STUDY OF MANUFACTURING THERMOCHROMIC WOOD

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Abstract. The development of new materials such as thermochromic wood provides an interesting option for the forest products industry. Poplar veneer was colored by ultrasonic impregnation using a thermochromic agent consisting of thermochromic dye, a chromogenic agent, 1-tetradecanol, and a sensitizing agent. In optimizing the process, the most significant influence on the extent of sample color change (ΔE) was found to be the mixing ratio of thermochromic dye to chromogenic agent. Next was the mixing ratio of thermochromic dye to 1-tetradecanol and last that of thermochromic dye to sensitizing agent. Analysis of variance showed that the influences of all experimental parameters on ΔE were significant at the 0.01 level. The optimum mixing ratio of thermochromic dye, the chromogenic agent, 1-tetradecanol, and the sensitizing agent was 1:8:50:1. The color of these new products changed from blue to wood color as temperature increased 26-34°C and reverted from normal wood color to blue as temperature decreased from 34-26°C.

Keywords: Thermochromic material, thermochromic wood, manufacturing process, *Populus euramericana*.

INTRODUCTION

Wood has been widely used in houses because of inherent desirable properties such as odor, color, and texture. With the advancement of technology and the enhancement of living standards, consumers increasingly desire multifunctional behavior from decorative materials. One problem, however, is that products with low technological content and low added value share a large proportion of the Chinese market (Wu et al 2004). Wood dyeing is a way to improve the appearance of wood products and enhance their value. Much research has been done in this field such as *Paulownia* veneer dyeing (Chen et al 2000), the relationship between wood structure and wood dyeing effects on plantation Chinese fir (Bao and Duan 2000), a computer color matching technique for use in wood dyeing (Li et al 2006), and the effects of wood dyeing in microwave processing (Chang et al 2008). Now some dyes and dyeing methods are being applied in the wood industry. However, research on dyeing wood to create products that change color with changing temperature near normal room conditions has not been reported. Thermochromic wood veneer represents a commercial opportunity provided the appropriate dyes and manufacturing conditions can be developed. In this study, poplar veneer was colored by ultrasonic impregnation using a thermochromic agent containing thermochromic dye, a chromogenic agent, 1-tetradecanol, and a sensitizing agent. The optimum manufacturing process of thermochromic wood veneer was determined within given experimental limits. This research makes possible the manufacture of a new material for use in items such as wood furniture and decorative panels.

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MATERIALS AND METHODS

Materials

Poplar (*Populus euramericana*) veneer with dimensions of 30 mm (longitudinal) × 0.7 mm (radial) × 45 mm (tangential) was studied. The total number of samples was 18. For treating solutions, 30% H_2O_2 was diluted to 10% and NaOH was dissolved using distilled water for a 5% solution. These solutions were mixed at a 1:1 ratio. The mixture was adjusted to pH 9-10 with 10% HCl, and the samples were treated for 4 h. After treatment, the samples were dried in an oven for 8 h at 70°C. The average sample moisture content was 9% as measured by DELTA-55 after reconditioning.

Experimental Set-Up

The experimental parameters included mixing ratios of thermochromic dye (Crystal Violet Lactone, purity 99.9%) and a chromogenic agent (Biphenyl A, purity 99.9%), thermochromic dye and 1-tetradecanol (purity 99.99%), and thermochromic dye, and a sensitizing agent (sodium thiosulfate, purity 94.0%). The experimental index requiring optimization was the color difference of the samples (ΔE), which is the extent of change of sample color with temperature. Three levels were set for every experimental parameter (Table 1).

The orthogonal test design is an efficient, fast, and economical experimental method for investigating multifactors and multilevels at the same time and for selecting the optimum factor and level. The orthogonal test design used in this study is shown in Table 2.

Experimental Procedure

The experimental procedure was carried out in eight steps:

1. Forty-mL beakers were labeled from 1 to 9, and 0.5 g of thermochromic dye was put in each.

Table 1. Experimental parameters and levels.

