Wood Veneer Dyeing Enhancement by Ultrasonic-assisted Treatment

Yi Liu,[a,b,c,d] Jihang Hu,[a] Jianmin Gao,[a,b,c,]* Hongwu Guo,[a,b,c,]* Yao Chen,[a,b,c]
Qingzheng Cheng,[d] and Brian K. Via [d]

To extend the potential application of ultrasonic treatment in dyeing low-quality wood to improve decorative value, wood veneers were dyed with an ultrasonic assisted dyeing system. The effects of ultrasonic power, dye concentration, dyeing time, and temperature of ultrasonic-assisted treatment on dye-uptake, chromatic value, crystallinity, thermal stability, chemical structure, and microstructure for dyed wood veneer were investigated. The dye-uptake, chromatic value, and dyeing rate were improved by ultrasonic-assisted treatment. The effect was strengthened with an increase in ultrasonic power, dye concentration, and dyeing time and temperature. After ultrasonic treatment, the dyed wood properties such as lignin degradation, crystallization and thermal stability decreased slightly, and part of the wood microstructure such as the pit membrane and parenchyma cells was mechanically damaged. Ultrasonic-assisted treatment enhanced the permeability of wood by creating new fluid channels and sorption sites, and it is believed to be an energy-efficient and environmental wood dyeing technique.

Keywords: Wood dyeing; Ultrasonic-assisted treatment; Improvement; Permeability

Contact information: a: MOE Key Laboratory of Wooden Material Science and Application, Beijing Forestry University, Beijing 100083, China; b: Beijing Key Laboratory of Wood Science and Engineering, Beijing Forestry University, Beijing 100083, China; c: College of Material Science and Technology, Beijing Forestry University, Beijing 100083, China; d: Forest Products Development Center, School of Forestry and Wildlife Sciences, Auburn University, Auburn, AL 36849, USA;
** Corresponding authors: jmgao@bjfu.edu.cn; ghw5052@163.com*

INTRODUCTION

Wood dyeing is an emerging technology to efficiently use fast-growing plantation wood. Dyed wood products are prepared through toning, dyeing, tri-dimensional digital modeling design, and the wood grain reconstitution process by using low-quality wood veneer as raw materials (Zhuang 2004; Hu *et al*. 2012). Wood dyeing processes can eliminate color differences within the veneers, resulting in a more homogenous color and a beautiful pattern (Duan 2002). This innovative technique for wood will satisfy the demand for a diverse collection of wooden decoration materials (Fang 2008). Dyed wood and modified dyed wood products have been applied in furniture, interior decoration, flooring and plywood secondary finishes, sports equipment, and handicrafts, which have industrialized production and created remarkable social and economic benefits (Zhuang 2004; Arai 2010; Arai and Nakajima 2011; Sun *et al.* 2011; Guo and Liu 2012; Fu *et al*. 2014; Zhao *et al*. 2014).

Atmospheric pressure impregnation is currently the most widely used method for wood dyeing. Although it is a simple, mature technology, some problems still exist, such as longer dyeing times, low dye-uptake rate, and poor wood permeability. So it is only applicable to the dyeing of thin wood veneers with a thickness less than 0.7 mm (Zhuang 2004). Wood dyeing is a process with continuous wetting, diffusion, and adsorption of the dye solution on wood surface, followed by proper infiltrating and fixing into wood fibers or tracheids (Li and Yu 2005). The extent of adsorption and penetration of dye molecules entering the wood structure is critical to the dyeing depth and quality of the dyed wood (Wei *et al*. 2008). However, there are limited channels available for dye penetration, especially in the transverse direction (Yu *et al*. 2002; Rowell 2012). In general, as the thickness of the wood veneer increases, it becomes more difficult for dyes to penetrate. Therefore, creating a new energy-efficient and environmental-friendly process for thick wood veneers is of utmost importance.

Ultrasonic chemistry is subject to mechanical, cavitation, and heat effects, and it can accelerate or control chemical reactions (Feng and Li 1992). Ultrasonic treatments have been shown to significantly improve the reaction rate, reduce the activation energy, shorten the induction time, and trigger new reactions by the unique interaction between sound energy and material. Currently, ultrasonic-assisted dyeing techniques are mainly used in textiles (Kamel *et al*. 2010). Ultrasonics have not only improved dye-uptake but have increased dye homogeneity and permeability, decreased dosage requirements of dyes and auxiliaries, and also lowered the required temperature or time during fabric dyeing (Abou-Okeil *et al*. 2010; Guesmi *et al*. 2013; Li *et al*. 2013). When ultrasonic power is applied in dye liquor, the power of the ultrasonic energy activated its chemical effect through the creation of substrate cavitations. These ultrasonic waves cause a rapid series of alternative compression and relaxation in the molecular structure of the medium due to cyclical forces (de laFuente-Blanco *et al*. 2006; Soria and Villamiel 2010; Merdan *et al*. 2012). Thus, using ultrasonic energy in fabric dyeing can result in energy savings, less water consumption, increased depth of color penetration, and better processing conditions (Öner *et al*. 1995; Shirsatha *et al*. 2012).

Recently, ultrasonic treatments have been implemented to improve the permeability of wood, which is mainly used in wood drying, extraction, and impregnation (Kaufmann and Christen 2002; Tanaka *et al*. 2010; He *et al*. 2013; Ramezanpour *et al*. 2014). It was found that an ultrasonic treatment can greatly reduce the overall processing time, increase the mass transfer rate, and also increase the effective liquid diffusivity. Micro-deformation of porous solid materials, caused by ultrasonic waves, is likely to be responsible for the creation of microscopic channels that enhance diffusion and increase convective mass transfer (Cui *et al*. 2012; He *et al*. 2013).

