Poplar-based thermochromic composites that change colour at 38 °C to 46 °C

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The red thermochromic dye (R-TD) is the tetradecanoic acid tetradecyl ester (C28H56O2) and methyl red (C15H15N3O2) mixture that has better permeability enabling its infiltration into wood and better thermochromic properties changing its colour at above 30 °C after about 0.5 min. Thicker poplar-based thermochromic composite specimens (R-PTC, thickness: 5.0 mm) were prepared by filling the R-TD into pre-treated poplar veneer (thickness: 5.0 mm) thus allowing better penetration after pre-treatment. After R-TD infiltration, the R-PTC samples were covered by polypropylene wax for preventing R-TD from overflowing from R-PTC under the action of phase-change temperature. This R-PTC, whose colour can change from light-red to dark-red at 38 °C to 46 °C, can recover to light-red at below 38 °C after about 14 h, and the peak of colour change is at about 42 °C. R-PTC will be suitable for materials used in thermochromic furniture that can indicate the surface temperature to potential users, thus allowing assessment of likely scalded pain when used the furniture.

Thermochromic wood, as a thermochromic material, can undergo a reversible change in colour with respect to temperature stimulus1–5, that has the advantages of renewability, low cost, easy preparation, easy modification and so on. Thermochromic wood can be used in many fields, such as: temperature sensors6–8, smart window frame9–11, temperature control coatings12,13, thermal energy storage14, camouflage15, etc. Infiltrating thermochromic dyes into wood materials will help to improve the seasonal visual effect of wood, that can enrich the decorative effect of wood materials, can be used as temperature indicators, and can provide a new solution to energy consumption for interior buildings16,17. Professor Fu Feng and coworkers have investigated the development of thermochromic wood18, the preparation and properties of thermochromic thin wood-based veneer (thickness: 0.7 mm)19–21, and multi-functional thermochromic energy-storage wood materials22. Xiaodong Zhu and coworkers have prepared a thin thermochromic wood-based veneer (thickness: 0.17 mm) that can be obtained after impregnation with a thermochromic compound suspension for 2.0 min at 65 °C16.

In the present research, a thicker, poplar-based, thermochromic composite (R-PTC, thickness: 5.0 mm) was prepared by infiltration of red thermochromic dyes (R-TD) into the pre-treated poplar veneer (thickness: 5.0 mm) and compacting the resulting poplar-based composite (Fig. 1). This type of R-PTC can undergo a colour change from light-red to dark-red at about 38 °C to 46 °C, can revert to light-red at below 38 °C after about 14 h, and the peak of colour change is at about 42 °C.

Results and discussion

Fourier transform infrared spectroscopy (FTIR) was used to investigate changes in the composition of the cell wall of poplar specimens before and after pre-treatment. FTIR spectra were measured using an FTIR-850 (Gangdong, Tianjin, China). In the FTIR spectrum, the band at 1505 cm−1 represents the aromatic skeleton vibration of the lignin28–31. The band at 1235 cm−1 represents the characteristic vibration of hemicelluloses, and that at 1735 cm−1 signifies the presence of a C=O functional group32–35. The 1505 cm−1, 1235 cm−1, and 1735 cm−1 peaks represent lignin, hemicelluloses, and C=O functional group, respectively. After pre-treatment, the 1505 cm−1, 1235 cm−1, and 1735 cm−1 peaks of pre-treated poplar specimens are lower than the peaks of the original poplar specimens in the FTIR spectra (Fig. 2), proving that lignin, hemicellulose, and the C=O functional group may had been changed therefrom. As Table 1 shows, the absolute-dry mass of original poplar specimens

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Longitudinal-cutting poplar veneer (thickness: 5.0 mm)

Figure 1. Preparation of R-PTC.

Figure 2. FTIR spectra: original, and pre-treated poplar specimens.

(60 mm × 60 mm × 5 mm) was about 4.244 ~ 4.391 g, and the absolute-dry mass of pre-treated poplar specimens (60 mm × 60 mm × 5 mm) was about 3.113–3.382 g, and the absolute-dry mass of pre-treated poplar specimens was less than that of the original poplar specimens, with the mass being reduced by about one-third of its original
value after pre-treatment. Therefore, to compare with the original poplar specimens, the lignin, hemicellulose, and the C=O functional group may have been largely removed in the pre-treated poplar specimens.

