Journal of Industrial and Engineering Chemistry 41 (2016) 68–74

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

journal homepage: www.elsevier.com/locate/jiec

Comparison of aging characteristics of the duplicated beeswax-treated and non-treated paper books during artificial thermal aging

Kyoung-Hwa Choi [a,*], Yeong Seok Kang [b], Byoung-Uk Cho [c,**]

[a] Changgang Institute of Paper Science and Technology, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon, Gangwon-do 24341, Republic of Korea
[b] Restoration Technology Division, National Research Institute of Cultural Heritage, 472 Munji-dong, Yuseong-gu, Daejeon 34122, Republic of Korea
[c] Department of Paper Science and Engineering, College of Forest and Environmental Science, Kangwon National University, 1 Kangwondaehak-gil, Chuncheon, Gangwon-do 24341, Republic of Korea

ARTICLE INFO

Article history:
Received 16 November 2015
Received in revised form 15 January 2016
Accepted 5 July 2016
Available online 21 July 2016

Keywords:
Aging characteristics
Volatile organic compounds (VOCs)
Acidic byproducts
Beeswax-treated volume
The Annals of Joseon Dynasty

ABSTRACT

Changes in mechanical and optical properties of the duplicated beeswax-treated and non-treated Hanji volumes during artificial aging were examined, and the VOCs emitted from the samples were analyzed using a GC/MS. In results, the decrease in mechanical and optical properties of the beeswax-treated volume during aging was approximately 2.5 times higher than that of non-treated volume. The quality and quantity of the VOCs emitted from the beeswax-treated volume were also greater than those from the non-treated volume. Especially, the amount of acetic acid from beeswax-treated volume after 90 days of aging was 20 times greater than that of non-treated volume.

Introduction

The Annals of the Joseon Dynasty are representative of paper-based national treasures in Korea. The 472 years (1392–1863) history of the Joseon Dynasty, which was the last sovereign Korean state, was documented in the Annals. UNESCO (the United Nations Educational, Scientific and Cultural Organization) registered these Annals as part of "The Memories of the World" in 1997 and have preserved these paper cultural heritages as world cultural artifacts since then. Among thousands of volumes of the Annals archived at multiple locations in Korea, a total of 2077 volumes have survived from numerous fires during wars with neighboring foreign dynasties and 1181 volumes called the JeongJok-San Annals have been kept in KyuJangGak in Seoul. Among them, 475 volumes were proactively beeswax-treated for the purpose of their long-term preservation when they were published in the Joseon Dynasty approximately 500 years ago. Preservation treatment methods using beeswax have rarely been found worldwide except for the Annals of the Joseon Dynasty. Ironically, however, the beeswax-treated volumes have been more deteriorated than non-treated ones called Hanji volumes [1–3]. Hanji is the traditional handmade paper of Korea made from the bast fiber of paper mulberry. The understanding of the deterioration differences between the beeswax-treated volumes and Hanji volumes of the Annals of the Joseon Dynasty has been needed to develop restoration technologies and better long-term preservation strategies for the beeswax-treated volumes, but even the mechanisms and factors associated with the deterioration of the beeswax-treated volumes have been not fully understood. Only a few studies had tried to examine fragmented debris of the original Annals in order to uncover the aging mechanisms of the entire beeswax-treated volumes of the Annals [4,5]. For instance, Lattuati-Derieux et al. [4] analyzed byproducts of the fragmented beeswax-treated pieces of the Annals using infrared spectroscopy (IR), high temperature gas chromatography (HT-GC) and high temperature gas chromatography/mass spectrometry (HT-GC/MS). Jeong et al. [5] investigated the carbonyl and carboxyl groups of bees-wax treated fragments using Gel permeation chromatography/multi-angle laser light scattering (GPC/MALLS) after fluorescence labeling of functional groups of paper cellulose. These studies based on original

* Corresponding author. Fax: +82 33 259 5621.
** Co-corresponding author. Fax: +82 33 259 5621.
E-mail addresses: bleaching@kangwon.ac.kr (K.-H. Choi), bucho@kangwon.ac.kr (B.-U. Cho).

http://dx.doi.org/10.1016/j.jiec.2016.07.009
1226-086X/

fragments of the Annals succeeded in providing the information for post-aging characteristics of the Annals after several centennial years, but the size and quantity of the study samples used in these studies hinder us to uncover the overall aging processes of the entire volumes of the Annals between initial stage and post-aging stages.

