

ASSESSMENT OF THE DYEING PROPERTIES OF MAPLE VENEER TREATED BY DICHLOROTRIAZINE REACTIVE DYE BASED ON FUZZY COMPREHENSIVE EVALUATION

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INTRODUCTION

Effects of dye concentration, dyeing temperature and time, volume ratio, and dyeing assistant and fixing agent, fixing time on the dye-uptake and K/S were investigated with orthogonal experiments. The major factors on dye-uptake and K/S were identified using visual and variance analysis. Dye-uptake and K/S were synthetically evaluated and optimally selected with fuzzy comprehensive evaluation. Results showed that dye concentration and temperature were significantly affected by all the seven factors during dyeing process on dye-uptake and K/S. The optimal parameters for the dye effect of maple veneer were: temperature 65.0°C, dye concentration 3.0 %, dyeing assistant 40.0 g.L⁻¹, dyeing time 3.0 hours, fixing agent 20.0 g.L⁻¹, fixing time 10.0 minutes, volume ratio 1:20. Additionally, attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDX) results indicated that reactive dyes were combined with maple fiber and diffused into the wood lumen and wood ray. X-ray diffraction (XRD) results indicated the intensive of crystallinity in the dyed wood was declined due to the dichlorotriazine reactive dye. Furthermore, thermogravimetric analysis (TGA) demonstrated that the residue of dyed veneer was higher than undyed, and the temperature at maximum degradation rate of dyed and undyed veneer was different.

KEYWORDS: Wood dyeing; dichlorotriazine reactive dye; fuzzy comprehensive evaluation.

INTRODUCTION

In recent years, the supply of the natural forest quality wood is reduced due to the decreasing of forest area. Plantation forest has attracted substantial attention lately due to their advantages over natural forest, such as low cost, excellent quality, and high yield. In order to improve the

efficient use of plantation forest, the decorative effect value by dyeing precious wood imitatively (Liu et al. 2015a, b, c). Moreover, dyed wood could be satisfied to people's requirements on color diversity. Therefore, dyeing is commonly used in the field of wood processing.

Rattee (1962) found that the reactive dyes had made possible the development of methods for linking the dyeing and finishing processes in 1962, which offered considerable economy in operating costs because of the simplicity of the operations and the streamlining of production, and at the same time dye consumption was markedly reduced as a result of the very high degree of fixation obtained. Due to these advantages, reactive dyes have become the main dyes for printing and dyeing, which gradually replaced direct dyes, sulfur dyes, vat dyes (Zhang and Yang 2008). Dichlorotriazine (DCT) type reactive dyes, first produced by British ICI company, are made by the reaction of dye with ammonium group and cyanuric chloride. Dichlorotriazine reactive dyes possess two chlorine substituent groups and the higher activity guaranteed their application at lower temperature. So compared to monochlorotriazine reactive dyes, the dichlorotriazine type reactive dyes have been widely used (Perkins 1996).

Compare to direct dyes, basic dyes and acid dyes, dichlorotriazinereactive dye was optimal dye to imitate rosewood (Huang and Luo 1997). Chen et al. (1999) proposed that reactive dyes contain reactive groups, which could reactive with the hydroxyl groups of wood by covalent bonds (Chen et al. 1999). Bifunctional reactive dyes had been considered in wood dyeing by Xu (2001), Deng et al. (2004), Liao et al. (2005; 2006). But little attention has been devoted to the mechanism between dyes and wood. In addition, there has been much research on vinyl sulfone reactive dyes, monochlorotriazine reactive dyes and double-monochlorotriazine reactive dyes by Zhou (2003), Li (2010, 2011), Lv (2012), Li (2014), Yu et al. (2015). However, little work has been devoted to considering the comprehensive evaluation of two results to obtain the optimal process even dye-uptake or color difference was tested. In addition, quite few researches has been done regarding the property of dichlorotriazine reactive dyes (Huang and Luo 1997; Guo and Cao 2009; Zhou 2003; Liu 2011; Guan 2011; Li 2013; Yu 2014; Yu et al. 2015). Guo and Cao (2009) studied on the effect of reactive dye on bonding performance of dyed veneers. Huang, Liu and Guan explored the effect of imitating color matching. The mechanism of reactive dyes and wood has been considered by Li (2013), Yu (2014), Yu et al. (2015).