Experimental levels[a]	Experimental parameters[b]		
	Mixing ratio A of DC	Mixing ratio B of DT	Mixing ratio C of DS
K_1	1:8	1:40	1:1
K_2	1:10	1:50	1:2
K_3	1:12	1:60	1:3

[a] K_1, first level; K_2, second level; K_3, third level.
[b] A, thermochromic dye and chromogenic agent; B, thermochromic dye and 1-tetradecanol; C, thermochromic dye and sensitizing agent.

Table 2. Orthogonal test design.

Test	The mixture ratio of different ingredients[a]			
	Mixing ratio A of DC	Mixing ratio B of DT	Experimental parameters	Mixing ratio C of DS
1	1 (1:8)	1 (1:40)	1	1 (1:1)
2	1 (1:8)	2 (1:50)	2	2 (1:2)
3	1 (1:8)	3 (1:60)	3	3 (1:3)
4	2 (1:10)	1 (1:40)	2	3 (1:3)
5	2 (1:10)	2 (1:50)	3	1 (1:1)
6	2 (1:10)	3 (1:60)	1	2 (1:2)
7	3 (1:12)	1 (1:40)	3	2 (1:2)
8	3 (1:12)	2 (1:50)	1	3 (1:3)
9	3 (1:12)	3 (1:60)	2	1 (1:1)

[a] A, thermochromic dye and chromogenic agent; B, thermochromic dye and 1-tetradecanol; C, thermochromic dye and sensitizing agent.

2. As described in Tables 1 and 2, a chromogenic agent, 1-tetradecanol, and a sensitizing agent were weighed and added to the beakers.
3. Each beaker was heated in an electric oven and stirred with a glass bar to completely mix the thermochromic agents.
4. The samples were treated in an ultrasonic bath at 75°C for 4 h at 160 W.
5. After the samples were dyed, they were cleaned with hot water and dried in the oven at 70°C for 8 h. The samples were at 11% MC.
6. The samples were placed in a conditioning cabinet at 65% RH to equilibrate at 12-34°C in 2°C steps.
7. The color parameters of brightness index (L), red–green index (a), and yellow–blue index (b) were measured using a CR-300 chroma meter (Minolta Co Ltd, Tokyo, Japan) according to CIE 1976 (Duan et al 2002). ΔE for each sample was calculated using:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \qquad (1)$$

8. The optimum parameters for the process within the limits of the experimental conditions were determined.

RESULTS AND DISCUSSION

Fabrication Process for Thermochromic Wood Veneer

Determining the optimum manufacturing process. The main controlling factor for sample ΔE and the optimum process were determined. Table 3 shows that the mixing ratio of thermochromic dye and the chromogenic agent had the strongest effect on sample ΔE among the different mixing ratios. The next strongest was the ratio of thermochromic dye to 1-tetradecanol, and the weakest was the ratio of thermochromic dye to the sensitizing agent. Within the limits of the experimental conditions, the optimum ratio of thermochromic dye to chromogenic agent to 1-tetradecanol to sensitizing agent was found to 1:8:50:1.

A thermochromic wood veneer was also made using the optimized conditions. The experimental results from the orthogonal test design using samples 1-9 and the result for sample 10 (using the optimum conditions) are shown in Table 4. It can be seen that ΔE at the optimum conditions was greater than that for any other combination of experimental parameters.

Influence of experimental parameters on sample ΔE. Three different mixing ratios of thermochromic dye and the chromogenic agent, thermochromic dye and 1-tetradecanol, and thermochromic dye and the sensitizing agent were used in this study. The ΔE average for each level is shown in Fig 1.

