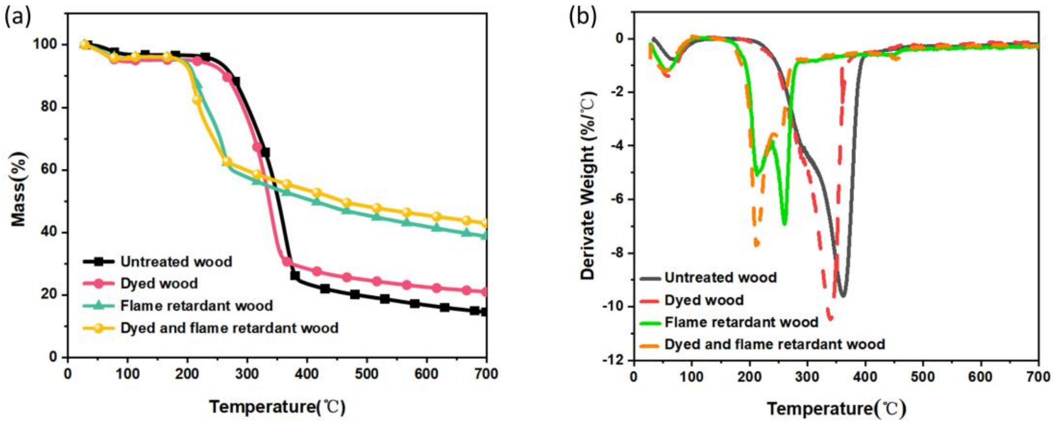

Fig. 11. Graphs of thermal stability of wood specimens after different treatments. a: TG curves; b: DTG curves

Table 3. Thermal Degradation Parameters of Untreated and Treated Wood

Samples	$T_{10\%}$ (°C)	T_{max} (°C)	Carbon Residue Ratio (%)
Control Wood	277.44	362.65	14.54
Dyed Wood	267.47	338.28	20.95
Flame Retardant Wood	210.32	261.15	38.80
Dyed and Flame Retardant Wood	203.91	212.41	43.08

Note: $T_{10\%}$ is the temperature corresponding to 10% loss of mass for different wood specimens. T_{max} is the temperature at which the rate of weight loss of different wood specimens reaches its maximum.

Cone Calorimetry Test

The morphology of untreated poplar plywood, dyed poplar plywood, fire-retardant poplar plywood, and fire-retardant dyed poplar plywood after burning is shown in Fig. 12. Untreated poplar plywood and dyed poplar plywood were more white powder and less charcoal black solid after burning. The black solid of the fire retardant-treated poplar plywood increased significantly after burning, indicating that the fire retardant treatment promoted the charring of wood.

Fig. 12. The appearance of wood after burning: (a) U-Pl, (b) D-Pl, (c) FR-P, (d) D/FR-Pl

Figure 13 shows the graphs of HRR and THR of untreated poplar plywood (U-Pl), dyed poplar plywood (D-Pl), fire-retardant poplar plywood (FR-Pl), and fire-retardant dyed poplar plywood (D/FR-Pl) with respect to the burning time; Fig. 14 shows the graphs of SPR and TSP of untreated poplar plywood (U-Pl), dyed poplar plywood (D-Pl), fire-retardant poplar plywood (FR-Pl), and fire-retardant dyed poplar plywood (D/FR-Pl) with respect to the burning time; Fig. 15 shows the graphs of mass versus burning time for untreated poplar plywood (U-Pl), dyed poplar plywood (D-Pl), fire-retardant poplar plywood (FR-Pl), and fire-retardant dyed poplar plywood (D/FR-Pl), and the results of the test data for the specific and detailed cone-heat-related parameters are shown in Table 4.