In this study, we aimed to investigate the effects of dichlorotriazinereactive dye on dyeing maple veneer. Effects of various factors were explored on dye-uptake and K/S. To obtain the optimal experimental parameters for dyeing maple veneer with fuzzy comprehensive evaluation. Additionally, FTIR, SEM, and EDX were used to explore the mechanism of interaction between dye molecules and wood fiber. TGA was used to investigate the stability of dyed maple veneer. XRD will help us to consider the changes of crystallinity with dyed maple veneer. The results of this study would provide better insight to scholars in the field of the combination of dichlorotriazine reactive dye and wood, and then, may help produce a dye which is suitable for dyeing wood.

MATERIAL AND METHODS

Materials

The maple was peeled and then tailored into 10×30×0.5 mm veneers. The veneers were air-dried to a moisture content of approximately 12 %. Reactive Brilliant Blue X-BR (C.I. Reactive Blue 4), which is a dichlorotriazine reactive dye mostly used in textile dyeing, was provided by Guang C. Dye Plant in Beijing, China. Sodium chloride was used as a dyeing assistant and sodium carbonate was used for fixing dyes. All of the additives were of reagent grade and provided by Yixiu B. Company (China).

Bleaching method

In order to eliminate the color difference between samples, the hydrogen peroxide (H_2O_2) was used as bleaching agent, and the sodium silicate as stabilizer. The maple veneers were treated in hydrogen peroxide solution with 3 % concentration, temperature 60.0°C, treating time 75.0 minutes, treating stabilizer 5.0 g.L⁻¹, and volume ratio ($V_{\text{wood veneer}}:V_{\text{bleaching bath}}$) 1:20.

Orthogonal dyeing experiment

A natural pressure dip-dye method was used for maple veneer dyeing. Wood veneers were horizontally immersed in the dye bath with spaces between each other to avoid overlapping and ensure leveling. Then, the dye bath was placed in an electro thermostatic water bath. Samples treated with varying experimental factors, such as dye concentration, dyeing time, temperature, amount of dyeing assistant and fixing agent, fixing time, and volume ratio ($V_{\text{wood veneer}}:V_{\text{dye bath}}$). After dyeing, the residual dyestuff on the surface of the dyed veneers was washed away by distilled water, and then dyed veneers air-dried to a moisture content of 12 %.

Then the major influencing factors on dye-uptake and K/S were identified via visual analysis and variance analysis. Finally, the dyeing process parameters were synthetically optimized by fuzzy comprehensive evaluation (FCE). The four levels of seven factors are listed in Tab. 1. The dye-uptake and K/S were measured according to the orthogonal table. Each combination was tested three times.

Tab. 1: Orthogonal factors and levels.

	Temperature (°C)	Dye concentration (%)	Dyeing assistant (g.L ⁻¹)	Dyeing time (h)	Fixing agent (g.L ⁻¹)	Fixing time (min)	Volume ratio ($V_{\text{wood veneer}}:V_{\text{dye bath}}$)
	T	DC	DA	DT	FA	FT	VR
1	35.0	0.5	20.0	0.5	10.0	30.0	1:15
2	45.0	1.0	30.0	1.0	15.0	45.0	1:20
3	55.0	2.0	40.0	2.0	20.0	60.0	1:30
4	65.0	3.0	50.0	3.0	25.0	75.0	1:40

Improving the dyeing quality of products is as important as reducing energy consumption, so dye-uptake which reflects the energy consumption and K/S which the dyeing quality should be comprehensively evaluated for the optimal dyeing process. Fuzzy comprehensive evaluation (FCE) was adopted to comprehensively evaluate two factors and determine the optimal dyeing parameters. It changed the qualitative evaluation into quantitative evaluation according to the fuzzy membership degree theory. And to make a comprehensive evaluation of multiple indices affected by various influence factors (Luo et al. 2014). The key of comprehensive evaluation is the weight vectors of evaluation indices. In this research, the expert evaluation method was used to determine the weight vectors. Expert evaluation, which is similar to peer review, is a method that the evaluation system and the weight vector of evaluation index is determined by intuitive assessment of the experts under their knowledge and experience. The evaluation results of this paper were the average results of eight experts in the field of wood dyeing. Considering the actual processing needs, the weight vectors of two comprehensive evaluation indices are as follows: (dye-uptake, K/S) are (0.2, 0.8), which means the dyeing effect is the primary review indicator.