However, few studies so far have addressed the application of ultrasonic-assisted dyeing of wood (Chang *et al*. 2008), which can be challenging since wood is a complex, natural, porous polymer, and its main components are cellulose, hemicellulose, and lignin (Liu and Zhao 2004; Rowell 2005; Yang 2009). The detailed study of dye-uptake and microstructure changes of wood veneer under the influence of ultrasonic waves is lacking in current literature. Furthermore, there are not any published studies available on the sonochemistry and fluid diffusion analysis of dyed wood veneer during ultrasonic-assisted treatment. Consequently, the dyeing properties of wood veneer due to ultrasonic-assisted treatments are not fully understood.

The aim of this study was to investigate the feasibility of using an ultrasonic-assisted treatment for the dyeing of wood veneers by using a wood dyeing facility with an ultrasonic-assisted system. The effect of ultrasonic power, dye concentration, and dyeing time and temperature on the dyeing properties of wood veneer was tested. The effect of these factors on the performance of the crystalline, thermal stability, chemical structure, and microcosmic structure of dyed wood veneer was also evaluated.

EXPERIMENTAL

Materials

Fast-growing poplar wood (*P. tomentosa* Carr.) was purchased from Heilongjiang Province, northeast of China. The sapwood was rotary cut and then prepared into 120 mm × 50 mm × 1.2 mm sized veneers. The moisture content of the veneers was air dried to less than 8%, and the density was 433 kg/m^3. All of the veneers were sanded with 200-mesh sandpaper to ensure smooth and flat surfaces. Acid Red GR (*C. I. Acid Red 73*) dye was provided by the Second Plant Dye Chemical Co. in Tianjin, China.

Methods

Ultrasonic-assisted dyeing system

A diagram of the ultrasonic-assisted dyeing system is shown in Fig. 1. This machine was modified from a wood ultrasonic-vacuum drying facility (Shanghai Laboratory Instrumental Works Co., Ltd., China). The vacuum pump, pressure controller, and pressure meter were used to control pressure. The electronic generator driving the ultrasonic transducer was comprised of a power amplifier, an impedance matching unit, and a resonant frequency control unit. This system was specifically designed to keep a constant power at the resonant frequency of the transducer during the dyeing process.

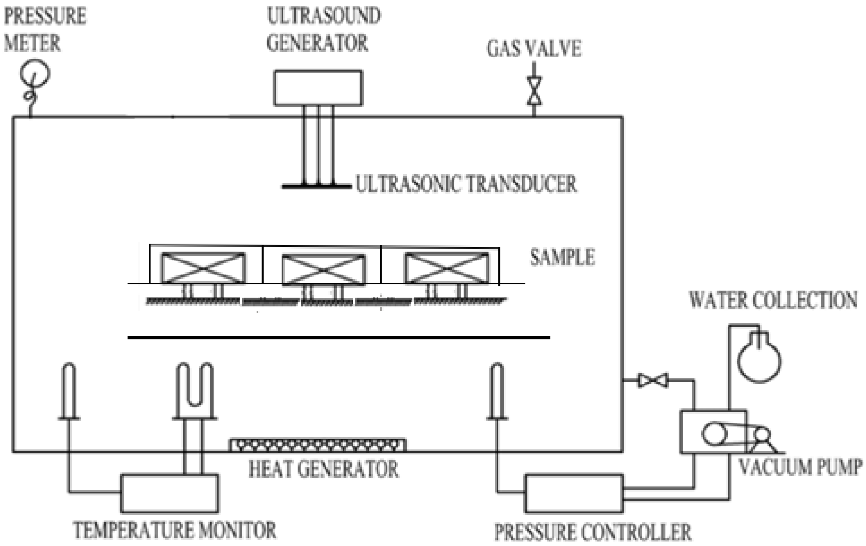

Fig. 1. The diagram of the ultrasonic-assisted dyeing system

The maximum power capacity of the ultrasonic generator was 1200 W. The volume of the ultrasonic bath was 4 L. The ultrasonic transducer with a weight of 0.9 kg and a diameter of 0.066 m was attached to the ultrasonic generator with corresponding power and frequency; it was also put on the wood specimen by its own weight to avoid ultrasonic energy attenuation. A gas valve was used to adjust the vacuum condition in the dyeing chamber. A temperature monitor was used to control the temperature according to the setting values. There were two sets of heat generators. The highest temperature achievable was 200 °C.

Dyeing method

An ultrasonic-assisted dip-dye method at atmospheric pressure was used for wood veneer dyeing. The dye-uptake of the dye liquor and chromatic value of the dyed samples were examined. The effect of ultrasonic power, concentration of dye liquor, and dyeing time and temperature on the properties of dyed wood was investigated afterwards.

Acid Red GR dye liquor 0.15%, 0.12%, and 0.09% (w/v) was prepared and 0.15% (w/v) anhydrous Na_2SO_4 was added as a buffering agent. The pH value of the dye liquor was adjusted to 4.0 by 10% H_2SO_4 (w/w). The ultrasonic transducer, with a frequency of 20 KHz, was installed and linked to the ultrasonic generator. The transmitting power was adjusted to 120, 240, or 300 W. Then, the frequency of the ultrasonic generator was configured to match the impedance of the ultrasonic transducer.

For each condition, nine wood veneers were vertically inserted into the groove of the ultrasonic-assisted dyeing machine, leaving gaps between the veneers so as to ensure maximization of ultrasonic waves obtained per unit area of the dyeing specimens. The bath ratio was 1:300 (V_{veneer}:$V_{\text{dye liquor}}$). The dyeing process was carried out at 60, 70, and 80 °C with ordinary pressure for 1, 2, 3, 4, or 5 h, respectively. The dye-uptake of the dye liquor and chromatic value of the dyed samples was measured before and after the experiment. The dye liquor was stirred clockwise every 20 min for even penetration. After dyeing, the raffinate of all the samples were washed away by tap water, and then the moisture content was air-dried to 8% in a cool place without light.

