The Thermal Stability of Amur Cork Tree-Dyed Paper

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Abstract

Amur cork trees are one of the most important traditional natural dyes used, especially for functional production in ancient Chinese papers, due to religious reasons, their aesthetic aspects and antibacterial properties. The properties of Amur cork tree-dyed papers under dry-heat accelerating aging conditions were investigated via optical observation, pH, scanning electron microscopy, thermal difference, tensile strength and folding endurance examinations. The results showed that the concentration of Amur cork trees greatly affected the properties of paper. The changes in surface color, pH, morphology and mechanical properties after the artificial dry-heat aging tests revealed that the paper thermal stability was affected by the Amur cork tree content. A suitable concentration of Amur cork tree colorant is good for maintaining paper's thermal stability due to chemical bonding. Agglomerated colorant dyes might decompose weak acidic materials, which accelerates paper degradation.

1. Introduction

Papers dyed with natural yellow plant dyes are one of the most important traditions in ancient China due to religious reasons, the high tinctorial strength of these plant dyes, the vividness of the yellow color and conservation considerations. In recent years, the analytical characterization of natural yellow dyes has attracted the attention of many researchers [1-7]. As one of the most important yellow natural dyes used widely in ancient China, the properties of Amur cork tree-dyed papers have been studied [8, 9]. The results showed that the Amur cork tree had a better effect than other botanical-sourced yellow dyes.

Nevertheless, natural dyes have some disadvantages, such as being faded and deteriorating easily by thermal, acid gases, UV light, etc. Until now, the fading of natural dyes induced by light has been studied widely [10-13]. However, valuable ancient books and other paper materials dyed with Amur cork tree dyes usually change color considerable after a long period of time, even under no light conditions. Therefore, the need for protection against the damaging effects of environmental conditions is a very important indoor conservation concern.

Considering all of those described above, a laboratory design that can somewhat simulate the possible degradation conditions under a controlled environment is needed. Until now, the thermal stability of Amur bark tree-dyed paper has been less understood. In this paper, we prepared Amur cork tree colorant dye and dyed handmade paper with it and without the use of a mordant. The dyed paper samples with different Amur cork tree colorant contents were aged under artificial dry-heat aging conditions. It was our intent in this research work to examine the thermal stability of Amur cork tree-dyed paper. The aim of this study was to investigate the causes of changes against the action of heat and to provide valuable useful knowledge for paper conservation.

2. Experimental Section

2.1 Materials

Daqian handmade paper (P) was supplied by the *Daqian* Paper Shop in Sichuan Province and had a grammage of 25.46 g/m² and thickness of 94 µm. Its paper pulp was not bleached and made according to the traditional Chinese handmade paper process.

Amur cork trees were purchased from the traditional herbal market in Chengdu, Sichuan Province. All materials were purchased commercially and used as received.

2.2 Preparation of colorant dyes

Detailed information on the preparation of Amur cork tree -dyed paper has been described in our previous paper [8]. The dyeing process was based on traditional Chinese recipes adopted for laboratory procedures [14, 15]. Amur cork trees (50 g) were cut into slices and soaked thoroughly in 500 mL of deionized water for a period of 12 h at room temperature, followed by boiling and simmering for 30 minutes. The extracted solution was filtered to obtain high-concentration extracts from the boiled dregs using a cloth sack. The obtained original Amur cork tree colorant liquid was labeled A0 and then used for dyeing at certain liquor ratios.

2.3 Preparation samples

Colorants with different concentrations of Amur cork tree dyes were obtained by diluting the original Amur cork tree colorant (A0) with deionized water. Amur cork tree-dyed paper was prepared by pulling papers in colorant dyes and hanging on glass rods at 23±1°C for 48 h. The paper samples at water/Amur cork tree ratios of 0:1, 1:1, 2:1 5:1, 10:1 (v/v) were prepared and labeled as P-A0, P-A1, P-A2, P-A5 and P-A10, respectively. Photographic images of the colorant dyed papers are presented in Fig. 1.

All the paper samples were conditioned according to ISO 187-1990 [16] before mechanical measurements at a temperature of 23±1°C and an RH of 50%±2% for 24 h. Tensile strength and folding endurance test samples were prepared by cutting samples that were 15-mm wide with sides within 0.1-mm and 250-mm long in the horizontal and vertical directions and 140-mm long in the horizontal and vertical directions, respectively. It was ensured that paper strips were free of abnormalities, wrinkles and creases.