Measurement of Dye -uptake

Dye-uptake was characterized by dye bath absorption, which expressed the degree of dye

transfer from dye bath to veneer. A double beam UV visible spectrophotometer (TU-1901, Beijing Purkinje General Instrument Co., Ltd, China) was used to measure the absorption at the maximum absorption wavelength (λ_{\max}). The maximum absorption wavelength of Reactive Brilliant Blue X-BR was 268 nm (Fig. 1). Ultimate dye-uptake stands for the percentage of the added dye that has transferred to the veneer. The dye-uptake was calculated as follows:

$$Ct = \frac{(A_0 - A_t)}{A_0} \times 100 \quad (1)$$

where: A_0 and A_t - the absorption of the dye liquor at λ_{\max} , which were from the control group and the experimental group, separately.

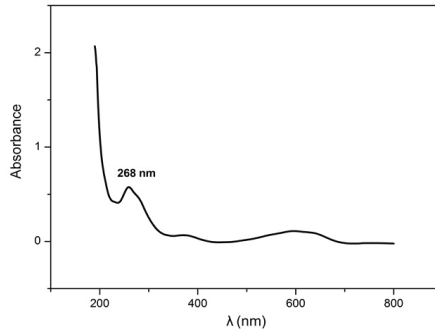


Fig. 1: Spectrum scanning curve of reactive brilliant blue X-BR.

Measurement of color

The surface reflectance of the samples was measured by colorimeters. The Kubelka-Munk equation provides for calculation of a ratio, K/S, from measured reflectance values as is shown in Eq. 2.

$$\frac{K}{S} = \frac{(1-R)^2}{2R} \quad (2)$$

where: K - the coefficient of absorption,
 S - the coefficient of scattering,
 R - the fractional reflectance at a specific wavelength.

This study was carried out at the maximum wave length. K/S associates the reflectance of the substrate with the dye concentration. The K/S spectrum as a function of wavelength can be used to identify the apparent absorption maxima. Typically, based on the Kubelka-Munk theory, we can assume that K/S is approximately linear to the variation of chromophores in this range of absorption values.

Scanning electron microscope (SEM) and Energy-dispersive X-ray spectroscopy (EDX)

The distribution of reactive dyes within the wood cell cavity and wood ray were observed with SEM (Hitachi S-3400N, Japan) at an accelerating voltage of 10 kV. The tangential sections of dyed and undyed wood veneers were placed on conductive adhesives and then coated with gold. Moreover, the dyed and undyed wood samples were analyzed with energy dispersive X-ray

analysis (EDX) to determine the content of characteristic elements. The dyed sample was treated in dye concentrate 2.0 %, dyeing temperature 45.0°C dyeing time 3.0 hours, dyeing assistant 30.0 g.L⁻¹, dye-fixing agent 10.0 g.L⁻¹, and volume ratio 1:30.

X-ray diffraction analysis (XRD)

XRD measurements were performed with a Cu-K α radiation ($\lambda = 0.1540$ nm) via a goniometer (Shimadzu X-ray 6000, Japan), operated at 40 Kv and 40 mA. The intensity was measured as function of the scattering angle 2θ by θ - 2θ scan. The angle range was 5~50° and the step was 0.02°. The dyed sample was treated in dye concentrate 2.0 %, dyeing temperature 45°C, dyeing time 3.0 hours, dyeing assistant 30.0 g.L⁻¹, dye-fixing agent 10.0 g.L⁻¹, and volume ratio 1:30.

Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

ATR-FTIR was used to characterize the surface chemical composition of the maple veneer treated with the dichlorotriazine reactive dye. All samples were placed on the diamond crystal of the ATR-FTIR spectrometer (Nico-let Nexus 670, USA) in the range of 4500 to 650 cm⁻¹. A total of 64 scans were performed at 4 cm⁻¹ resolution. The dyed sample was treated in dye concentrate 2.0 %, dyeing temperature 45.0°C, dyeing time 3.0 hours, dyeing assistant 30.0 g.L⁻¹, dye-fixing agent 10.0 g.L⁻¹, and volume ratio 1:30.