Measurement of dye-uptake

The amount of dye-pickup by the wood veneer during dyeing was measured to determine the absorption of the dyes. A Spectrumlab 22pc spectrophotometer (Shanghai Lengguang Technology Co. Ltd., China) was utilized to determine the absorption. The maximum absorption wavelength ($\lambda_{\max}$) was 509 nm for the Acid Red GR dye (Dong *et al.* 2009). Percent exhaustion (C_t, %) of the dye solution was calculated based on the following formula:

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

where A_0 and A_t are the absorbance of the dye solution at $\lambda_{\max}$ before and after wood veneer dyeing, respectively.

Measurement of color parameters

The CIE $L^*a^*b^*$ color system was applied to evaluate the color parameters L^*, a^*, and b^* of the samples' surface. The color index was recorded with a ZB-A colorimeter

(Hangzhou Paper States Instrument Co. Ltd., China), using a D65 standard illuminant. The color parameters were measured two times for each sample (triplicates for each condition). The average value was recorded. The color difference (ΔE^*) was used to evaluate the dyeing effect of the wood veneer. ΔE^* was calculated with Eq. 2,

$$\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2} \tag{2}$$

where ΔE^* indicates the degree of total color change, L^* stands for the lightness from 0 (for black) to 100 (for white), a^* represents the red-green chromaticity coordinates ($+a^*$ is for red, $-a^*$ for green), and b^* denotes the yellow-blue chromaticity index ($+b^*$ is for yellow, $-b^*$ for blue); ΔL^*, Δa^*, and Δb^* are the differences of the sample values (before and after dyeing) of L^*, a^*, and b^*, respectively.

ATR-FTIR, XRD, DSC, and SEM analysis

Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy was performed to characterize the surface chemical structure of the dyed wood veneer. The samples were directly applied to the diamond crystal of the FTIR spectrometer (Bruker VERTEX 70v, Germany), and the spectra were collected in transmittance mode by 32 scans in the range of 1800 to 800 cm^{-1} at a resolution of 2 cm^{-1}. The crystallinity of the powder (40- to 60-mesh) from untreated and treated wood veneers was evaluated by an X-ray diffractometer (Shimadzu XRD 6000, Japan). The patterns were obtained within a 5 to 50° diffraction angle (2θ) interval, with a 0.02° step and a scan speed of $2°\bullet\text{min}^{-1}$. The degree of crystallinity was determined as the ratio of the intensity difference in the selected peak positions. The degradation characteristics of the dried powder samples (40- to 60-mesh) were established by a differential scanning calorimeter (DSC; TA Q2000, USA). The temperature was first programmed from ambient temperature to 20 °C, and then raised from 20 to 215 °C under a 50 mL/min flow of nitrogen atmosphere at a heating rate of 20 $°\text{C}\bullet\text{min}^{-1}$. A scanning electron microscope (SEM; JSM 5900, Japan) operating at an accelerating voltage of 5 to 10 kV was used to observe the morphology of the dyed wood veneer.

RESULTS AND DISCUSSION

Effect of Ultrasonic-assisted Treatment on Dye-Uptake and ΔE* of Dyed Wood Veneer

Obvious promotion effects of ultrasonic-assisted treatment were obtained (Fig. 2). It was found that the dye-uptake (C_t) and ΔE^* of the samples dyed with ultrasonic-assisted treatment were much higher than those of the untreated. The dye-uptake gradually increased with increased ultrasonic power for lower power ranges. The effect became more pronounced when the ultrasonic power was higher. This suggested that the diffusion of the dyes into the interior of wood becomes increasingly significant with increasing ultrasonic power. For ΔE^*, a rapid increase occurred between 0 and 120 W. However, there was only a slight increase at higher power (240 and 300 W). The fact that the ΔE^* values reached a plateau might be attributed to dye liquor diffusion from the surface to the interior, due to the greater accessibility. Another explanation was the color dyeing depth reached an equilibrium level or a saturation degree.

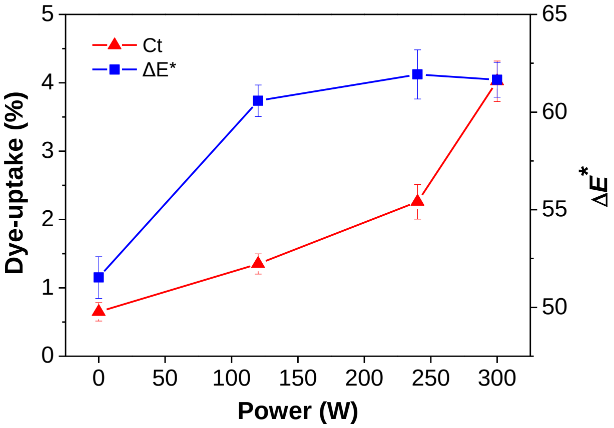

Fig. 2. Effect of ultrasonic power on the dye-uptake (Ct) and Δ*E** of dyed wood veneer. Data reported as the mean ± standard deviation. Dye concentration, 0.15%; dyeing time, 2 h; and dyeing temperature, 80 °C

The process of wood dyeing includes the dyes continuous penetration, diffusion, and sorption on the wood surface. These factors promote penetration into the internal structure. When the dye-uptake of the wood veneer was low, the Δ*E** of the wood surface increased along with an increase of dye-uptake. However, as the absorbed dye molecules became saturated, the dyes still continued to diffuse and penetrate into the wood structure. On the other hand, application of increased ultrasonic power improved the permeability of the wood, resulting in an increase in dyes infiltration and penetration. In addition, an improvement in the ultrasonic power promoted the activation of the dye molecules, which resulted in a higher proliferation potential. All of these factors contributed to the improvement of wood dyeing uptake rate.