2.4 Thermal stability studies

Samples were preconditioned according to ISO 187-1990 [16] (23±1°C and 50%±2% RH) for 24 h) and cut into suitable sizes for tests. The thermal degradation temperature was chosen based on the standards ISO 5630-1-1991 (Paper and board-accelerated aging- Part 1: Dry heat treatment at 105°C) similar to the natural aging of paper [17]. Dry-heat accelerated aging was performed in a constant climate chamber KMF 240 (Binder GmbH, Germany) at a temperature of 105±1°C for 80 days. At predetermined periods, specimens for each test were removed from the oven and conditioned for 24 h.

2.5 Characterization

pH tests

The pH of the colorant dyes was tested by a portable pH measurement (Horiba, LAQUA twin-pH-22). Three to four drops of colorant dyes were allowed to rest on the flat sensor until the measured value was displayed.

The pH values of the paper samples were measured by cold extraction according to ISO 6588-1:2012 [Paper, board and pulps-Determination of pH of aqueous extracts-Part 1: Cold extraction] [18]. For this method, air-dried paper samples were soaked in cold distilled water for a period of time. The upper layer liquid was taken after shaking. Then, the pH value of the cold extract was analyzed using a Mettler Toledo S400-B SevenExcellence™ pH meter (Mettler Toledo, Switzerland). The accuracy in these measurements was an average pH ± 0.02 units (n =5).

Colorimetric measurement

A solid reflection spectrophotometer (CM-700D from Minolta Co., Japan) was used to measure the color changes caused by the effect of accelerated dry-heat aging according to the standard ISO 11475:2004 [19]. The measurements were performed by a 10° observer and a D₆₅ light source. The CIE L*a*b* color space was used to determine the color difference (ΔE) by the equation $\Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$, where Δa is the red/green difference, Δb is the yellow/blue difference, and ΔL is the lightness difference. The average data and standard errors of ten measurements were calculated.

Mechanical property measurements

The mechanical property test samples were conditioned according to ISO 187-1990 [16] before testing.

Tensile strength tests were performed according to the TAPPI T-494 and ISO 1924 standards [20, 21] with a TMI 84-56 tensile tester (horizontal) (Testing Machines, Inc., Holland) at a temperature of 23 $\pm$ 1°C, RH of 50 $\pm$ 2% and a test speed of 25 mm/min using an extensometer gauge of 180 mm $\times$ 15 mm. The reported values are the mean from ten determinations.

The folding endurance experiments were performed on a TMI 31-23 double folding endurance tester (Testing Machines, Inc., USA) according to TAPPI/T511 [22] and ISO 5626:1993 [23]. The applied force was 0.5 kg, and the double-fold force was 175 per minute. The folding endurance tests were carried out in a standard atmosphere (at a temperature of 23 $\pm$ 1 °C and an RH of 50% $\pm$ 2%).

Microscope examination

Scanning electron microscopy (SEM) images were recorded using a Philips FEI INSPECT F instrument operated at a 5 kV working voltage after specimen coating with a gold layer by sputtering under vacuum. The surfaces of the paper specimens before and after aging conditions were examined.

Degree of polymerization (DP) test

The degree of polymerization (DP) was determined from the measured change in the intrinsic viscosity, a fast and convenient method to estimate the average DP of cellulose, using the empirical Mark-Houwink equation [24, 25].

$$[\eta] = 0.91DP^{0.85}$$

1

$[\eta]$: intrinsic viscosity, mL/g.

Intrinsic viscosity $[\eta]$ was measured using an Ubbelohde viscometer using copper as the solvent at 25 ± 0.1 °C according to standard GB/T37838-2019 (Pulps-Determination of limiting viscosity number in cupriethylenediamine (CED) solution) [26]. CED was supplied by the China National Pulp and Paper Research Institute. The detailed procedure has been described in our previous paper [27].