Thermogravimetric analysis

The thermal stability of the unstained and stained maple veneer veneers was evaluated by TGA. Non-isothermal degradation measurements were performed on a Q5000 TGA device (TA Instruments, USA). Tests were run from room temperature to 600°C at a heating rate of 10°C.min⁻¹ under a nitrogen atmosphere (100 mL.min⁻¹) to avoid thermo-oxidation. The maximum degradation rate was calculated as the mass (%) at peak temperature divided by peak temperature. The dyed sample was treated in dye concentrate 2.0 %, dyeing temperature 45.0°C, dyeing time 3.0 hours, dyeing assistant 30.0 g.L⁻¹, dye-fixing agent 10.0 g.L⁻¹, and volume ratio 1:30.

RESULTS AND DISCUSSION

Visual analysis of orthogonal test results

Fig. 2 shows the visual analysis of dye-uptake when seven factors changed. Dye concentration and temperature were mainly attributed to dye-uptake, while dyeing assistant and fixing agent had slightly effect on dye-uptake. The results indicated that the increasing of dyeing temperature was favor to advance completely reaction of dyes and wood fibers (Song and Shen 2009). The dye-uptake was biggest when the temperature was 65.0°C. The dye-uptake decreased with dye concentration increasing, because the interaction among the dye molecules was greater than that between dye and wood fibers (Liu 2011). The dye-uptake decreased with the increasing dosage of dyeing assistant, but increased after the dosage of dyeing assistant was 30.0 g.L⁻¹. At first, the dyeing assistant would cause the aggregation of dyes which led to decreasing of the dye-uptake. The addition of assistant such as sodium chloride was believed to increase the activity of dichlorotriazine reactive dyes in water (Song and Shen 2009). So the dye-uptake was the highest when the dyeing assistant was 50.0 g.L⁻¹. With dyeing time increasing, the dye molecules

diffused sufficiently in wood tube cells and pits, then they could fully interact with wood fibers (Cao 2009). Na^+ could enhance the activity of reactive dyes, so the addition of sodium carbonate could improve the dye-uptake. But excessive Na^+ would lead to dye molecules aggregation and even deposition, so excess sodium carbonate would lead to dye-uptake decreased. Therefore, when the fixing agent was $15.0 \text{ g}\cdot\text{L}^{-1}$, the dye-uptake was optimum (Fang and Wang 2013). The low volume ratio was conducive to the increase of dye concentration, so the dye-uptake was optimum when the volume ratio was 1 to 15 (Xia 2014).

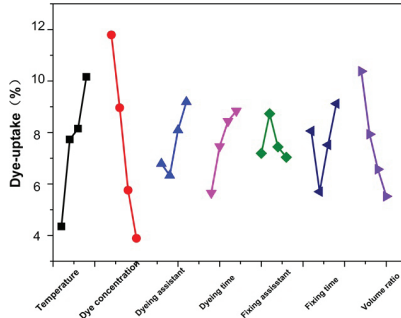


Fig. 2: Visual analysis of dye-uptake.

Fig. 3 shows the visual analysis of K/S when the seven factors change. The K/S was affected greatly by dyeing temperature and dye concentration, and slightly by volume ratio and fixing agent. The K/S increased with the temperature increasing, but K/S decreased at 55.0°C . Resulting from the dye molecules diffused into the veneer at 55.0°C (Cao 2009).

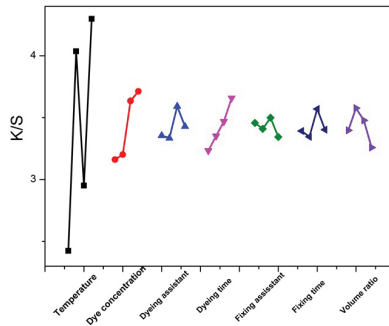


Fig. 3: Visual analysis of K/S.