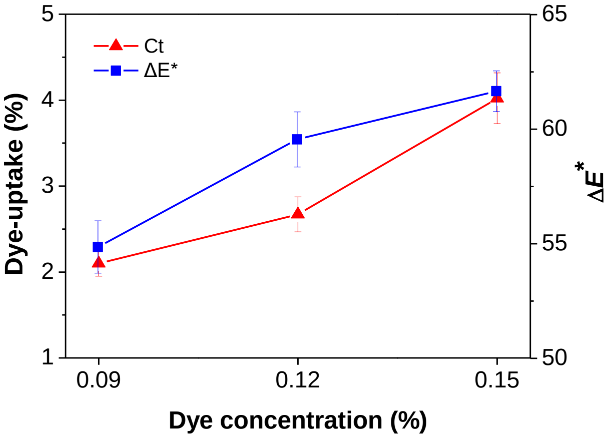

Fig. 3. Effect of dye concentration on the dye-uptake (*C*t) and Δ*E** of dyed wood veneer. Data reported as the mean ± standard deviation. Ultrasonic power, 300 W; dyeing time, 2 h; and dyeing temperature, 80 °C

Figure 3 demonstrates the relationship between increased dye concentration and dye-uptake, and ΔE^* of the dyed wood veneer. Under the same ultrasonic power, the higher the dye concentration, the greater the dye-uptake and dyeing rate, which resulted in a better dyeing performance of the samples. This was mainly attributed to a larger concentration difference between wood cells and dye liquor obtained when a higher dye concentration of dye liquor was used. This concentration difference was advantageous to the dye liquor infiltration into the wood interior, which resulted in an improvement in the dye-uptake and dyeing depth. Another explanation was that the higher the dye concentration, the higher the aggregation degree of the dye molecules in the dye liquor (Li *et al*. 2013). When ultrasonic energy was applied, the dye agglomeration decreased, and the solubility as well as the diffusivity increased. The third theory was that adsorption increases with increasing dye concentration can sometimes be regarded as evidence of a relatively low affinity of adsorption. In cases where there is low affinity between an adsorbate and a cellulosic surface, the self-association between adsorbate molecules (such as a dye) can play a large role in determining the outcome. Therefore, it is believed that the effect of applied ultrasonic treatment will be more obvious in a high concentration of dye liquor.

The ΔE^* of the wood veneer was 58.44 after dyeing for 1 h with ultrasonic-assisted treatment (Fig. 4), while it was 51.53 after 2 h by the atmospheric impregnation dyeing method (Fig. 2). This result indicated that ultrasonic-assisted treatment in wood dyeing saves time and energy.

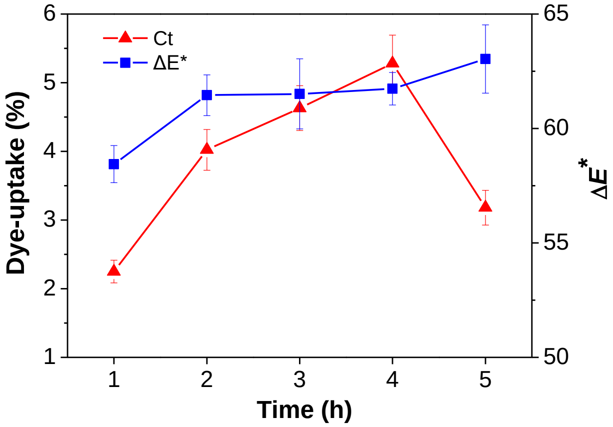

Fig. 4. Effect of dyeing time on the dye-uptake (C_t) and ΔE^* of dyed wood veneer. Data reported as the mean ± standard deviation. Ultrasonic power, 300 W; dye concentration, 0.15 %; and dyeing temperature, 80 °C

The dye-uptake of wood veneer gradually increased from 2.25 to 5.28% with the extension of dyeing time at the beginning, and then decreased after 4 h (Fig. 4). This was reasonable, as the wood dyeing process is a dynamic sorption and desorption equilibrium process of dye molecules onto the wood surface and internal structure (Yu *et al*. 2002; Guo and Liu 2012). During initial dyeing, the wetting of the wood surface coupled with adsorption played a dominant role resulting in an increase in the wood dyeing rate. After that, the dye molecules began to penetrate below the wood surface. Additionally, the cavitation and thermal effects of the ultrasonic waves also helped to promote the sorption process of dye molecules into the wood cell wall. However, the ultrasonic treatment also accelerated the dissolution of wood inclusions, such as extractives. Both factors jointly increased wood intracellular concentration, which led to an increase in the desorption rate of dye molecules. As a result, with an extended dyeing time, the adsorption and desorption between the wood and dye liquid tended to be balance until it reached an equilibrium dye uptake.

It was found that increasing the dyeing temperature enhanced the dyeing effect of wood (Fig. 5). When the temperature was 80 °C, the ΔE^* increased by 11.1% more than those at 60 °C. Previous studies have shown that the most advantageous temperature for the cavitation bubbles formation, *via* ultrasonic vibration in water solution, is 50 to 60 °C (Feng and Li 1992). The number of cavitation bubbles was reduced when the temperature increased, which was attributed to the high temperature of the liquor which exacerbates molecular thermal motion. This irregular movement disrupted the formation of cavitation bubbles, resulting in a more homogenous liquor.

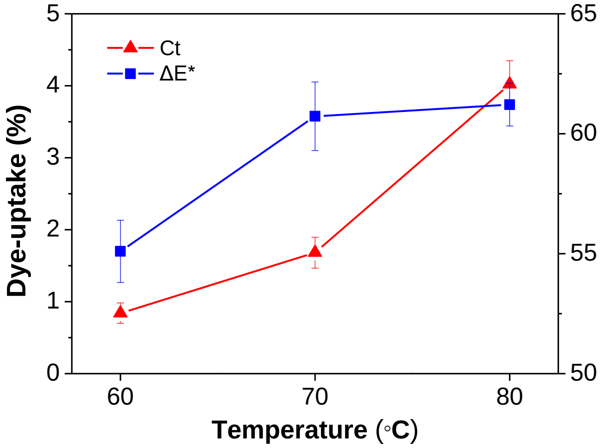

Fig. 5. Effect of dyeing temperature on the dye-uptake (C_t) and ΔE^* of dyed wood veneer. Data reported as the mean ± standard deviation. Ultrasonic power, 300 W; dye concentration, 0.15%; and dyeing time, 2 h

