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COLORIMETRIC AND THERMOCHROMIC PROPERTIES OF REVERSIBLE THERMOCHROMIC WOOD

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ABSTRACT

To endow wood materials with a thermochromic function, an organic thermochromic agent consisting of thermochromic dye, bisphenol A (BPA) and long-chain alcohols (1-tetradecanol (TD), or 1-hexadecanol (HD)) was used as a dye to prepare reversible thermochromic wood (RTCW). The colorimetric properties, including total color difference (ΔE^*_{ab}), lightness index (L*), red-green index (a*), and yellow-blue index (b*), were investigated at different temperatures. The color change temperature range and color hysteresis of RTCW were also analyzed. The color difference unit of National Bureau of Standards (NBS) was used to determine the color change temperature range and the achromic (chromic) temperature. In the decolorization process, with the temperature increasing, the values of ΔE^*_{ab}, L* and b* of the RTCW samples increased, and the values of a* decreased, but the values of ΔE^*_{ab}, L*, a*, and b* were just opposite in the colorization process. Meanwhile, the color of the RTCW with TD or HD could repeatedly change between red and light brown (wood colore) within a color temperature range of 25-35°C or 37-49°C respectively, presenting a "color hysteresis" phenomenon over a heating (decolorization) and cooling (colorization) cycle. The achromic and chromic temperature of the RTCW samples with TD was 31°C and 25°C respectively while RTCW samples with HD was 43°C and 37°C.

KEYWORDS: Thermochromic wood, thermochromic properties, reversibility, colorimetric properties, color difference, color hysteresis.

INTRODUCTION

Chromogenic materials change their visible optical properties in response to an external stimulus (Seeboth et al. 2007). According to the stimulus, chromogenic materials are classified as thermochromic, photochromic, electrochromic, piezochromic, halochromic, biochromic (Klanjšek Gunde 2010). Among the chromogenic materials, thermochromic materials (TCM) play a remarkable role in the next future (Seeboth et al. 2007). TCM respond to change of temperature by color change (Kulčar et al. 2010). TCM have been becoming increasingly important for various applications in security printing, smart packing, textile, wood materials (Jiang et al. 2013a; Liu et al. 2011). Reversible thermochromic wood (RTCW) is a new functional material, which can decolorize at high temperatures and transform into original dyeing color on cooling. The RTCW materials will be applied to furniture, floors, and decorative panels, which will improve the added value of products (Jiang et al. 2013a).

As a new functional material, RTCW was developed by our research team in past ten years. In our research, RTCW was manufactured by impregnating wood or veneers with a thermochromic agent which consisting a color former, color developer and solvent (Jiang 2013, Liu 2010). Common color formers are electron-donating, leuco dye, such as crystal violet lactone (CVL), thermochromic dye (Red) or thermochromic dye (Yellow). Frequently used color developer are electron-accepting, weak acid, as exemplified by bisphenol A (BPA), gallates or phenols. Frequently used solvents are esters and alcohols such as 1-dodecanol (DD), 1-tetradecanol (TD) or 1-hexadecanol (HD) which reported to be suitable because of their low volatility and wide range of applications (White and LeBlanc 1999). In the previous studies, the mixing ratio of thermochromic agent, manufacturing technology, thermochromic properties and light fastness of RTCW were studied (Fu et al. 2013, Jiang et al. 2013b, Liu et al. 2012). It was found that RTCW had good thermochromic properties, that is, the color of RTCW can repeatedly change between the dyeing color and the color of the wood surface over a specific temperature range. The color change temperature was usually determined by visual observation of researchers (Liu 2010). However, it was not rigorous as there were errors with different testers though it was a convenient and effective method. Thus, it is necessary to figure out how temperature effected the color change and the colorimetric properties changed with different temperatures. Whilst according to the literatures and the authors' results in previous research works, the melting point of the solvent component controls the temperature at which the color of the leuco dye-developer-solvent composites, thermochromic changes (Tang et al. 2010, White and LeBlanc 1999). Therefore, the relationship of color change temperature to melting point of solvents could be expounded.