The K/S increased with dye concentration increasing, because of the increasing amount of dye molecules in the dye bath, which improved the reaction rate of dye molecules and wood fiber (Li 2013). As shown in Fig. 3, the K/S reached the highest point when the dosage of dyeing assistant was $40.0 \text{ g}\cdot\text{L}^{-1}$. Sodium chloride just weakens the repulsive force among dye molecules, as well as the force between wood fibers and dye molecules. With dyeing time increasing, dyes could react with wood fibers sufficiently, therefore, the K/S increased. The amount of fixing agent had an effect on the rate of fixing, so the change in K/S with fixing agent exhibited the similar trend to the change in K/S with dyeing time. When the fixing agent was $20.0 \text{ g}\cdot\text{L}^{-1}$ and the fixing time was 60.0 minutes, the K/S was optimum. The low volume ratio was conducive to the dye-uptake,

thus improving the K/S. But over low volume ratio was not conducive to dyeing property, so the K/S was optimum at the volume ratio 1 to 20.

Variance analysis of orthogonal test results

Tabs. 2 and 3 list the variance analysis results of dye-uptake and K/S, respectively. Clearly, dyeing temperature and dye concentration were significant factors. In addition, influence order of the seven factors on dye uptake was obtained (dye concentration>temperature>volume ratio>fixing time>dyeing time>dyeing assistant>fixing agent). Dyeing temperature significantly affects the K/S. Moreover, the order of the seven factors influenced on K/S was obtained (temperature>dye concentration>dyeing time >volume ratio>dyeing assistant >fixing time >fixing agent). The results of variance analysis and visual analysis were consistent.

Tab. 2: Variance analysis of dye-uptake.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Temperature	0.013924	3	0.004641	<u>7.74</u>
Dye concentration	0.029266	3	0.009755	<u>16.27</u>
Dyeing assistant	0.004039	3	0.001346	2.25
Dyeing time	0.004833	3	0.001611	2.69
Fixing agent	0.001429	3	0.000476	0.79
Fixing time	0.004926	3	0.001642	<u>2.74</u>
Volume ratio	0.010588	3	0.003529	<u>5.89</u>
Error	0.005995	10	0.000599	
Total	0.074999	31		
	Orders of priorities of factors influence			
	Dye concentration>Temperature>Volume ratio>Fixing time>Dyeing time>Dyeing assistant>Fixing agent			

Boldtype with underline: overpass $F_{0.01}(3,10) = 6.55$, Boldtype: overpass $F_{0.1}(3,10) = 2.73$.

Tab. 3: Variance analysis of K/S.

Source of variation	Sum of squares	Degrees of freedom	Mean square	F
Temperature	18.903514	3	6.3011712	9.24
Dye concentration	1.971004	3	0.6570014	0.96
Dyeing assistant	0.326964	3	0.1089881	0.16
Dyeing time	0.789048	3	0.2630161	0.39
Fixing agent	0.107351	3	0.0357835	0.05
Fixing time	0.231575	3	0.0771918	0.11
Volume ratio	0.435511	3	0.1451704	0.21
Error	6.815846	10	0.6815846	
Total	29.5808137	31		
	Orders of priorities of factors influence			
	Temperature>Dye concentration>Dyeing time >Volume ratio>Dyeing assistant >Fixing time>Fixing agent			

Boldtype with underline: overpass $F_{0.01}(3,10) = 6.55$

Optimum schemes

The optimum schemes for different indices are listed in Tab. 4. As can be seen deduced from Figs. 2 and 3, the maximum values are the optimal dyeing parameters.

Tab. 4: Optimum scheme for single index.

Optimum index	Optimum scheme	Optimum parameters
Dye-uptake	$T_4DC_1DA_4DT_4FA_2FT_4VR_1$	Temperature (65.0°C),
		Dyeing concentration (0.5 %),
		Dyeing assistant (50.0 g.L ⁻¹),
		Dyeing time (3.0 h),
		Fixing agent (15.0 g.L ⁻¹),
		Fixing time (75.0 min),
K/S	$T_3DC_4DA_3DT_4FA_2FT_4VR_4$	Volume ratio (1:15)
		Temperature (55.0°C),
		Dyeing concentration (3.0 %),
		Dyeing assistant (40.0 g.L ⁻¹),
		Dyeing time (3.0 h),
		Fixing agent (15.0g/L),
Fixing time (75.0 min),		
		Volume ratio (1:40)

The optimal dyeing parameters, which were analyzed with FCE method, are shown in Tab. 5.