3. Results And Discussion

The temporal appearance of the dyed paper with different Amur cork tree colorant concentrations is shown in Fig. 1. The undiluted Amur cork tree dyed paper showed a bright yellow color. It became lighter with a decrease in Amur cork tree concentration. The effect of color changes on paper samples under dry-heat aging is shown in Fig. 2. The color changes with different Amur cork tree concentrations were considerable during aging. The initial bright yellow color for P-A0 before aging became dark brown after dry-heat aging for 50 days. The color difference values (ΔE) could indicate that the influence of aging was more significant. The ΔE values of all samples are shown in Figure 3. With dry-heat aging time, the color change of undyed paper could not be detected ($\Delta E < 3$) even after 50 days. On the other hand, the Amur cork tree dyed paper became brownish after only 5 days. The ΔE increased quickly with dry-heat aging times for the Amur cork tree-dyed papers. The higher the Amur cork tree concentration was, the greater the color change was. The dying mechanism of Amur cork tree-dyed paper is due to its major color component, berberine, a kind of cationic alkaloid charged positively with protons, forming a chemical bond with the hydroxyl groups of the paper fibers through nitrogen. However, yellow berberine turns slowly under heating to deep red–brown–black crude products, including berberrurine [28–31]. In this experiment, all of the dyed paper samples changed to brown to various degrees. The color of the P-A0 sample changed to a slightly red–brown–black color after dry-heat aging for 50 d, which meant that berberine decomposed to some degree during this aging time. With the decrease in the Amur cork tree concentration, the color did not change much, which meant that berberine did not decompose easily when the Amur cork tree concentration was not as high. These results corresponded with the description that when dyeing paper with Amur cork tree, one should not add too much colorant or the color will darken after a long period of time [32].

Colorant fading is associated with changes in the characteristics, such as pH, mechanical properties and morphology. Mechanical properties are an important direct indication of polymer properties. The

mechanical properties of handmade paper is different on the orientation along the transverse direction (TD) and longitudinal direction (LD). The average values of tensile strength and folding endurance of different concentrations of Amur cork tree-dyed paper were tested, and the results are shown in Fig. 4. The values of tensile strength and folding endurance index reflect the detailed structure of the paper. After dyeing, the tensile strength and folding endurance of the original paper increased greatly. As the Amur cork tree concentration decreased, the mechanical properties of the dyed papers decreased gradually. However, even the tensile strength and folding endurance of P-A10 were both slightly higher than those of undyed paper.

During the aging process, paper fibers can be depolymerized and lead to a loss of mechanical properties. Two types of mechanical properties, tensile strength and folding endurance, were measured in this study and are shown in Figs. 5 and 6. The results showed that the mechanical properties of different samples decreased linearly with increasing aging time. Apparently, the patterns of the change for undyed paper and Amur cork tree-dyed papers were similar, at least in the dry-heat aging time range studied in this work. Even though the thermal stability was not sufficient, samples with a suitable concentration of Amur cork had higher thermal stability than other samples.

The morphologies of the samples during dry heating could be elucidated by SEM. Representative SEM images of the pure paper and dyed papers with different Amur cork tree concentrations before and after being subjected to dry heat for 80 days are shown in Fig. 7. The results showed that the fibers were deposited by toning particle materials after dyeing. Agglomeration of toning particles was clearly observed on the surface of P-A0 and P-A1. The agglomerated color component materials clump together in bundles, do not form chemical bonds with the paper fibers and might decompose easily. Figure 7 shows that all samples were destroyed to various degrees after thermal aging for 80 days. Broken fibers were observed clearly on the surface of the undyed paper. Broken fibers and large holes could be observed on the P-A0 and P-A1 surfaces after aging for 80 d (P-A0-80 and P-A1-80), while only some small holes were observed on the P-A2-80 surface, which meant that P-A2 was not destroyed as much as the other paper samples. The representative SEM images of the dyed samples revealed that colorant materials on the surfaces of P-A2 and P-A5 had better dispersibility than those of P-A0 and P-A1. The serious agglomeration of the Amur cork tree illustrated the importance of the colorant material concentration for good dispersion.

The paper's pH is considered one of the most important factors determining the paper's stability toward natural and accelerated aging [27]. The pH of different Amur cork tree concentrations of colorant dyes showed that Amur cork tree colorant dyes were weakly acidic (Fig. 8). Because the undyed paper (P) demonstrated weak alkalinity (pH 7.8), Amur cork tree-dyed papers demonstrated weak acidity to weak alkalinity, which might be ascribed to the presence of alkaline materials in the paper during the papermaking process. Under dry-heat aging conditions, the pH of all samples decreased (shown in Fig. 9). According to Fig. 9, the decrease in pH for P-A0 and P-A1 was greater than that for other samples and resulted in a pH below 6. These results indicated that there should be some acid produced, which corresponded with Cheun's results [29]. The decomposition of berberine produced weakly acidic

materials, which accelerated the degradation of paper under weakly acidic conditions and led to a mechanical decrease. However, for P-A2, no serious agglomeration of toning particles was observed by SEM. The electrovalent bonds between paper fibers and colorant dyes prevented colorant decomposition. For P-A5, there were not enough colorant dyes to form chemical bonds between the paper fibers, so P-A5 had lower mechanical properties than the other samples.

