ABSTRACTS (PH D THESIS)

Color Change of Lignocellulosic Materials during Natural Aging and Heat Treatment

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Introduction

Lignocellulosic materials can be deteriorated by biodegradation, weathering, and natural aging. Their service life, especially of paper and wood, can exceed thousands of years under the proper conditions where biodegradation and weathering are avoided. In such conditions, natural aging becomes a major source of deterioration of the materials. Understanding the mechanism of natural aging is important not only for the purpose of basic research on lignocellulosic materials but also for the preservation and restoration of culturally significant properties made of them.

Natural aging of lignocellulosic materials is considered as ill-defined deterioration which proceeds slowly in the materials under participation of the omnipresent oxygen and water. Some reports have characterized the properties of naturally aged materials in comparison with those of recent materials. However, these reports remain to be the observation of phenomena that occur during natural aging. To understand the mechanism of natural aging within experimentally available time span, heat treatment below thermal decomposition points of the materials has been very useful to accelerate aging.

The objective of this study is to elucidate natural aging of lignocellulosic materials by comparing the property of naturally aged samples with heat-treated samples. Color, which is one of the physical properties that change during natural aging and heat treatment, was elucidated by means of kinetic analysis. Furthermore, as a possible application of heat treatment, heat-treated materials was evaluated as artificially aged materials.

Materials and Methods

The materials used in this study were cellulose filter paper, Chinese Xuan paper, hinoki (*Chamaecyparis obtusa* Endl.) wood, keyaki (*Zelkova serrata* Makino) wood and sugi (*Cryptomeria japonica* D.Don) wood. The specimens were prepared from naturally aged samples stored in the ambient indoor conditions for the aging durations ranged from approx. 35 years (Xuan paper) to approx. 1600 years (hinoki wood). For control and heat-treated samples, specimens prepared from recently manufactured or harvested samples were dried and then heated in an air-circulating oven at 90, 120, 150 and 180°C for the durations of 10 min. (for keyaki and sugi wood at 180°C) to approx. 3 years (for Xuan paper at 90°C). Color was measured by using spectrophotometer and spectroscopic imaging system and expressed in terms of the CIELAB color parameters (L^*, a^*, b^* and ΔE^*_{ab}). Obtained color data were discussed by means of kinetic analysis applying the time-temperature superposition (TTSP) method for accurate analysis. Heat treatment was also applied to make artificially aged Xuan paper which has preferable characteristics for calligraphy. Specimens of Xuan paper were heated in an air-circulating oven at 180°C for the durations ranging from 0.5 hour to 48 hours. A calligrapher subjectively evaluated the quality of heat-treated specimens by brush handwriting. The moisture content and the water

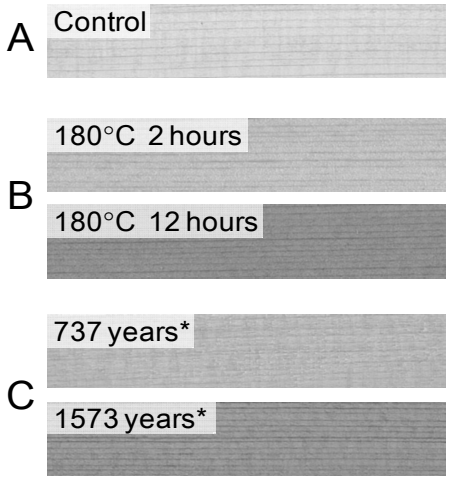

Figure 1. Color changes of hinoki wood during heat treatment and natural aging. A: control (harvested in 1988), B: specimens treated at 180°C for 2 or 12 hours, C: specimens aged in the ambient condition for 737 or 1573 years. *Aging duration was determined by dendrochronology and radio carbon dating.

absorptiveness were also measured as the properties which concern the qualities of paper for calligraphy.

Results and Discussion

As shown in Figure 1 as an example, color changes that occur during natural aging were similar to those during heat treatment for all materials. Color changes were expressed by decreasing L^*, increasing ΔE^*_{ab}, and changes in a^* and b^* characteristic of each material, with increasing treatment duration. Measured color data was successfully analyzed with high accuracy. In the temperature range from 90°C to 180°C, the reaction of color changes followed the Arrhenius equation for all materials, which indicated that color changes in this temperature range can be explained by the apparently same reaction mechanism (Figure 2 (1)) [1]. Comparing color changes measured from naturally aged samples with those at the ambient temperature predicted from kinetic analysis of heat-treated specimens, color changes of hinoki wood during natural aging can be explained mainly as the same reaction as heat treatment, i.e., thermal oxidation (Figure 2 (2)). While, color changes of keyaki wood during natural aging were significantly faster than predicted, suggesting that either thermal oxidation was accelerated or there were other different reactions involved. Color changes and calculated activation energy of cellulose filter paper were similar to those of Xuan paper and wood, indicating that color changes of cellulose significantly contributed to those of Xuan paper and wood [2,3].

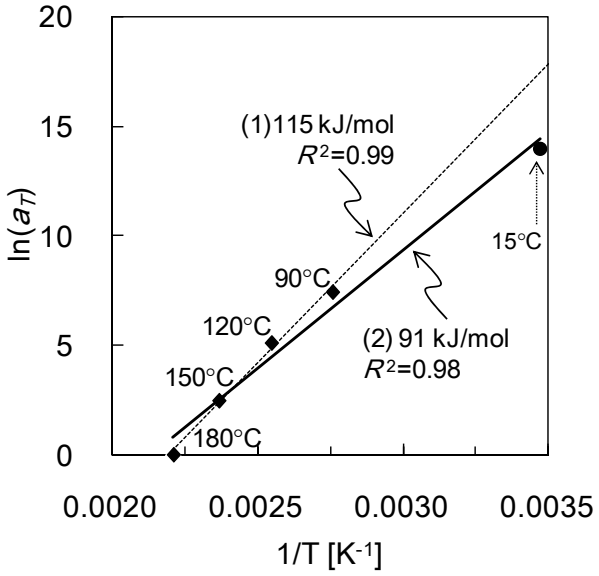

Figure 2. Arrhenius plots of changes in L^* with regression lines, coefficients of determination (R^2) and apparent activation energies calculated from (1) heat-treated hinoki wood and (2) both heat-treated and naturally aged hinoki wood.

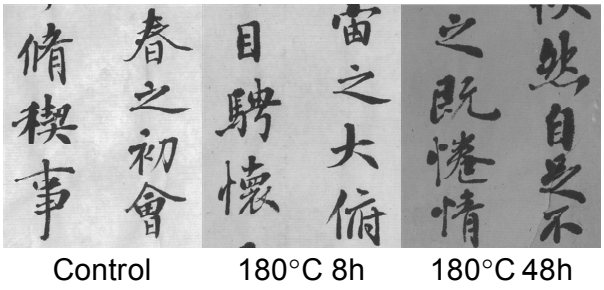

Figure 3. Brush handwriting on heat-treated Xuan paper by a calligrapher (臨書:王羲之「蘭亭序」, Study of a masterpiece: "*Lanting Xu*" by *Wang Xi Zhi*). The numbers below the figure indicate treatment temperature and durations.

Figure 3 shows the heat-treated Xuan paper with brush handwriting by a calligrapher. The calligrapher judged that 3-, 5- and 8-hour-heated specimens had the good quality for calligraphy. Equilibrium moisture contents decreased with the increasing treatment duration. Water absorption of Xuan paper treated for 0.5-8 hours was lower than untreated specimens and then increased with increasing treatment duration. These results indicated that heat treatment with appropriate duration allows to produce Xuan paper which has preferable properties for calligraphy.

References

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