Tab. 5: Comprehensive optimum scheme of dyeing parameters.

Weight vector	(Dye-uptake, K/S)=(0.2,0.8)
Optimum scheme	$T_3DC_4DA_3DT_4FA_2FT_4VR_4$
Optimum parameters	Temperature (55.0°C), Dyeing concentration(3.0 %),
	Dyeing assistant (40.0 g.L ⁻¹), Dyeing time (3.0 h),
	Fixing agent (15.0 g.L ⁻¹), Fixing time (75.0 min),
	Volume ratio (1:40)

SEM and EDX Analysis

Fig. 4 shows the morphologies of the undyed wood (Figs. 4a and c) and the dyed wood (Figs. 4b and d) with dichlorotriazinere active dye. Noticeably, the surface of xylem ray cells in undyed wood veneer was smooth, which could be seen from Fig. 4a. Contrary to the dyed wood, numerous dye molecules aggregated around the surface of xylem rays; these changes can be seen in Fig. 4b. Empty vessel walls were obvious in undyed wood (Fig. 4c), while the empty places in the dyed wood were filled with a small amount of dye molecules (Fig. 4d).

By SEM-EDX, the elemental composition of the undyed wood and dyed wood samples were determined, and the results are shown in Tab. 6. From the data in Fig. 4a, it can be determined that the agglomerates were dye molecules (Fig. 4b). Comparing the data between Figs. 4c and d, the characteristic elements in the dye wood were obviously increased (Fig. 5), which means the molecules were dye molecules.

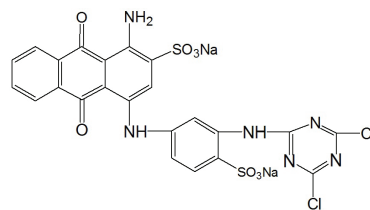
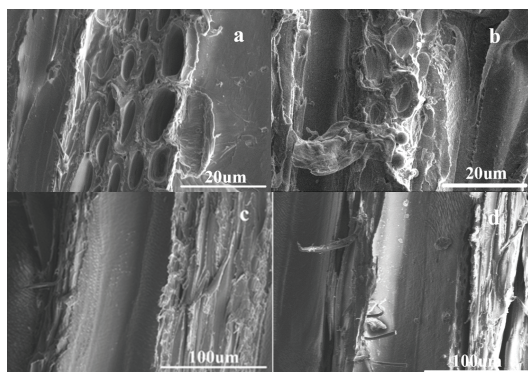


Fig. 4: Scanning electron micrographs: a) and c) undyed maple samples; b) and d) dyed maple samples.

Tab. 6: SEM-EDX Values of nitrogen, sulfur, and chlorine in Fig. 4.

Area (wt %)	Nitrogen	Sulfur	Chlorine
a	0	1.001	1.067
b	3.070 ↑	2.230 ↑	1.752 ↑
c	0	0.832	0.851
d	1.213 ↑	1.402 ↑	1.160 ↑

XRD analysis

The XRD scans for undyed and dyed wood are shown in Fig. 6. The characteristic peaks of maple were found at $2\theta=16^\circ$, 22° , and 35° , corresponding to the crystal plane diffraction peaks of (101), (002) and (040) in cellulose, respectively.

It can be seen from Fig. 6, compared with undyed maple veneer, the crystallinity of dyed maple veneer was declined. The crystallinity of undyed maple veneer was 21.7 %, while the dyed wood reduced to 18.8 % (Fig. 5). The decomposition of cellulose molecular chain or chain hydrogen bonding chain, which led to the regular structure of cellulose crystalline region was damaged. To a certain, this phenomenon would result in a decline of polymerization for cellulose. The cellulose crystalline region gradually transformed into amorphous region, so that diffraction intensity dropped, and the crystallinity decreased (Li 2014, 2003).