In the textile industry, the temperature of ultrasonic-assisted dyeing is generally between 45 and 65 °C (Kamel *et al*. 2010; Parvinzadeh *et al*. 2010; Ferrero and Periolatto 2012). However, wood fibers can swell in hot water, resulting in an increase in the thermo-plasticity of wood. When wood fibers were highly swollen, the layers of cellulosic material might become further separated from each other; this led to certain van der Waals interactions might be less. Under the influence of the vigorous thermal motion of water molecules, the gap between wood fibers increased. This is a benefit for the dye molecular penetration into the internal structure of wood (Liu and Zhao 2004; Yang 2009). Furthermore, the micro-environment of high temperature, high pressure, and high microjet, formed by the collapse of cavitation bubbles conducive to dye liquor infiltration and diffusion inside the wood, led to an improvement in the dye-uptake of the wood veneer. As a result, compared to the most favorable temperature for cavitation, it is valid to improve the dye-uptake by increasing the dyeing temperature appropriately in the wood ultrasonic-assisted dyeing process.

It can be concluded that wood dyeing with ultrasonic-assisted treatment reached the dyeing quality at reduced dyeing concentrations, temperatures, and times compared to conventional methods. This was attributed to ultrasonic cavitation and thermal effects caused by the ultrasonic waves in the dye solution, which made the kinetic energy and the collision impulse of molecules increase. This beneficially improved the permeability of the wood structure. The lower viscosity and higher liquidity of the dye liquor enhanced the interface of wood, which led to an increase in the chance of dyes adsorption into wood tissue. As a result, it is believed that even when the dyeing conditions (*i.e.*, temperature, time, and concentration) were reduced, the wood veneer still exhibited an acceptable appearance at lower ultrasonic power.

XRD Analysis

According to the results of XRD (Fig. 6), the crystallinity of poplar wood was 44.12%, while the dyed wood and ultrasonic-assisted treated dyed wood were 45.24% and 43.78%, respectively. Comparing the three curves, the position of the diffraction peaks did not change, which indicates that the structure of the cellulose in the dyed wood was consistent with those of the raw materials (Mulinari *et al*. 2010; Chen *et al*. 2014).

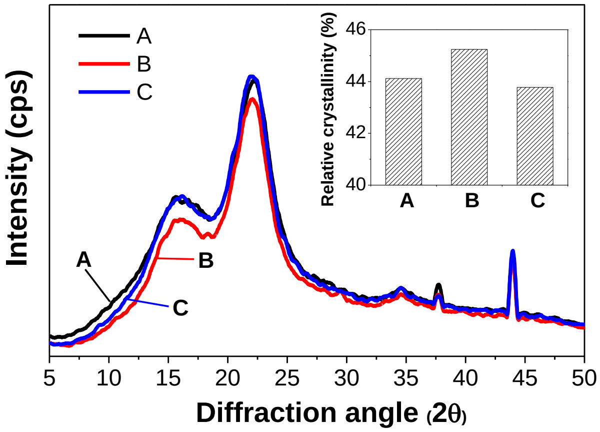

Fig. 6. Poplar wood XRD curves and relative crystallinity of (A) untreated, (B) dyed at 80 °C for 2 h, and (C) dyed at 80 °C with an ultrasonic assistance of 300 W for 2 h

The increased crystallinity of the dyed wood was attributable to the hydrothermal dyeing process. As the dyeing temperature increased and the processing time extended, it is hypothesized that the water molecules got into the non-crystalline region of cellulose. The surface activity of microfibrils in the non-crystalline region was strengthened. This made the molecular chains of the microfibrils more orderly, and resulted in solid hydroxyl combinations between each other. Thereby, one part of them formed a new crystalline region, and the crystallinity of the cellulose increased. In general, woody materials with increasing crystallinity lead to a decrease in the dye-uptake rate (Li 2003). This can be used to explain why the dyeing rate of wood veneer at 5 h was lower than that of 4 h in Fig. 4. However, after treatment by ultrasonic waves, the crystallinity of the dyed wood decreased. This was attributed to two reasons: first, there could have been a small concentration of cellulose on the surface, which suffered significant degradation by acid hydrolysis due to a reaction in the acidic dye solution. This would result in a decline in the degree of polymerization for cellulose (Yang 2009). Second, it is possible that the ultrasonic stress played a continuing role on void formation, which starts at the non-crystalline region, then results in a fatigue crack on the fiber surface, which then results in a partially or completely destroyed fiber (Li 2003).

ATR-FTIR Analysis

Compared with the conventional method, the ultrasonic treatment has apparent effects on the surface chemical structure (Fig. 7). The chemical structure of lignin for a large number of unsaturated functional groups (1650 cm^{-1}, 1592 cm^{-1}, 1504 cm^{-1}, 1458 cm^{-1}, 1423 cm^{-1}) (Table 1) exhibited serious degradation via phenoxy radical reactions. Pranovich *et al*. (1998) studied the sonochemistry of lignin model compounds and reported the formation of various products as a result of the hydroxyl radical that attacked the aromatic ring. Furthermore, the degradation of cellulose (1423 cm^{-1}, 1373 cm^{-1}, 898 cm^{-1}) and hemicellulose (1738 cm^{-1}, 1373 cm^{-1}, 1234 cm^{-1}) was also apparent. In most cases, the higher the dye concentration, the longer the dyeing time, the greater the ultrasonic power, and the higher the dyeing temperature, resulted in more serious degradation of the dyed wood veneer samples. The chemical structure of the wood destructed to a certain extent, and the wood macromolecule components degraded to small molecules, which were conducive to how dye liquor penetrates inside the wood structure. These factors are conducive to improving the dyeing effect.