Original, and pre-treated poplar specimens were cut from the longitudinal direction, these sections were examined by using Sigma 300 scanning electron microscopy (Zeiss, Germany). Figure 3a,b are SEM images of longitudinal direction from original, and pre-treated poplar specimens, respectively. As the red arrows show (Fig. 3), the cell cavity space was obviously enlarged after pre-treatment, that improved the channel of R-TD infiltration.

DSC test of R-TD and R-PTC. The phase-change temperature of thermochromic dyes can affect the temperature during dye-infiltration and the colour-change temperature of a thermochromic material 19,20. A differential scanning calorimeter (DSC) can be used to measure phase-change temperature (Fig. 4): the peak value of phase-change temperature was 46.97 °C in R-TD, and the peak value was 41.78 °C in R-PTC. As Fig. 4 shows, the phase-change temperature range of R-TD is about 30 °C to 62 °C, and the phase-change temperature range of R-PTC is about 38 °C to 46 °C. In R-PTC, the covalent bond between wood fibers and R-TD that potentially improved the starting temperature of phase-change temperature range, and the water molecule of wood that possibly reduced the peak value and range of phase-change temperature. Therefore, comparing with R-TD, the R-PTC had lower peak value of phase-change temperature, and narrower phase-change temperature range.

| Sample 1 (g) | Sample 2 (g) | Sample 3 (g) |
|-------------|-------------|-------------|
| Absolute-drying mass: original poplar (60 mm × 60 mm × 5 mm) | 4.244 | 4.362 | 4.391 |
| Absolute-drying mass: pre-treated poplar (60 mm × 60 mm × 5 mm) | 3.113 | 3.214 | 3.382 |

Table 1. The absolute-drying masses: original, and pre-treated poplar specimens.

Figure 3. SEM images: original, and pre-treated poplar specimens.

Figure 4. The DSC curve of R-TD and R-PTC.
Thermochromic properties of R-PTC. According to CIELab measurements (International Lighting Committee, 1976) and the environmental temperature range of R-PTC, the R-PTC specimens were placed into a constant-temperature box for about 10 min at a specific temperature from 20 to 60 °C (Table 2), and the colour parameters \((L, a, b)\) of R-PTC surface were measured using a CR-400 colorimeter (Konica Minolta, Japan) at each specific temperature (Table 2). Each colour parameter is the average value of three measurements at different positions (●, ■, and ▲) on the R-PTC surface (Fig. 5a). In Table 2, \(\Delta E_{ab}\) is the value of the colour difference, and the magnitude of \(\Delta E_{ab}\) affects the strength of human vision (Table 3)\(^{36,37}\); \(\Delta E_{ab}\) is given by:

\[
\Delta E_{ab} = \sqrt{(L_n - L_0)^2 + (a_n - a_0)^2 + (b_n - b_0)^2}
\]

where \(L_0, a_0,\) and \(b_0\) are the colour parameters of the R-PTC surface at 20 °C; \(L_n, a_n,\) and \(b_n\) are the colour parameters of the R-PTC surface at 22 °C, 24 °C, 26 °C, …, 58 °C, and 60 °C, respectively.

As shown in Table 2 and Fig. 5b, at 38 °C to 42 °C, \(\Delta E_{ab}\) exceeded 3.0 and gradually reached 12 (Table 2). Data in Table 3 show that the colour differences in R-PTC changed at 38 °C and did so to a much greater extent at 42 °C to the human eye. In Fig. 5a, the colour of the R-PTC surface is seen to have changed from light-red (at < 38 °C) to dark-red (at ≥ 42 °C). The thermochromic properties of R-PTC basically accord with the DSC test of R-PTC, the peak value all appeared at about 42 °C, and the range all appeared at about 38 °C to 46 °C.

After heating the R-PTC specimens in a constant-temperature box (Symor, Heifei, China) for about 150 h at 80 to 100 °C, the weight of heat-treated R-PTC was reduced about 21% of original R-PTC. As Fig. 5c shown, at ●, ■, and ▲ positions on the R-PTC surface, the colour parameter of three positions were measured before and after the R-PTC specimens were exposed to ultraviolet light (120 mw/cm²) for about 150 h, and its \(\Delta E_{ab}\) was 5.7, recognition change.