Table 4. Cone Calorimetry Test Result Data of the Untreated and Dyed and Flame-retardant Treated Poplar Plywood

Samples	TTI (s)	HRR (kW/m^2)		THR (MJ/m^2)	TSP (m^2)	Mass (%)	CO production rate (kg/kg)	CO$_2$ production rate (kg/kg)
		average value	peak value					
U-Pl	14	111.04	489.56	112.71	1.44	16.27	0.2324	4.9661
D-Pl	15	106.93	436.92	119.39	1.81	18.63	0.2413	4.7877
FR-Pl	13	99.02	440.59	103.77	2.65	19.52	0.3319	4.6018
D/FR-Pl	12	99.43	362.59	106.07	2.39	20.59	0.2826	3.8960

From Table 4 it can be seen that the ignition time of U-Pl and D-Pl is 14 s and 15 s, respectively, after treatment with 30% concentration of flame retardant. The ignition time of FR-Pl and D/FR-Pl is 13 s and 12 s, respectively, and the ignition time is shortened by 1 s and 2 s compared to that of U-Pl, which indicates that the flame retardant treatment does not play a role in prolonging the ignition time. This is because ammonium phosphate flame retardants generate acidic substances under heating conditions, and the wood decomposes in advance (Hu et al. 2015; Zheng and Guo 2020).

The Heat Release Rate (HRR) is the amount of heat released per unit time when a sample burns at a fixed intensity of radiant flux. The higher the average HRR and the higher the peak HRR, the more likely the material is to ignite. Total Heat Release (THR) is the total heat released from ignition to extinction of the specimen under a given intensity of thermal radiation flow. The total heat release reflects the degree of combustion of the sample and the higher the value, the more complete the combustion and the greater the risk factor.

As can be seen from Fig. 14, the combustion process of different plywood specimens is basically the same: in the first 400 s, it is mainly caused by the combustion of veneer of different specimens; in the range of 400 s~600 s, it is mainly caused by the combustion of plywood substrate; and after 600 s, the specimens basically burn out and enter the final charring stage. Combined with the data in Table 4, it can be seen that the average and maximum heat release rate peaks of U-Pl were 111.04 kW/m^2 and 489.56 kW/m^2, respectively, and the average and maximum heat release rate peaks of D-Pl were 106.93 kW/m^2 and 436.92 kW/m^2, respectively, which shows that the addition of dyes does not play a positive role in the flame retardancy of untreated poplar plywood. After the flame-retardant dye treatment, the average and maximum heat release rates of D/FR-Pl were 99.43 kW/m^2 and 362.59 kW/m^2, respectively, which were 10.46% and 25.94% lower than those of U-Pl, indicating that the flame-retardant treatment reduced the heat release rate of U-Pl and played a better flame-retardant effect.

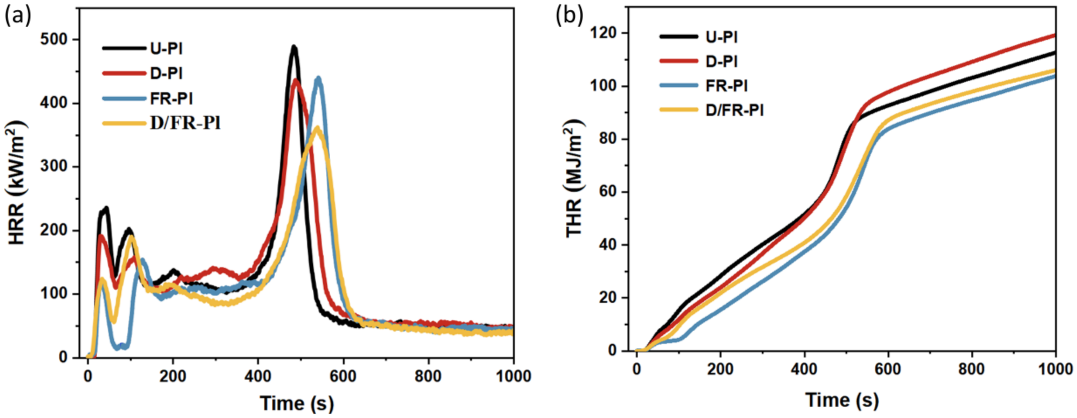

Fig. 13. Curves of U-Pl, D-Pl, FR-Pl and D/FR-P. a: HRR; b: THR

In addition, similar to the results obtained by HRR, the THR of the samples after flame retardant dyeing treatment decreased significantly, with the THR of U-Pl being 112.71 MJ/m^2 and that of D-Pl increasing compared to U-Pl, but the change was not significant. After flame retardant treatment, the THR of FR and D/FR-Pl was obviously lower than that of U-Pl, and the THR curve also gradually slowed down, and the onset of the faster rate of increase was also shifted back compared to that of U-Pl. This is mainly because the phosphorus-containing compounds in the flame retardant and the charcoal layer formed a cross-linking structure between them, which reduced the total amount of combustible gases (CO, CH_4, C_2H_6) and was able to effectively inhibit or mitigate the continuous and further combustion reaction of the wood, and improved the fire resistance of the wood to a great extent (Pan *et al*. 2021; Phromsaen *et al*. 2014).

