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능가사 출토 종이와 섬유의 해부학적 성질 및 미량원소 분석

Agnieszka Helman-Wazny, 박원규*
순수미술원 보존수복학부, 폴란드 바르샤바
**충북대학교 산림과학부, 충북 청주시 개신동*

Anatomical Characteristics and Trace Elements of Historical Papers and Cloths from Neunggasa Temple in Korea

Agnieszka Helman-Wazny and Won-kyu Park*
Faculty of Conservation and Restoration, Academy of Fine Arts, 00-379 Warsaw, POLAND
**School of Forest Resources, Chungbuk National University, Cheongju 361-763, KOREA*

초록 본 연구의 목적은 전남 고흥 능가사 대웅전과 천왕문에서 발굴된 종이와 섬유의 해부학적 특성과 미량 화학성분을 광학현미경, 화상해석, 주사전자현미경(SEM-EDS)으로 분석하는 것이다. 모든 종이는 닥나무로 식별되었다. 인피섬유에서 분리된 투명막의 존재가 특징적이었다. 대웅전 벽에 붙여 있는 종이가 가장 손상이 심하였으며 천왕문에서 발굴된 책의 종이 세포는 비교적 보존 상태가 양호하였다. 천왕문의 동방지국상 아래에서 발굴된 섬유는 매우 좁은 세포폭을 갖는 실크이었다. SEM-EDS 분석에서 높은 실리카 함량이 발견되었다. 종이 내에서 발견된 칼슘, 철, 염소, 그 밖의 미량원소 분석 결과를 연대, 생산지 및 보존처리와 관련하여 고찰하였다.

ABSTRACT The objective of this study is to examine the characteristics of historical papers and cloths found at Neunggasa temple, Goheunggun, Chonnam Province, Korea, using light microscopy, image analysis and SEM-EDS for fiber morphology and trace metal composition. All papers were made from paper mulberry. Transparent membrane, which was separated from bast fiber, was unique in these fibers. The papers found on the wall of Daewungjun were most highly degraded and those of the books, which were excavated under Cheungwangmun, were relatively well preserved. The cloths found under the statue 'Dong-bangjiguk' were silk, very narrow fiber without any marks. In the analysis of SEM-EDS, high content of silica was detected. Also small content of calcium was taken into consideration. Content of iron and chlorine were discussed from the viewpoint of potentially harmful elements for the conservation of paper. The composition of trace elements could not be used to determine the origins of papers.

Introduction

First step for the conservation of historical materials made of paper is the identification of fiber composition. Fibers constitute the basic component of a paper leaf, and determination of fiber composition is essential to characterize the paper. The microscopic analysis make possible the identification of most fibers present, but bast fibers in highly beaten pulp are difficult to identify because stamping and drying can fundamentally change the shape of cell.

Typical bast fibers have thick walls, but thin-walled fibers located near to cambium collapse during pulping, while thick-walled ones have a tendency to retain their cylindrical shape.[1] Bast fibers in pulp can be identified by the morphology of fiber and by the structural features of the associated elements like parenchyma cells or vessels, which may be present in pulp. Color of staining by Herzberg or "C" solution is also very important to identify fiber origin.

In the identification of fiber in pulp, attention has to be paid to the following features:

1) General shape of fibers.
2) Dimension of fibers (length and width).
3) Cross-markings (more apparent after staining with Herzberg stain).
4) Shape and dimension of lumen.
5) Shapes of fiber ends.
6) Irregularities in fiber walls.
7) Kind and size of vessel elements (associated element).
8) Size and shape of parenchyma cells (associated element).

It is much harder to identify fibers in historical papers. Main problems are connected with different degree of fiber deterioration during time (aging process). It can also change the morphology of fiber like dimension and shape of fiber, width of lumen, etc. Sometimes it is impossible to recognize the morphology in high-degraded pulp. Also the presence of non-plant components in the paper like glue, fungi and other impurities can make these analysis difficult.

The purpose of this study is to characterize the papers attached on the wall of Daewungjun, the papers of two books which were excavated under Cheungwangmun, and the cloths excavated under the statue "Dongbangjiguk" of the Neunggasa temple located at Goheunggun, Chonnam Province, Korea.