The colour of methyl red (C₁₅H₁₅N₃O₂) is red and acid form (HMR) when its pH value was ≤ 4.4 and its wavelength was at 520 nm, and the colour of methyl red (C₁₅H₁₄N₃O₂) is yellow and alkaline form (MR) when its pH value was ≥ 6.2 and its wavelength was at 430 nm\(^{38–41}\). R-TD is the tetradecanoic acid tetradecyl ester (C₂₈H₅₆O₂) and methyl red (C₁₅H₁₅N₃O₂) mixture. In R-TD, C₂₈H₅₆O₂ is the hide-colour solvent, and C₁₅H₁₅N₃O₂ is the developer. As Fig. 5a,d shown, the R-TD was light-red and its developer was acid form (HMR) at about 20 °C, and the R-TD was dark-red and its developer was alkaline form (MR) at about 42 °C.

Mechanical characteristics of R-PTC. The longitudinal compressive strength and tensile strength, and radial hardness of R-PTC were measured. Compared to the original poplar specimens, the R-PTC had a slightly lower longitudinal compressive strength, tensile strength, and radial hardness (Fig. 6). The mechanical characteristics of pre-treated poplar were reduced after the loss of the lignin during pre-treatment: this also influenced the mechanical characteristics of the R-PTC specimens, therefore, improving the mechanical characteristics of R-PTC without affecting its thermochromic properties will form a focus of future research.

Microscopic features of R-PTC. The microscopic features of R-PTC were examined by SEM. Figure 7a,c show SEM images of radial-cut and longitudinal-cut pre-treated poplar specimens, respectively. Figure 7b,d show SEM images of radial-cut and longitudinal-cut R-PTC, respectively. Compared with Fig. 7a,c,b,d show that the

| Temperature (°C) | \(L_n\) | \(a_n\) | \(b_n\) | \(\Delta E_{ab}\) |
|-----------------|-------|-------|-------|-----------|
| 20              | 52    | 43    | 18    | 0         |
| 22              | 51    | 42    | 18    | 1.4       |
| 24              | 53    | 42    | 17    | 1.7       |
| 26              | 53    | 44    | 18    | 1.4       |
| 28              | 51    | 43    | 19    | 1.4       |
| 30              | 51    | 44    | 19    | 1.7       |
| 32              | 51    | 44    | 17    | 1.7       |
| 34              | 53    | 42    | 17    | 1.7       |
| 36              | 53    | 44    | 19    | 1.7       |
| 38              | 54    | 45    | 20    | 3.5       |
| 40              | 47    | 48    | 25    | 9.9       |
| 42              | 44    | 48    | 26    | 12.4      |
| 44              | 40    | 49    | 30    | 18        |
| 46              | 38    | 51    | 34    | 22.7      |
| 48              | 35    | 50    | 39    | 27.9      |
| 50              | 27    | 43    | 32    | 28.7      |
| 52              | 28    | 41    | 33    | 28.4      |
| 54              | 26    | 44    | 30    | 28.7      |
| 56              | 28    | 42    | 34    | 28.9      |
| 58              | 27    | 42    | 32    | 28.7      |
| 60              | 27    | 42    | 31    | 28.2      |

Table 2. The colour parameters of the R-PTC surface at temperatures from 20 to 60 °C.
R-PTC was able to be infiltrated by R-TD, which as the red arrows show, R-TD had been attached to the cell wall of wood. In R-PTC, the R-TD gathered around the fibers and on the surface of cell wall, and the R-TD liked irregular ball-like object that combined with the fibers of wood (Fig. 8).

**Conclusions**

The colour of the newly-developed R-PTC could change from light-red (below 38 °C) to dark-red (above 42 °C), can gradually revert to light-red at below 38 °C after about 14 h, and the peak of colour change is at about 42 °C. When the temperature of object at ≥ 42 °C, the user will feel scalded pain after touching the object. Therefore, R-PTC could be used in material used to make furniture capable of indicating the surface temperature to potential users, allowing them to assess likely scalded pain. Furthermore, future work will focus on improvement of its mechanical characteristics.

**Experimental.** Materials and chemicals. The original poplar (60 mm × 60 mm × 5 mm) was purchased from Mudan Wood Co., Ltd. (Suqian, China), Sodium hypochlorite (NaOCl, > 98%), deionised water, and absolute ethyl alcohol (C₂H₆O, > 99.5%) were purchased from Aladdin Biochemical Technology (Shanghai, China). Tetradecanoic acid tetradecyl ester (C₂₈H₅₆O₂, > 99%) and polypropylene wax were purchased from Shandong Usolf Chemical Technology Co., Ltd. (Linyi, China). Methyl red (C₁₅H₁₅N₃O₂, > 99%) was purchased from Fangzheng Reagent Factory (Tianjin, China).