The aim of this study is to develop a RTCW colored by a leuco dye-developer-solvent composites consisting Leuco dye TF-R1 (color former), BPA (color developer), and TD or HD (solvent). The colorimetric properties of RTCW were characterized. Moreover, On the basis of the color unit rating of National Bureau of Standards (NBS), the color change temperature is distinguished by the total color difference (ΔE^*_{ab}) using a chroma meter with an aim to offer a new evaluation method for determining the color change temperature range of RTCW.

MATERIAL AND METHODS

Materials

Sliced veneers of *Betula alnoides* (mixed sapwood and heartwood) with dimensions of approximately 50 × 30 × 0.7 mm (R × T × L) were provided by Treessun Flooring Co., Ltd. (China). The average density and moisture content of veneers was 660 $kg \cdot m^{-3}$ and 7±2%, respectively. The total number of samples was 9. Leuco dye TF-R1 (TF-R1, 3-diethylamino-7, 8-phenyl-fluoran, $C_{28}H_{23}NO_3$, laboratory reagent) was purchased from Perking University Delichem Co., Ltd. (China), 1-hexadecanol (HD, $C_{16}H_{34}O$, purity 98.0%) and bisphenol A (BPA, purity 99.0%) were obtained from Tianjin Guangfu Fine Chemical Research Institute (China), and 1-tetradecanol (TD, $C_{14}H_{30}O$, purity 99.0%) was purchased from Tianjin East China Chemical Reagent Factory (China). All were used without further purification.

Methods

Preparation of reversible thermochromic wood

Reversible thermochromic compounds was mixed with TF-R1, BPA, and TD (or HD). The mixing ratio of TF-R1 to BPA to TD (or HD) was 1:4:40. All of them were weighed and added to the beakers. Each beaker was heated in an electric oven and stirred with a glass bar to mix the three components completely. And then the wood samples were put into the beakers in an ultrasonic bath at 75°C for 1 h at 160W (Jiang 2013). After the samples were dyed, they were dried in the oven at 30°C for 4 h. The samples were placed in a temperature and humidity chamber at 50% RH to equilibrate at 15°C. Three replicate veneers were dyed for each type of RTCW, and a total of 9 veneers for the experiments (3 veneers for the control experiment).

Colorimetric properties measurement

Color changes were characterized using the Commission Internationale de L'Eclairage L*a*b* (CIE L*a*b*) color space. The CIE L*a*b* color space is currently one of the most popular and widely used color spaces and it is well suited for the determination color differences. The advantage of the CIE L*a*b* system is that color differences can be expressed in units that can be related to visual perception. With the CIELAB (1976) system, the colorimetric properties of lightness index (L*), red-green index (a*), and yellow-blue index (b*) were measured with the Chroma Meter (CR-400, Konica Minolta Sensing Inc., Japan).

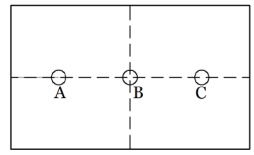

Fig. 1: Testing figure for colorimetric properties. The test points were distributed at the midline position. A 10 mm margin was set apart on both sides along the length of the samples

The colorimetric properties at the points A, B, and C (Fig. 1) were measured three times and calculated mean value during heating from 15°C up to 59°C and cooling down to 15°C. in 2°C steps. The test temperature was control by a temperature and humidity chamber and it maintained 10 minutes after reaching the desired temperature. The colorimetric properties were measured quickly in the temperature and humidity chamber. The total color difference (ΔE^*_{ab}) was calculated as follows (Koksal and Dikbas 2008, Razzoog et al. 1994, Rosentritt et al. 1998).