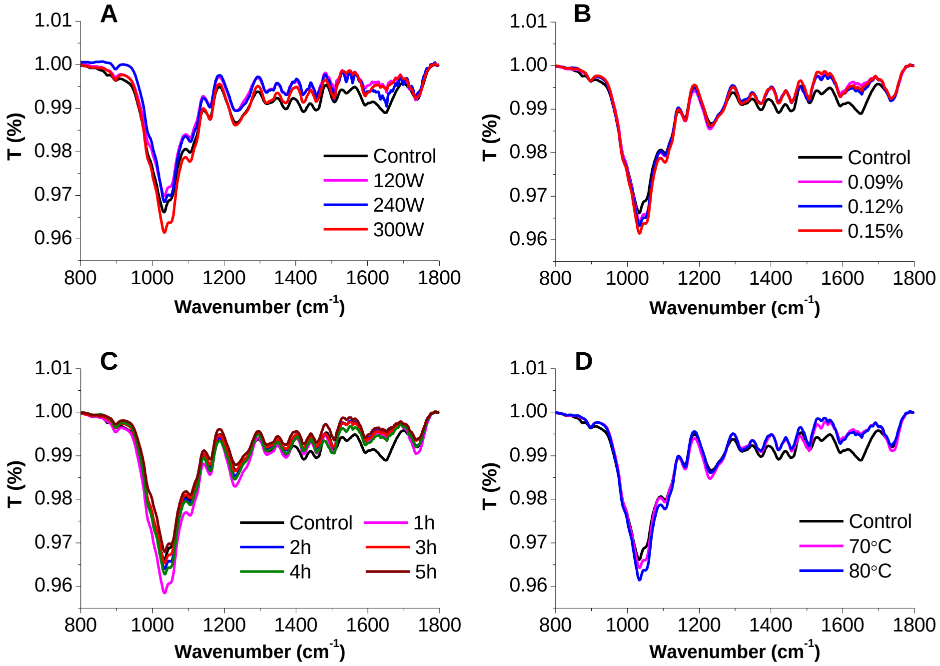

Fig. 7. The ATR-FTIR spectra of the dyed wood veneer treated by ultrasonic waves under different (A) ultrasonic power, (B) dye concentration, (C) dyeing time, and (D) dyeing temperature. The dyeing parameters of control group: Ultrasonic power, 0 W; dye concentration, 0.15%; dyeing time, 2 h; and dyeing temperature, 80 °C

Table 1. Characteristic Band Assignments of ATR-FTIR Spectra of Dyed Wood

Wavenumber (cm^{-1})	Chemical Structure Assignment
1738	C=O stretching of non-conjugated carbonyl (Xylan)
1650	C=O stretching of conjugated carbonyl (Lignin)
1592	C=C Stretching of aromatic skeleton (Lignin)
1504	C=C Stretching of aromatic skeleton (Lignin)
1458	-CH_3 and -CH_2 unsymmetrical bending (Lignin)
1423	C-H Stretching of aromatic skeleton bending (Lignin, Cellulose)
1373	C-H bending (Cellulose, Hemicellulose)
1234	CO-OR stretching of acyl-oxygen bond (Hemicellulose) Stretching of benzene-oxygen bond (Lignin)
1122	S-O stretching of sulfonate groups (Dyes)
1034	C-O-C stretching of aliphatic ether bond (Xylan, Lignin)
898	C_1-H bending of anomeric carbon (Xylan)

DSC Analysis

An endothermic peak observed in wood, untreated dyed wood, and dyed wood with ultrasonic-assisted treatment between 20 and 215 °C was obvious at 123.29 °C, 127.21 °C, and 122.45 °C (Fig. 8), respectively. These results suggest that the thermal stability of wood improved after dyeing for 2 h, while they were reduced after ultrasonic treatment. This was consistent with the results of XRD (Fig. 6).

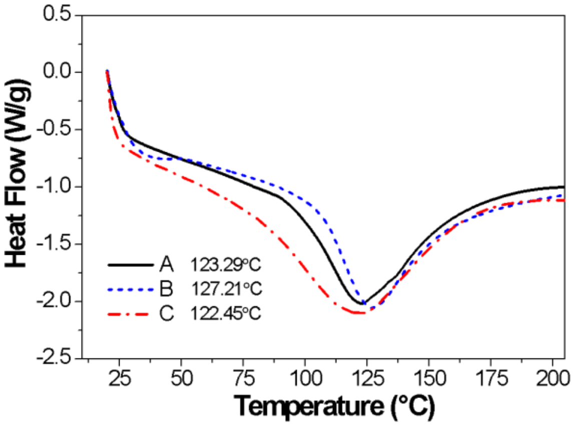

Fig. 8. The poplar wood DSC curves of (A) untreated, (B) dyed at 80 °C for 2 h, and (C) dyed at 80 °C with an ultrasonic assistance of 300 W for 2 h

SEM Analysis

Figure 9 shows the SEM micrographs of dyed wood veneer after treatment with ultrasonic energy.

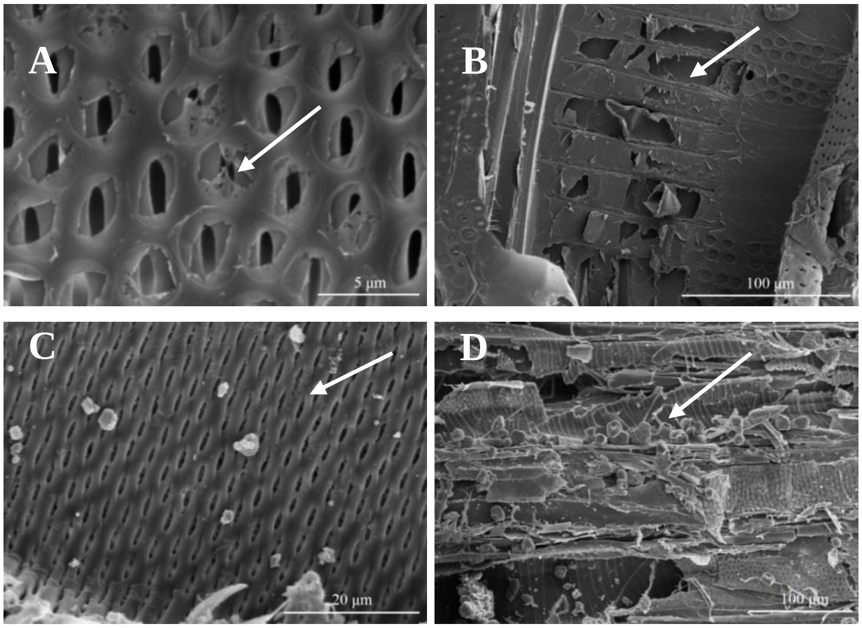

Fig. 9. SEM micrographs of poplar wood veneer dyed at 80 °C with an ultrasonic assistance of 300 W for 2 h