The aging of paper under dry-heat conditions involves several main processes, namely, heat absorption, chemical bond cleavage and formation of oligomer fragments. Therefore, the factors that affect the thermal aging tendency of paper would control the degradation of paper. In the case of Amur cork tree-dyed papers, when the colorant materials dispersed on the paper surface, electrovalent bonds could be formed easily between paper fibers and colorant dyes to prevent paper fiber depolymeration. On the other hand, the agglomerated colorant dyes could be decomposed under thermal conditions, and the produced weak acid would trigger the depolymeration of paper fibers.

The DP was primarily dependent on the molecular chain length [27, 33]. The DP results of the paper samples were determined and are shown in Fig. 10. Interestingly, the DP of P-A2 and P-A5 was slightly higher than that of the undyed paper before aging. However, the DP of P-A0 and P-A1 was slightly lower than that of undyed paper. These results further indicated that the dispersion of colorant materials on paper was very important to the properties of the dyed paper. The DP decreased greatly when the paper samples were subjected to dry-heat aging. The decrease in DP was more pronounced at higher Amur cork tree concentrations than at lower Amur cork tree concentrations. After dry-heat aging for 50 days, the DP of P-A0 was below half the original values.

4. Conclusions

This study was an in-depth investigation of Amur cork tree-dyed paper under dry-heat artificial aging conditions. Compositional and structural characteristics were determined by color, pH, SEM, molecular weight, and mechanical properties changes. Micro-observation revealed that a high Amur cork tree colorant concentration induced agglomeration on the paper surface. The pH, molecular weight and mechanical properties at different aging times depended on the dispersion of the Amur cork tree. A suitable amount of Amur cork tree could form a strong interaction between colorant dyes and paper fibers, which could prevent the decomposition of paper to some degree. The decomposed Amur cork tree produced weakly acidic materials, which accelerated the decomposition of the paper.

The thermal stabilities of Amur cork tree-dyed paper were affected by the concentration of Amur cork tree colorant dyes under accelerating artificial dry-heat aging conditions. It is important to consider the Amur cork tree concentration when it is used as a colorant dye for paper conservation materials.

Abbreviations

LD: longitudinal direction; TD: transverse direction; SEM: Scanning electron microscopy; CIE: International Commission on Illumination; P: undyed paper samples; A: Amur cork tree; P-A0, P-A1, P-A2, P-A5, P-A10: indicated the water/Amur cork tree colorant ratios of 0:1, 1:1, 2:1, 5:1 and 10:1, respectively.

Declarations

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Authors' contributions

Data of the research work were collected by TYW, YFW. QW and YBL prepared the manuscript. YBL revised it. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Competing interests

Not applicable for that statement.

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Figures

Figure 1

Photographic images of the colorant dyed papers are presented in Fig. 1.

Figure 2

Aged samples at different aging times.

Figure 3

The color difference values (ΔE) could indicate that the influence of aging was more significant. The ΔE values of all samples are shown in Figure 3.

Figure 4

The average values of tensile strength and folding endurance of different concentrations of Amur cork tree-dyed paper were tested, and the results are shown in Fig. 4.

Figure 5

Two types of mechanical properties, tensile strength and folding endurance, were measured in this study and are shown in Figs. 5.

Figure 6

Two types of mechanical properties, tensile strength and folding endurance, were measured in this study and are shown in Figs.6.

Figure 7

SEM photography of the different samples' surface before (0 day) and dry-heat 80 days.

Figure 8

The pH of different Amur cork tree concentrations of colorant dyes showed that Amur cork tree colorant dyes were weakly acidic (Fig. 8).

Figure 9

Under dry-heat aging conditions, the pH of all samples decreased (shown in Fig. 9).

Figure 10

The DP results of the paper samples were determined and are shown in Fig. 10.