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} = \sqrt{(L^*_n - L^*_0)^2 + (a^*_n - a^*_0)^2 + (b^*_n - b^*_0)^2} \quad (1)$$

where: ΔL^* - the lightness index difference,
Δa^* - the red-green index difference,
Δb^* - the yellow-blue index difference.,
L^*_0 - the lightness index at 15°C,
a^*_0 - the red-green index at 15°C,
b^*_0 - the yellow-blue index at 15°C,
L^*_n - the lightness index at a desired temperature,
a^*_n - the red-green index at a desired temperature,
b^*_n - the yellow-blue index at a desired temperature.

The total color difference (ΔE^*_{ab}) changes with the change of temperatures, therefore the relative color difference (ΔE) was used to distinguish the color of samples at different temperatures. The relative color difference (ΔE) was calculated by:

$$\Delta E = \left|(\Delta E^*_{ab})_{T_i} - (\Delta E^*_{ab})_{T_{i-1}}\right|, i = 2, 3, \ldots, n \quad (2)$$

RESULTS AND DISCUSSION

Colorimetric properties of reversible thermochromic wood

The CIELAB values of the RTCW samples were measured by Chroma Meter (CR-400, Konica Minolta Sensing Inc., Japan) during heating from 15°C to 59°C and cooling down to 15°C. The lightness index (L*), red-green index (a*), and yellow-blue index (b*) of RTCW samples at different temperatures were seen in Fig. 2 and Fig. 3.

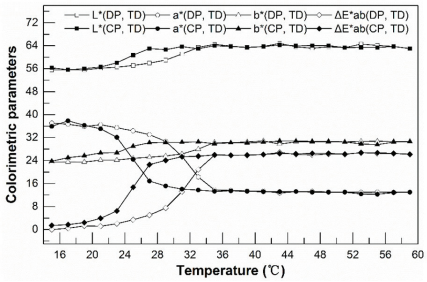

Fig. 2: CIELAB ΔE^*_{ab} (rhombus), L (squares), a* (circles), b* (triangles) of RTCW samples with TD in the decolorization process (DP, open signs) and colorization process (CP, solid signs)*

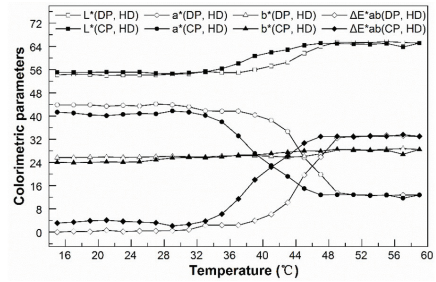

Fig. 3: CIELAB ΔE^*_{ab} (rhombus), L (squares), a* (circles), b* (triangles) of RTCW samples with HD in the decolorization process (DP, open signs) and colorization process (CP, solid signs).*

In the decolorization process, with the temperature increasing, the values of L* and b* of the RTCW samples increased, and the values of a* decreased, but the values of L*, a*, and b* were just opposite in the colorization process. It is found that the colorimetric properties of RTCW samples with TD and HD have the same changing tendency and the results are consistent with other studies on thermochromic printing inks (Kulčar et al. 2012). Whilst the RTCW samples treated with thermocycling fatigue experiment still had good repeatability (Jiang 2013).

Color change temperature and color hysteresis

The CIE L*a*b* color space is currently one of the most popular and widely used color spaces and it is well suited for the determination color differences. The total color difference (ΔE^*_{ab}) was calculated from Eq. 1 previously mentioned. In the decolorization process, the effect of temperature on the values of ΔE^*_{ab}, ΔL*, Δa*, and Δb* of RTCW samples with TD and HD was small in the range of 15-25°C (Fig. 4) and 15-37°C (Fig. 5), respectively.