Wood is a kind of porous material, and the function of ultrasonic cavitation and heat effects resulted in sharp moisture vaporization in the wood cell cavity, causing an outward diffusion of vapor pressure to act on the cell wall. This leads to the weak organizations, such as pit membrane (Fig. 9A), to rupture. The instantaneously increasing internal pressure also made some of the wood ray cells (Fig. 9B), such as parenchyma cells, break. These breaks formed new radial fluid channels for dye liquor and steam, thereby increasing the permeability of the wood. Furthermore, a lot of tiny cracks and acid etching on the wood fiber surface (Fig. 9C) were generated during the dyeing treatment assisted by ultrasonic waves, which obviously increased the internal surface area of the veneer (Fig. 9D), providing more adsorption sites for the dyes.

CONCLUSIONS

1. Ultrasonic-assisted treatment obviously improved the dye-uptake and chromatic value of the dyed wood veneer, and the effect was generally strengthened as the ultrasonic power, dye concentration, dyeing time, and dyeing temperature increased.
2. After ultrasonic-assisted treatment, the dyed wood components, lignin in particular, degraded, and the crystallization and thermal stability decreased slightly. Some damage of the microstructure of the dyed wood, such as pit membrane and parenchyma cells, was observed by SEM.
3. Ultrasonic-assisted treatment enhanced the permeability of the wood veneer, creating new fluid channel and sorption sites. This is believed to be an energy-efficient and environmental-friendly wood dyeing method.

ACKNOWLEDGMENTS

The authors would like to acknowledge Zhengbin He, Xueyong Ren, Bin Luo, and Zhenghua Shang for their help in the development of the experiment. This research was financially supported by the Beijing Municipal Education Commission Joint Project for Scientific Research and Graduate Training, the Special Fund for Forestry Research in the Public Interest of China (No. 201204702), the China Scholarship Council (No. 201306510015), and the Forest Products Development Center within the School of Forestry and Wildlife Sciences.

REFERENCES CITED

Abou-Okeil, A., El-Shafie, A., and El Zawahry, M. M. (2010). "Ecofriendly laccase-hydrogen peroxide/ultrasound-assisted bleaching of linen fabrics and its influence on dyeing efficiency," *Ultrasonics Sonochemistry* 17(2), 383-390. DOI: 10.1016/j.ultsonch.2009.08.007

Arai, K. (2010). "Ribbon-like variegation of *Pinus radiata* using the adsorption of basic dyes in the capillary penetration process III. Creating radial and/or tangential variations of color," *Journal of Wood Science* 56(5), 347-354. DOI: 10.2488/jwrs.56.347

Arai, K., and Nakajima, K. (2011). "Ribbon-like variegation of *Pinus radiata* using the adsorption of basic dyes in the capillary penetration process IV. Dying wood in parallel colored strips through the process of capillary penetration," *Journal of Wood Science* 57(1), 34-41. DOI: 10.2488/jwrs.57.34

Chang, J., Wang, J., Wang, Q., Li, C., and Wang, Z. (2008). "Effects of wood dyeing with microwave processing," *Scientia Silvae Sinicae* 44(6), 109-112.

Chen, H., Lang, Q., Bi, Z., Miao, X., Li, Y., and Pu, J. (2014). "Impregnation of poplar wood (*Populus euramericana*) with methylolurea and sodium silicate sol and induction of in-situ gel polymerization by heating," *Holzforschung* 68(1), 45-52. DOI: 10.1515/hf-2013-0028

Cui, X., Zhang, X., Tang, H., Zhang, L., Xu, C., and Sun, S. (2012). "Study on extracts of active substances from larch bark by FTIR spectroscopy," *Spectroscopy and Spectral Analysis* 32(7), 1810-1814. DOI: 10.3964/j.issn.1000-0593(2012)07-1810-05

Dong, C., Shuang, S., and Wei, Y. (2009). *Green Pigment and Application*, Chemical Industry Press, Beijing.

Duan, X. (2002). *Wood Color Control Technology*, China Building Materials Industry Press, Beijing.

Fang, G. (2008). *Wood Functional Improvements*, Chemical Industry Press, Beijing.

Feng, R., and Li, H. (1992).*Ultrasonic Chemistry and Its Applications*, Anhui Science and Technology Publishing House, Hefei.

Ferrero, F., and Periolatto, M. (2012). "Ultrasound for low temperature dyeing of wool with acid dye," *Ultrasonics Sonochemistry* 19(3), 601-606. DOI: 10.1016/j.ultsonch.2011.10.006

Fu, Z., Liu, Y., Xing, F., and Guo, H. (2014). "Changes in chemistry component structure and microstructure characterization of acetylated wood before and after UV radiation," *Spectroscopy and Spectral Analysis* 34 (11), 2944-2947. DOI:10.3964/j.issn.1000-0593(2014)11-2944-04

de la Fuente-Blanco, S., Riera-Franco deSarabia, E., Acosta-Aparicio, V. M., Blanco-Blanco, A., and Gallego-Juarez, J. A. (2006). "Food drying process by power ultrasound," *Ultrasonics* 44, e523-e527. DOI: 10.1016/j.ultras.2006.05.181

Guesmi, A., Ladhari, N., and Sakli, F. (2013). "Ultrasonic preparation of cationic cotton and its application in ultrasonic natural dyeing," *Ultrasonics Sonochemistry* 20(1), 571-579. DOI: 10.1016/j.ultsonch.2012.04.012

Guo, H., and Liu, Y. (2012). *Photochromic of Coated Dyeing Wood*, China Environmental Science Press, Beijing.