To date, various techniques have been suggested for allowing us to examine changes in physical and chemical properties associated with the degradation of paper archives as well as restorative or proactive methods for paper cultural artifacts [6,7]. Among them, analyses of volatile organic compounds (VOCs) emitted from paper cultural heritage artifacts using the gas chromatography/mass spectrometry (GC/MS) have been recognized as one of the new approaches for understanding the aging processes of paper cultural heritages [8]. In particular, solid phase microextraction (SPME) is a popular method that can measure the VOCs emitted from grandfathered papers and books due to its simplicity and convenience [9,10], but this method also has disadvantages such as data contamination by environmental factors and technical difficulties in quantification of VOCs. Thus, it is notable that dynamic chamber system (DCS) popularly used in measuring indoor air quality may be able to be used as an alternative non-destructive tool in examining paper cultural heritage. Recently, NRICH (the National Research Institute of Cultural Heritage) of the Republic of Korea collected the VOCs emitted from the Annals of the Joseon Dynasty using the DCS [11]. However, VOCs emitted from the beeswax-treated volumes of the Annals aged excessively for several centennial periods could not sufficiently show the aging pathway of the volumes because the quantity and type of VOCs emitted from organic materials have decreased over time. Thus, better methods should be devised for the examination of the VOCs emitted from the Annals associated with paper deterioration in more detail.

In this study, an entire beeswax-treated volumes and Hanji volumes were duplicated as comparativeness to the previous studies that analyzed a tiny pieces only, and the VOCs emitted from the duplicated beeswax-treated volumes were compared with those from the duplicated Hanji volumes in the process of aging in order to get better understanding of the reason why the proactive beeswax-treatment to the Annals of the Joseon Dynasty resulted in more serious deterioration.

Materials and methods

Samples

A beeswax-treated volume and a Hanji volume were duplicated using the same raw materials and methods utilized for the Annals of the Joseon Dynasty called SeJong Silok. The base paper was the Hanji, which is traditional handmade paper from the bast fiber of paper mulberry (*Broussonetia Kazinoki Sieb.*) in Korea, with a thickness of 102 μm and a basis weight of 61.3 g/m^2. Korean beeswax was used to produce the beeswax-treated paper. Beeswax was applied onto the base paper using a heating auto-coating machine. The thickness of the beeswax treated Hanji was 150 μm and the basis weight was 114.7 g/m^2. And then 30 pages of Hanji with these identified mechanical properties were bound as each volume based on the five holes sewing.

Artificial aging

Samples of beeswax-treated volumes and Hanji volumes were aged at 105 °C for 30, 60, and 90 days, respectively, based on ISO standard method 5630-1. The thermal aging was conducted at DCS in a constant temperature and humidity chamber. During thermal aging, the VOCs emitted from each material were collected for analysis. The artificially aged samples were cooled and subsequently exposed to 23 °C and 50% of relative humidity over 24 h. Then mechanical and optical properties of each book sample were evaluated.

In this study, both an aging test and VOCs analysis were carried out two times. Mechanical and optical properties of each aged sample were measured 10 times. All data were calculated the average and then represented in this paper.

Measurement of mechanical and optical properties

Mechanical and optical properties of all book volume samples before and after aging were measured. For mechanical properties, tensile strength and burst strength were evaluated in accordance with ISO standard methods 1924-2 and 2758, respectively. The average optical properties of brightness and color (L^*, a^*, b^*) were measured using a spectrophotometer (ELREPHO) based on ISO standard methods 5631 and 2470. The color deviation (ΔE) was calculated with Eq. (1):

$$\Delta E = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$$

where $\Delta L^* = L^*_{\text{after aging}} - L^*_{\text{before aging}}$, $\Delta a^* = a^*_{\text{after aging}} - a^*_{\text{before aging}}$ and $\Delta b^* = b^*_{\text{after aging}} - b^*_{\text{before aging}}$.

VOC sampling using DCS

The DCS was used for sampling the VOCs from each aged duplicated volume of the Annals (Fig. 1). This system consisted of a square chamber, sampling pumps (Sibata ∑30, Japan), an N_2 gas cylinder, flowmeter, and Tenax TA tubes (Supelco, USA) as an adsorbent. The square chamber was made of stainless steel with dimensions of 60 mm (L), 60 mm (W), and 10 mm (H). The inner wall of the chamber was electrolytically polished to prohibit

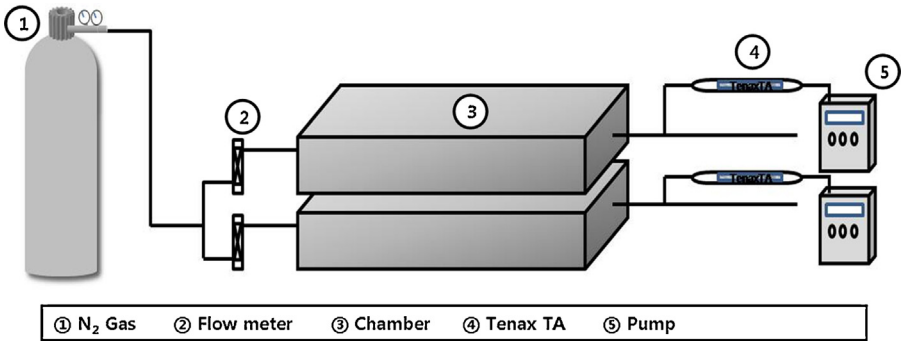

Fig. 1. A schematic of the DCS for sampling the VOCs emitted from the duplicated beeswax-treated and non-treated Hanji volumes.