Figure 1 shows the effect of different mixing ratios on ΔE, which was greatest when the mixing ratio of thermochromic dye to chromogenic agent was 1:8. Next was the 1:12 ratio, and the least was the 1:10 ratio. ΔE for the three levels was 70.11, 63.19, and 51.91, respectively. The effect of adding auxiliaries on thermochromic green dye has been published (Wang et al 2002), and a similar conclusion was obtained. For the three mixing ratios of thermochromic dye to 1-tetradecanol (1:40, 1:50, 1:60), the ΔE were 63.30, 67.97, and 53.95, respectively (ΔE was greatest at the 1:50 ratio). ΔE was greatest (66.56) at the 1:1 ratio of thermochromic dye to sensitizing agent. The mechanism of reversible thermochromic behavior in composite materials has been studied, and the amount of agent significantly impacting the color concentration was also published in an earlier article (Song and Li 1998).

Table 3. The range analysis of experimental results.

	The mixture ratio of different ingredients[b]		
Range analysis[a]	A (DC)	B (DT)	C (DS)
K_1	70.11	63.30	66.56
K_2	51.91	67.97	58.26
K_3	63.19	53.95	60.83
Range	18.20	14.02	8.30

[a] K_1, first level; K_2, second level; K_3, third level.
[b] A, thermochromic dye and chromogenic agent; B, thermochromic dye and 1-tetradecanol; C, thermochromic dye and sensitizing agent.
Mixing ratio of A (DC) > B(DT) > C(DS).
Optimum conditions: Mixing ratio of thermochromic dye, chromogenic agent, 1-tetradecanol, and sensitizing agent was 1:8:50:1 (A1B2C1).

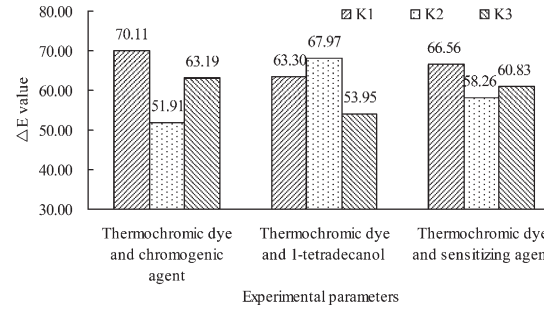

Figure 1. Effect of experimental parameters on ΔE of samples.

Table 4. ΔE of thermochromic veneer for the experimental series in Table 2.

Sample no.	1	2	3	4	5	6	7	8	9	10
ΔE	71.41	71.00	60.60	56.96	61.62	36.55	62.37	62.39	66.27	73.31

Analysis of experimental parameters in terms of ΔE. Analysis of variance was carried out to show the significance of the influences of the experimental parameters on sample ΔE. The results in Table 5 show that variations in all three parameters were significant at the 0.01 level.

Preparation and Properties of Thermochromic Veneer

Preparation of thermochromic wood veneer. The thermochromic agent was introduced using ultrasonic impregnation, and thermochromic wood veneer was successfully made using the optimum conditions determined in this study. The new material is blue at a lower temperature (26°C) and the color of wood at a higher temperature (34°C). Between these limits, the color changes gradually from blue to wood color when temperature is increased and from wood color to blue when temperature is decreased.

Properties of thermochromic wood veneer. Thermochromic wood veneer was produced using the optimum process. Relative to their values at 12°C, the color parameters L, a, b (and calculated ΔE) at other temperatures were investigated. Table 6 and Fig 2 show that the effect of temperature on all optical parameters was small in the range 12-24°C. At higher temperatures, the changes became very large, and the responses leveled out after 34°C. ΔE, ΔL, and Δb generally increased with increasing temperature, and the color of the samples gradually changed from blue to yellow. Δa (red to green) decreased with increasing temperature. It is clear from Fig 2 that the temperature range over which the color changed was 26-34°C. Relationships between ΔE and subjective visual assessments are shown in Table 7 (Guo 2006). The color changed gradually from blue to wood when the temperature increased 26-34°C. As the temperature decreased 34-26°C, there was a gradual change back from wood color to blue. This reversible transition occurred conveniently close to room temperature. The same result was visually observed in the course of the experiments.