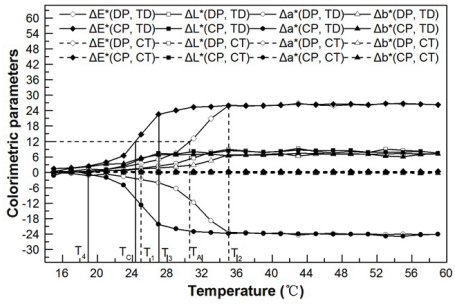

Fig. 4: CIELAB ΔE^*_{ab} (rhombus), ΔL (squares), Δa* (circles), Δb* (triangles) of RTCW samples with TD in the decolorization process (DP, solid signs) and colorization process (CP, open signs)*

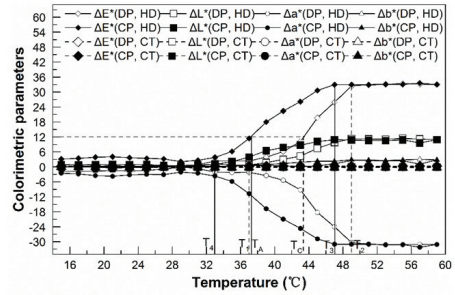

Fig. 5: CIELAB ΔE^*_{ab} (rhombus), ΔL (squares), Δa* (circles), Δb* (triangles) of RTCW samples with HD in the decolorization process (DP, solid signs) and colorization process (CP, open signs).*

With the increasing temperature, the changes became large, and the responses leveled out after 35°C (Fig. 4) and 49°C (Fig. 5), respectively. The values of ΔE^*_{ab}, ΔL*, and Δb* of RTCW samples with TD and HD generally increased and Δa* decreased with the increasing temperature from 25°C to 35°C (Fig. 4) and from 37°C to 49°C (Fig. 5) respectively, and the color of the RTCW samples generally changed from red to light brown (wood color). While in the colorization process, the change values of ΔE^*_{ab}, ΔL*, Δa*, and Δb* of RTCW samples with TD and HD were small in the range of 59-27°C (Fig. 4) and 59-47°C (Fig. 5) respectively. And the same as that below 19°C (Fig. 4) and 33°C (Fig. 5). With the decreasing temperature, the changes became large, and the responses leveled out below 19°C (Fig. 4) and 33°C (Fig. 5). And the color of the RTCW samples generally changed from light brown (wood color) to red. The values of ΔE^*_{ab}, ΔL*, Δa*, and Δb* of control (CT) samples were similarly constant during the decolorization and colorization process.

The phenomenon of decolorization and colorization of the RTCW samples occurred in the temperature-rise and temperature-fall period. In previous studies, the researchers usually determined the color change temperature by visual observation (Liu 2010). The method of visual observation, however, was not rigorous as the criteria of perceptibility adopted by each researcher were different. Whilst the color change temperature was defined as switching (Seeboth et al. 2007), decolortization (MacLaren and White 2003a, MacLaren and White 2003b), or activation temperature (Kaiserman et al. 2001). The definitions of the color temperature are not scientific because the color change process is dynamic and reversible. That is, the temperature at which the color change takes place should contain two definitions of achromic temperature and chromic temperature in decolorization and colorization process, respectively. Therefore, to counter such differences and disagreements in the criteria used, the National Bureau of Standards (NBS) rating system is a frequently used method to determine the degree of color difference since it offers absolute criteria by which color difference values can be converted to remarks (Koksal and

Dikbas 2008, Razzoog et al. 1994). In the present study, therefore, corresponding NBS units were calculated to assess the color differences caused by temperature.

Tab. 1: National Bureau of Standards (NBS) ratings of color differences.

NBS unit	Critical remarks of color differences	
0-0.5	Trace	Extremely slight change
0.5-1.5	Slight	Slight change
1.5-3.0	Noticeable	Perceivable change
3.0-6.0	Appreciable	Marked change
6.0-12.0	Much	Extremely marked change

It was found that the value of the total color difference (ΔE^*_{ab}) was more than 1.5, meaning that color change was "noticeable" (Tab. 1), and when the value of ΔE^*_{ab} was more than 12.0, meaning that color change was "very much", that is, the color changed to the other color (Tab. 1). So the temperature at which the value of ΔE^*_{ab} was more than 12.0 was taken as the achromic (T_A) and chromic temperature (T_C). The temperature at which the relative color difference value (ΔE) was more than 1.5 was taken as the initial achromic or chromic (T_1 or T_3) and final achromic or chromic (T_2 or T_4) temperatures. According to the foregoing analysis, the T_A and T_C temperature of RTCW samples with TD was 31°C and 25°C respectively while RTCW samples with HD was 43°C and 37°C (Fig. 6).