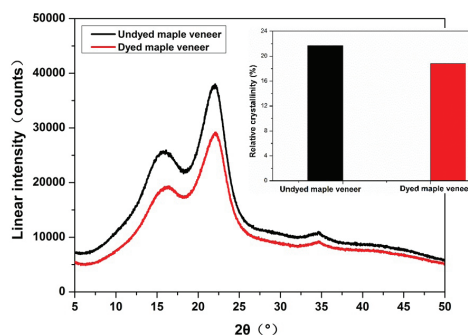


Fig. 6: XRD patterns of undyed and dyed maple veneer.

ATR-FTIR analysis

There are a strong absorption peak of O-H stretching at 3300~4000, C-H stretching at 2800~3000, and several distinct peaks in the finger print region between 500 and 1750 cm^{-1} . Most of these bands have contribution from holocellulose (cellulose and hemicellulose) and lignin. The peak at 1735 cm^{-1} assigned for C=O stretching in hydroxyl and carboxyl of holocellulose, as well as a functional peak of C=C in aromatic skeleton at 1504 cm^{-1} . The bands at 1458 and 1422 cm^{-1} also have significant contribution from lignin. The peaks at 1371, 1159 and 898 cm^{-1} are mostly resulting from carbohydrates and have no significant contribution from lignin (Pandey 1999; Pandey and Pitman 2003).

The ATR-FTIR diagram of dyed and undyed maple veneer only had intensity changes, except the peaks of 1558 and 1321 cm^{-1} , which indicated primary amine ($-\text{NH}_2$) and carbon nitrogen bond (C-N), respectively (Wu and Wang 2013). Compared with unstained maple veneer, dichlorotriazine reactive dye had apparent effects on the surface chemical structure of maple veneer. The absorption peaks of dyed veneer were reduced at 1735, 1234, and 1034 cm^{-1} . In particular, the absorption peak of 1735 cm^{-1} almost disappeared, indicating the reactive dye had damaged the carbonyl of wood. However, the absorption peak around at 3350, 2919, 1592, 1458, 1422 and 1371 cm^{-1} increased after dyeing. These changes can be seen in Fig. 7, there were many benzene rings and carbon oxygen bond (C=O) in dye molecules, moreover, Cl atoms in the dichlorotriazine reactive dye was a leaving group, while the nucleophilic substitution reacted between the dye molecules and wood fibers (Fig. 8).

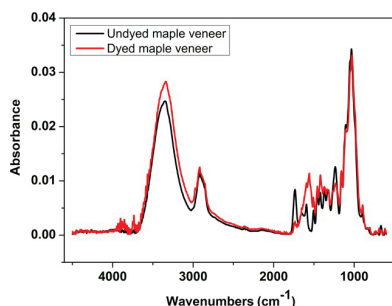


Fig. 7: ATR-FTIR spectra of undyed and dyed wood veneer.

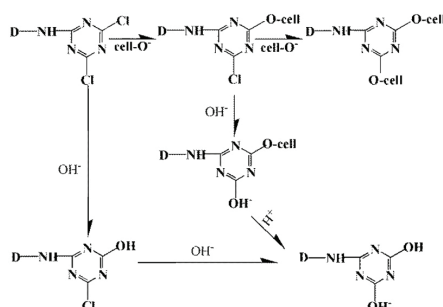


Fig. 8: The mechanism of reaction between the dye and wood.

Tab. 7: Characteristic band assignments of ATR-FTIR spectra of dyed wood.

Wave numbers (cm^{-1})	Functional group	Instruction
3350	-OH	stretching vibration of -OH
2919	$-\text{CH}_3, \text{CH}_2$	stretching vibration of C-H
1735	C=O	stretching vibration of C=O of non-conjugated carbonyl (xylan)
1592	C=C	stretching vibration of aromatic skeleton (lignin)
1558	$-\text{NH}_2$	bending vibration
1504	C=C	stretching vibration of aromatic skeleton (lignin)
1458	$-\text{CH}_3, \text{CH}_2$	unsymmetrical bending (lignin)
1422	$\text{CH}_3-\text{C}, \text{CH}_2$	bending vibration of C-H in lignin and polysaccharide

1371	C-H	bending vibration of C-H in cellulose and hemicellulose
1321	C-N	stretching vibration
1234	C-O	CO-OR stretching of acyl-oxygen bond (hemicellulose), stretching of benzene-oxygen bond (lignin)
1159	C-O-C	asymmetric stretching vibration in cellulose and hemicellulose
1034	C-O-C	stretching vibration of C-O-C in cellulose, hemicellulose, and lignin
898	C-H	deformation in cellulose

TG Analysis

Thermogravimetric tests in inert atmosphere (N_2) were achieved to evaluate the pyrolytic behavior of the dyed and undyed wood. Thermogravimetric curves have been measured from room temperature to $600^\circ C$ at heating rate of $10^\circ C \cdot min^{-1}$ for undyed and dyed maple veneers, which are plotted in Fig. 8.