He, Z., Yang, F., Peng, Y., and Yi, S. (2013). "Ultrasound-assisted vacuum drying of wood: Effects on drying time and product quality," *BioResources* 8(1), 855-863. DOI: 10.15376/biores.8.1.855-863

Hu, B., Guo, H., Liu, G., and Liu, Y. (2012). "The application of technical wood in modern interior decoration," *Furniture and Interior Design* 4, 14-15.

Kamel, M. M., Helmy, H. M., Mashaly, H. M., and Kafafy, H. H. (2010). "Ultrasonic assisted dyeing: Dyeing of acrylic fabrics C.I. Astrazon Basic Red 5BL 200%," *Ultrasonics Sonochemistry* 17(1), 92-97. DOI: 10.1016/j.ultsonch.2009.06.001

Kaufmann, B., and Christen, P. (2002). "Recent extraction techniques for natural products: Microwave-assisted extraction and pressurised solvent extraction," *Phytochemical Analysis* 13(2), 105-13. DOI: 10.1002/pca.631

Li, J. (2003). *Wood Spectroscopy Technology*, Science Press, Beijing.

Li, H., and Yu, Z. (2005). "Combinative mechanism between dyes and wood," *Journal of Beijing Forestry University* 27(4), 78-81.

Li, M., Yao, J., and Cui, S. (2013). *New Technology of Dyeing and Finishing*, Science Press, Beijing.

Liu, Y., and Zhao, G. (2004). *Woody Materials Science*, China Forestry Publishing House, Beijing.

Merdan, N., Saclıoglu, M. Z., Kocak, D., and Sahınbaskan, B. Y. (2012). "Investigation on colour and fastness properties of wool fabrics dyed with colours obtained from the flowers of the *Papaverrhoeas* l. (common poppy)," *Advances in Environmental Biology* 6(2), 750-755.

Mulinari, D. R., Voorwald, H. J. C., Cioffi, M. O. H., Rocha, G. J., and Silva, M. L. C. P. D. (2010). "Surface modification of sugarcane bagasse cellulose and its effect on mechanical and water absorption properties of sugarcane bagasse cellulose/HDPE composites," *BioResources* 5(2), 661-671. DOI: 10.15376/biores.5.2.661-671

Öner, E., Başer, I., and Acar, K. (1995). "Use of ultrasonic energy in reactive dyeing of cellulosic fabrics," *Journal of the Society of Dyers and Colourists* 111(9), 279-281.

Parvinzadeh, M., Memari, N., Shaver, M., Katozian, B., Ahmadi, S., and Ziadi, I. (2010). "Influence of ultrasonic waves on the processing of cotton with cationic softener," *Journal of Surfactants and Detergents* 13(2), 135-141. DOI: 10.1007/s11743-009-1158-y

Pranovich, A. V., Reunanen, M., and Holmbom, B. (1998). "Sonochemistry of lignin model compounds in water," in: *Advances in Lignocellulosics Chemistry for Ecologically Friendly Pulping and Bleaching Technologies*, 5th European Workshop on Lignocellulosics and Pulp, University of Aveiro, Aveiro, Portugal, pp. 421-424.

Ramezanpour, M., Tarmian, A., and Taghiyari, H. R. (2014). “Improving impregnation properties of fir wood to acid copper chromate (ACC) with microwave pretreatment,” *iForest - Biogeosciences and Forestry* 7(5), 286-291. DOI: 10.3832/ifor1119-007

Rowell, R. M. (2012). *Handbook of Wood Chemistry and Wood Composites*, Second edition, CRC Press, Boca Raton, FL. DOI: 10.1201/b12487

Soria, A. C., and Villamiel, M. (2010). “Effect of ultrasound on the technological properties and bioactivity of food: A review,” *Trends in Food Science and Technology* 21(7), 323-331. DOI: 10.1016/j.tifs.2010.04.003

Shirsatha, S. R., Sonawanea, S. H., and Gogateb, P. R. (2012). “Intensification of extraction of natural products using ultrasonic irradiations - A review of current status,” *Chemical Engineering and Processing: Process Intensification* 53, 10-23. DOI: 10.1016/j.cep.2012.01.003

Sun, D., Sun, D., and Yu, X. (2011). “Ultrasonic-assisted dyeing of poplar veneer,” *Wood and Fiber Science* 43(4), 442-448.

Tanaka, T., Avramidis, S., and Shida, S. (2010). “A preliminary study on ultrasonic treatment effect on transverse wood permeability,” *Maderas-Cienciay Tecnologia* 12(1), 3-9.

Wei, S., Wang, D., and Gu, J. (2008). “Permeability and adsorption of acid dyes in birch wood,” *Journal of Northeast Forestry University* 36(3), 45-48.

Yang, S. (2009). *Plant Fiber Chemical*, Third edition, China Light Industry Press, Beijing.

Yu, Z., Zhao, L., and Li, W. (2002). “Study on permeable mechanism with dyes during wood dyeing,” *Journal of Beijing Forestry University* 24(1), 79-82.

Zhao, Y., Tan, X., Wan, X., Yuan, Y., Yu, Z., and Tang, J. (2014). “Dyeing of acetylated wood with disperse dyes,” *Wood and Fiber Science* 46(3), 1-11.

Zhuang, Q. C. (2004). *Engineered Wood-Reconstituted Decorative Lumber*, China Forestry Publishing House, Beijing.

Article submitted: October 23, 2014; Peer review completed: December 15, 2014; Revised version received and accepted: December 16, 2014; Published: January 5, 2015.