In real life fires, people's lives are endangered mainly by the smoke and toxic gases in the fire, which can cause death by asphyxiation or poisoning to the point of life-threatening. From Fig.14 combined with the data in Table 4, it can be seen that the SPR peak of D-Pl does not change much compared to that of U-Pl, while the SPR peaks of FR-Pl and D/FR-Pl are higher than that of U-Pl after flame retardant treatment, and the rate of smoke production in the early stage of combustion is accelerated, which is mainly related to its smoke particles composed of small molecules such as NH_3, P, PO, PO_2 and HPO2 produced in the process of combustion. related. At the end of the test, the TSP of U-Pl was 1.44m^2 and D-Pl, FR-Pl and D/FR-Pl increased by 25.69%, 84.03% and 65.97% respectively compared to U-Pl. Among them, the amount of smoke generation increased significantly after the fire retardant treatment, which was mainly due to the fact that the wood would be extinguished quickly after ignition, resulting in the phenomenon of cloudy ignition, in addition, the char layer produced during the combustion process would decompose at high temperatures, leading to an increase in the SPR and TSP of the wood.

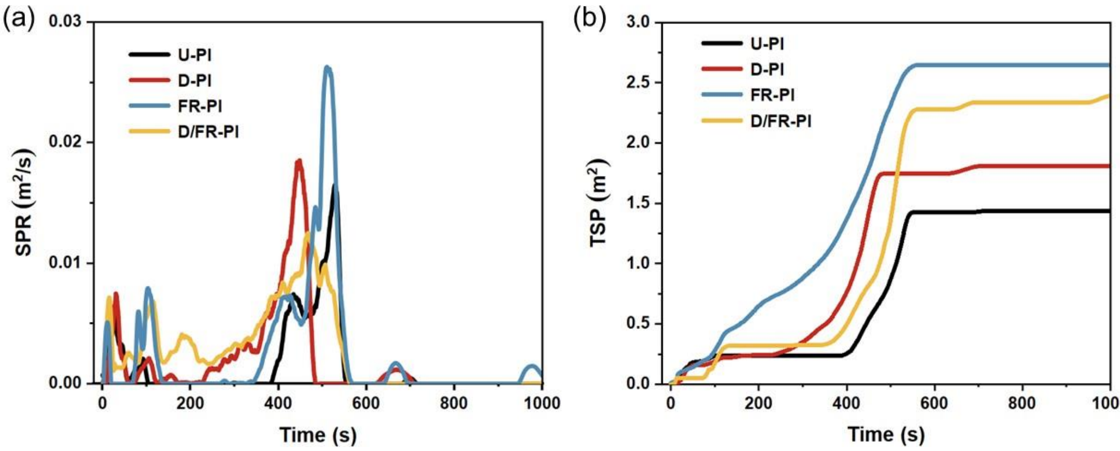

Fig. 14. The curves of U-Pl, D-Pl, FR-Pl, and D/FR-Pl. a: SPR; b: TSP

Residual mass (mass) refers to the mass of material remaining after combustion over time during the combustion process and is often expressed as a percentage (%). The greater the loss of mass, the more combustible the material and the greater the fire hazard.

From Fig.15, it can be seen that the trend of the mass change curves of U-Pl, D-Pl, FR-Pl, and D/FR-Pl is basically the same, and the mass loss is mainly concentrated in the first 600 s. When the mass loss is the same, the time corresponding to FR-Pl and D/FR-Pl is longer than that corresponding to U-Pl, which indicates that the flame retardant treatment can slow down the mass loss time of the samples so that the samples are more difficult to burn. In addition, the residual mass of U-Pl is 16.27% and that of D/FR-Pl is 20.60%, which is 27.84% higher than that of U-Pl. The results show that the specimens treated with flame retardant can delay the time of mass loss, increase the amount of residual carbon after burning, and improve the flame retardant property.