**Table 3.** The relation between ΔEₐₐ and identification ability of human vision.

| ΔE_ab | Human vision       |
|-------|--------------------|
| 0–0.5 | Unnoticeable change|
| 0.5–1.5| Slight change     |
| 1.5–3.0| Appreciable change|
| 3.0–6.0| Recognition change|
| 6.0–12.0| Obvious change    |
| > 12.0 | Very obvious change|

**Figure 5.** (a) The colours of the R-PTC surface changed from light-red (below 38 °C) to dark-red (above 42 °C). (b) The curve of ΔE_ab. (c) The colours of the R-PTC surface changed before and after ultraviolet light treatment. (d) The thermochromic mechanism of R-TD.
The preparation process of R-PTC included pre-treatment of the specimens, preparation of R-TD, R-TD infiltration, and compaction (Table 4).

Sample pre-treatment. After drying the original poplar specimens in a constant-temperature box (Symor, Heifei, China) for about 3 h at 80 to 90 °C, the sample was dipped in NaOCl solution (0.81 mol L−1 in deionised water) for about 48 h at 15 to 25 °C. Then, the specimens were steamed over deionised water for about 6 h at 100 to 120 °C. After repeating these pre-treatment, all added chemicals were removed from the specimens by rinsing in hot distilled water, and subsequent preservation in C₂H₆O.

Preparation of R-TD and R-TD infiltration. R-TD was prepared by mixing C₂₈H₅₆O₂ (10 g) and C₁₅H₁₅N₃O₂ (0.1 g) for about 0.5 h at about 75 to 80 °C. The pre-treated poplar specimens were then removed from the C₂H₆O and dried in a constant-temperature box for about 1 h at 80 to 90 °C. Then, the specimens were steamed over deionised water for about 6 h at 100 to 120 °C. After repeating these pre-treatment, all added chemicals were removed from the specimens by rinsing in hot distilled water, and subsequent preservation in C₂H₆O.

Preparation of R-TD and R-TD infiltration. R-TD was prepared by mixing C₃₀H₅₈O₃ (10 g) and C₁₅H₁₅N₃O₂ (0.1 g) for about 0.5 h at about 75 to 80 °C. The pre-treated poplar specimens were then removed from the C₂H₆O and dried in a constant-temperature box for about 1 h at 80 to 90 °C. Then, the specimens were steamed over deionised water for about 6 h at 100 to 120 °C. After repeating these pre-treatment, all added chemicals were removed from the specimens by rinsing in hot distilled water, and subsequent preservation in C₂H₆O.

Compaction and painting treatment. After R-TD infiltrating the sample, the poplar-based thermochromic composite (R-PTC) specimens were compacted in a 150 T universal test press (Suzhou, Shanghai, China) under an applied stress of 4.5 MPa for about 0.5 h at 15 to 25 °C, and the R-PTC samples were covered by polypropylene wax for preventing R-TD from overflowing from R-PTC under the action of phase-changed temperature.

Statement. All methods were performed in accordance with the relevant guidelines and regulations.
Figure 7. SEM images: pre-treated poplar specimens (a, c) and R-PTC specimens (b, d).

Figure 8. SEM image: the R-TD in R-PTC specimen.

Table 4. The chemical formula and method of preparation of R-PTC.

| Treatment method (s)                              | Chemicals (g, ml)                      | Temperature (°C) | Time (h) |
|---------------------------------------------------|----------------------------------------|------------------|----------|
| Pre-treatment of Sample 1 (dipping sample)        | NaOCl (30 g), Deionised water (500 ml) | 15–25            | 48       |
| Pre-treatment of sample 2 (steaming sample)       | Deionised water (2500 ml)             | 100–120          | 6        |
| Preparation of R-TD and R-TD infiltration         | C_{28}H_{56}O_{2} (10 g), C_{15}H_{15}N_{3}O_{2} (0.1 g) | 75–80            | 2.5      |
| Compaction and painting treatment                 |                                        | 15–25            | 0.5      |
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**Author contributions**

W.Z. wrote the main manuscript text and D.S. helped write the manuscript, W.Z. and D.S. conceived of the idea, W.Z., Z.W., P.Z. carried out the experimental work. Figures 1, 2, 3, 4, 5, 6, 7 and 8 were drawn by W.Z., Z.L., P.Z., all authors reviewed and edited the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

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