In agreement with previous findings (Antal and Varhegyi 1995), the DTG curve of untreated wood shows two main regions. Because the temperature intervals of hemicellulose and cellulose decomposition partially overlap each other, the hemicellulose decomposition usually appears as a more or less pronounced “shoulder” instead of a well-defined peak which appears at around $250\sim 350^\circ C$ (Fig. 9). The second region at around $380\sim 400^\circ C$ is associated with the attainment of the maximum, which mainly from cellulose decomposition, and then, followed by a rapid decay and a long tail. Compared to the DTG curve of undyed maple, the DTG curve of dyed maple showed only one region at around $250\sim 330^\circ C$. It seems that the reactive dye causes vast amounts of cellulose decomposition, and the hemicellulose and cellulose decomposition partially overlapeach other. But the temperature at maximum degradation rate of undyed and dyed was different, which was 363.86 and $318.38^\circ C$, respectively, indicating the maple veneer had a chemical reaction with dichlorotriazine reactive dye. As listed in Tab. 8, the degradation of untreated wood began at initial temperature of $259.3^\circ C$, and the dyed wood started at $242.18^\circ C$, owing to the stability of the ester bond between the fiber and dichlorotriazine reactive dye is weaker than the chemical bond of the fiber. However, the residue of dyed wood veneer was greater than that of the undyed veneer (Tab. 8), indicating the combination of dyes and veneer reduced the degradation of the veneer.

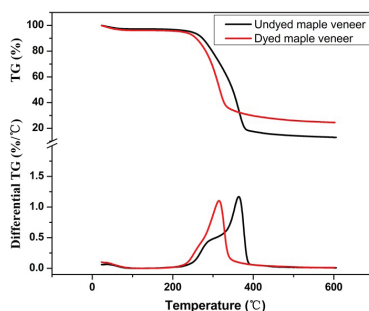


Fig. 9. TG and differential TG patterns of dyed and undyed maple veneer.

Tab. 8: Thermogravimetric parameters for thermal degradation of dyed and undyed maple veneer.

Sample	T ^a (°C)	T _{max} ^b (°C)	Residue ^c (%)
Undyed maple veneer	259.30	363.86	17.22
Dyed maple veneer	242.18	318.38	28.91

^a Initial temperature of degradation

^b Temperature at maximum degradation rate

^c Values determined at 600°C at heating rate of 10°C min⁻¹.

CONCLUSIONS

1. From the dye-uptake and K/S, Reactive brilliant blue has a good staining effect on maple. With variance analysis and visual analysis, dyeing temperature had stronger influence on K/S than other factors, and the dye concentration and temperature had stronger influence on dye-uptake. The optimal dyeing process parameters of maple determined by FCE on dye-uptake and K/S were temperature 55.0°C, dyeing concentration 3.0 %, dyeing assistant 40.0 g.L⁻¹, dyeing time 3 h, fixing agent 15.0 g.L⁻¹, fixing time 75.0 min, volume ratio 1:40.
2. The results of SEM showed that the dichlorotriazine reactive dye molecules distributed and aggregated in lumens and xylem rays of maple veneer, respectively. The EDX results indicated that a successful dispersion of reactive dyes in maple veneer occurred.
3. The new absorption peaks at 1558 and 1321 cm⁻¹ appeared relative to undyed wood, as measured by ATR-FTIR, because there were primary amines (-NH₂) and carbon nitrogen bonds (C-N) in the dichlorotriazine reactive dye molecules. Comparing to the undyed wood, the residue, the temperature at the initial degradation and maximum degradation rate of dyed wood had changed (TGA), which indicated a chemical reaction occurs between wooden fibers and dichlorotriazine reactive dye molecules and supported the FTIR results.

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