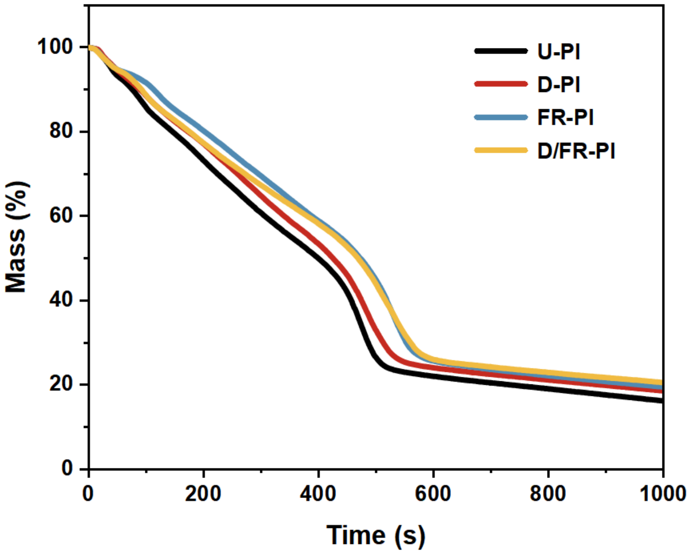

Fig. 15. Mass loss curves of U-Pl, D-Pl, FR-Pl, and D/FR-Pl

CONCLUSIONS

With the increase of flame retardant concentration, dye concentration, temperature and impregnation time, the dye-uptake and color difference showed the rule of change of first increase and then decrease. When the flame retardant concentration, dye concentration, temperature, and impregnation time were 15%, 1.5%, 80 ℃, and 2 h, respectively, the dye-uptake reached the maximum value. When the flame retardant concentration, dye concentration, temperature, and impregnation time were 20%, 2%, 80 ℃, and 3 h, respectively, the colour difference reached the maximum value. However, the oxygen index was increasing with the increase of flame retardant concentration, decreasing with the increase of dye concentration, increasing firstly and then decreasing with the increase of temperature, and increasing firstly significantly and then increasing slightly with the prolongation of impregnation time, and tending to a flat trend. The oxygen index was maximized at flame retardant concentration, dye concentration, temperature, and impregnation time of 30%, 0.5%, 80 °C, and 4 h, respectively.

ADP is both a flame retardant and a dye promoter. When dissolved in water, it produces a large number of NH_4^+ ions, which can accelerate the rate of transfer of dye molecules to the wood, thus increasing the utilization of the dye and the dye-uptake. However, too much ammonium dihydrogen phosphate will hinder the diffusion and penetration of dye molecules into the wood, resulting in a decrease in the dye-uptake. The increase in dye concentration does not favor the penetration of flame retardant molecules into the wood interior, leading to a decrease in oxygen index.

Too high a concentration of ammonium dihydrogen phosphate tended to cause intermolecular agglomeration, larger aggregated particles, and blocking the entry of dye molecules. Ammonium dihydrogen phosphate reacts chemically with wood to produce a new absorption peak, P-O-P, while no chemical reaction occurs with acid dyes. Improved crystallinity of flame retardant dyed poplar veneer compared to untreated poplar veneer. After ADP treatment, the wood had good thermal stability, which can delay the thermal degradation of wood and promote the catalytic formation of charcoal.

The average heat release rate and the peak maximum heat release rate of the flame retardant dyed poplar plywood were 99.43 kW/m^2 and 362.59 kW/m^2, respectively, which decreased by 10.46% and 25.94% compared with that of the untreated poplar plywood, and the total heat release was also decreased from 112.71 to 106.07 MJ/m^2, and the mass of the residue was increased from the untreated poplar plywood by 27.84%. The phosphorus-containing compounds in the fire retardant formed a cross-linking structure with the charcoal layer, which could effectively inhibit or mitigate the continuous and further combustion reaction of the wood and improve the fire resistance of the wood to a large extent. However, after treatment with 30% concentration of ammonium dihydrogen phosphate, the amount of smoke production increased significantly, and the total smoke production (TSP) of fire retardant dyed poplar plywood increased by 65.97% compared with that of untreated poplar plywood.

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