Thermochromic mechanism of thermochromic wood veneer. The thermochromic mechanism can be interpreted as follows. Electrons are exchanged between thermochromic dye and chromogenic agent with changing temperature. When the temperature is lower than 26°C, chromogenic agent receives electrons from the thermochromic dye and the color of the samples is blue. When the temperature is higher than

Table 5. Variance analysis of experimental results.

Property	Experimental parameters	DF	Sum of squares	Mean squares	F	Pr > F
ΔE	A	2	1097.3	548.6	68.0	<0.0001
	B	2	805.7	402.9	49.9	<0.0001
	A × B	2	177.3	88.6	11.0	0.0001
	C	2	296.5	148.3	18.4	<0.0001
	Error	45	363.0	8.1		
	Total	53	2739.9			

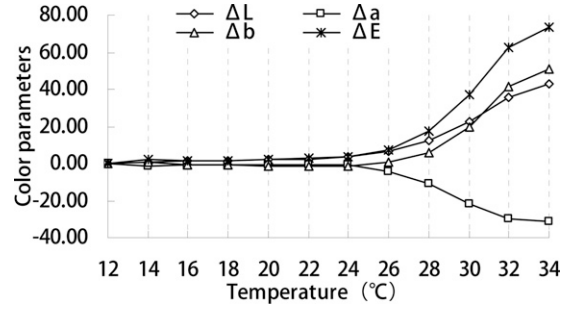

Figure 2. Influence of temperature on ΔL, Δa, Δb, and ΔE.

Table 6. Change of sample color parameters at different temperatures.

Color parameters	Test temperature (°C)											
	12	14	16	18	20	22	24	26	28	30	32	34
ΔL	0	1.05	1.13	1.24	1.91	2.40	3.36	6.28	12.18	22.51	35.90	43.07
Δa	0	−1.69	−0.73	−0.76	−0.65	−0.87	−1.01	−4.18	−10.77	−21.76	−30.02	−31.02
Δb	0	0.97	−0.58	−0.55	−1.42	−1.36	−1.74	0.51	6.07	19.39	41.67	51.18
ΔE	0	2.21	1.46	1.55	2.47	2.89	3.92	7.56	17.35	36.83	62.66	73.73

Table 7. Relationship of ΔE and vision.

ΔE	Visual assessment
0-0.5	Unnoticeable change
0.5-1.5	Slight change
1.5-3.0	Appreciable change
3.0-6.0	Recognizable change
6.0-12.0	Obvious change
Over 12.0	Very obvious change

34°C, the thermochromic dye does not transfer electrons to the chromogenic agent and the veneer has a natural wood color. When the temperature gradually increases from 26-34°C, the veneer changes from blue to natural wood color. When the temperature gradually decreases from 34-26°C, the color changes from wood color to blue. The explanation is consistent with the electron exchange mechanism of some other organic thermochromic materials. Rawat and Norula (1987) showed that the oxidation and reduction peaks of thermochromic dye and chromogenic agent are very close. The balance of the oxidation-reduction reaction changes with changing temperature, altering the wavelengths at which the dye absorbs or reflects light.

CONCLUSIONS

To achieve the maximum ΔE within the chosen experimental conditions, the optimum mixing ratio of thermochromic dye to chromogenic agent to 1-tetradecanol to sensitizing agent was determined to be 1:8:50:1. Based on this optimum process, a new kind of thermochromic material (thermochromic wood veneer) was successfully made. The color change of thermochromic wood veneer was visually obvious. The color started to change at 26°C and stopped at 34°C. When the temperature gradually increased 26-34°C, the color changed from blue to natural wood. Conversely, when temperature gradually decreased from 34-26°C, the veneer changed from natural wood color to blue.

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