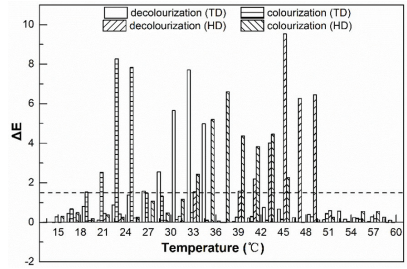

Fig. 6: ΔE of RTCW samples with TD and HD at different temperatures.

Similarly, the color change temperature interval was easily calculated. As was seen from Fig. 4 and Fig. 5, the achromic temperature interval (T_1-T_2) and chromic temperature interval (T_3-T_4) of RTCW samples with TD was 25-35°C and 27-19°C respectively while RTCW samples with HD was 37-49°C and 47-33°C.

According to the foregoing analysis, the RTCW samples underwent color reversible change during the decolorization and colorization process. No abrupt change was observed as both processes were continuous (Fig. 2 to 5). RTCW samples could lose their color during heating and regain it during the cooling. The reversible color change process depended on the temperature which can be shown by the change of ΔL*, Δa* and Δb* as a function of temperature (Figs. 4 and 5). When the samples were heated, ΔE^*_{ab} , ΔL*, and Δb* became higher, and the Δa* became lower. Whereas, it was opposite when the samples were cooling. Most of the decolorization process were already accomplished to a certain degree above T_A where, ΔL*, Δa*, and Δb* remained approximately the same with further increment of temperature. The reverse process occurred during cooling but at lower temperatures. The entire, ΔL*, Δa*, and Δb* curve had a form of a loop. The results were not consistent with the result obtained on previous experiments (Liu et

al. 2011). Such results showed that color of RTCW samples did not only depend on temperature, but also on the thermal history. Therefore, it was not possible to characterize the properties of such a sample in a selected time only by temperature. The thermochromic system had memory – it was not possible to predict its output without knowing the path that it followed before the current state was reached. Such a phenomenon was called color hysteresis.

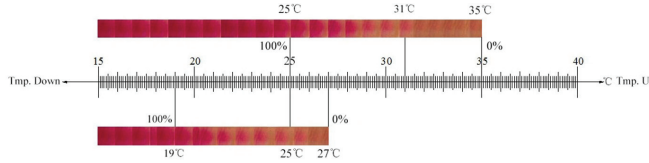

Fig. 7: Diagram of reversible color change of RTCW samples with TD in the decolorization and colorization process.

Fig. 7 showed that the color of RTCW samples with TD appearing on heating was not equal to those on cooling. RTCW belonged to several physical systems with hysteresis. It was color hysteresis that described the color of a RTCW sample as a function of temperature.

CONCLUSIONS

The colorimetric properties of two organic higher aliphatic alcohol-based thermochromic wood samples were analyzed. The samples decolorized at high temperatures and transform into original dyeing color when cooling. The color changes depended on temperature and thermal history, which was named color hysteresis that the colors appearing on heating are in general not equal to those on cooling.

According to the color difference unit of NBS, it was feasible and dependable to determine the achromic (chromic) temperatures and initial to final achromic (chromic) temperatures during the decolorization (colorization) process. The achromic and chromic temperature of the thermochromic wood samples with TD was 31°C and 25°C respectively while thermochromic wood samples with HD was 43°C and 37°C. And the achromic and chromic temperature interval of the thermochromic wood samples with TD was 25-35°Cand 27-19°C respectively while thermochromic wood samples with HD was 37-49°Cand 47-33°C in the decolorization and colorization process.

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