General Description of Samples

Sample 1 (Fig. 1, no. 1)

Sample 1 is some papers (notes) for monks attached on the wall in the main building (Deawungjun). The paper color was dark yellow to brown. On the surface, some calligraphy letters was written with black ink. Paper material (surface layer) was brittle and weak. Paper pulp contained high quantity of glue (layer gluing papers to the wall) and impurities. That sample contains also fragments of inner paper. Before the paper with "Notes for

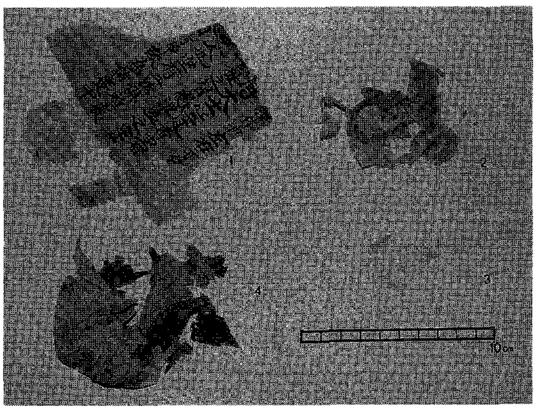

Fig. 1. The samples from Neunggasa temple. The scale represents 10 cm.

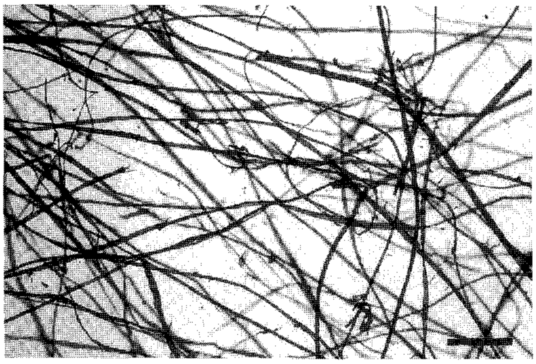

Fig. 2. Stained fibers of paper mulberry in sample 2. The bar represents 300 micrometers.

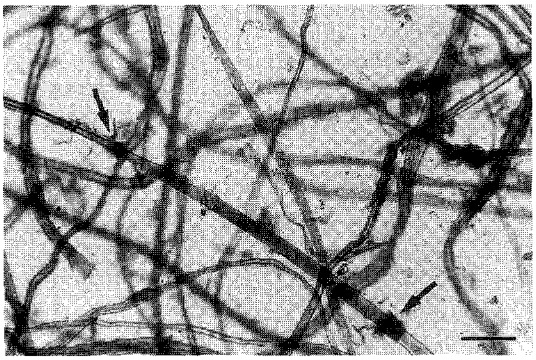

Fig. 3. Paper mulberry fibers with jagged membrane on fiber surface. The bar represents 100 micrometers (sample 1).

monks" was glued on the wall in temple, there had added few paper layers as a ground.

Sample 2 (Fig. 1, no. 2)

This sample was taken from a printed book excavated in Cheungwangmun (an entrance gate building with four wooden statues). First letters of this book start with "Sari". This sample contained three pieces of dirty paper with sand and dust particles. Fragments of letters printed with red ink are present in the sample. The paper was very thin and composed with long fibers.

Sample 3 (Fig. 1, no. 3)

Sample 3 was taken from another printed book also excavated in Cheungwangmun. First letters of this book start with "Yookja". The paper was very thin, composed with long fibers and well preserved.

Sample 4 (Fig. 1, no. 4)

The sample was taken from clothes excavated under the chair for the statue "Dongbangjiguk" in Cheungwangmun. The specimen of cloth is pale blue with brown stain of dirt. The specimen was composed with alternate fibers.

Methods

(A) Preparation of samples

Light Microscopy

The samples were divided into small pieces, placed in a small beaker and covered with distilled water and boiled in autoclave. The water was decanted and the samples were drained off to be dry. Small portion (about 0.2 g) of paper was defibered on the slide glass. Fibers were treated with Herzberg stain. The stain (2 drops) was applied to the fiber field on the slide glass, and cover glass on it.

Scanning Electron Microscope

Small piece of paper was placed horizontally, directly on the wet graphite glue on the SEM stub. The specimens were dried in a drying oven at 100 °C for about 10 hours and coated by gold in vacuum (Ion Coater Eiko IB-3).

(B) Observation

Light Microscopy

The stained material was observed under the microscope with transmitted light (OLYMPUS BX 50). The slide was examined for different fibers (according to TAPPI Standard

T401), with attention given to their morphological characteristics (details of anatomical structure) and staining. Results were compared with reference materials. OLYMPUS camera attached to the microscope with transmitted light and Kodak color film (ISO 100) were used. The photographs were made in magnificence 40×, 100×, 200× and 400×.

Image Analysis

Paper was examined for the size of fibers. Stained fibers on the slide glass were measured for length and width of fiber. Each kind of fiber in sample was measured 20 times for length and width, respectively. Minimum, maximum, median and mean values were calculated. Results were compared with the key for fiber identification.

(C) Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy (SEM)

Paper was observed with SEM (HITACHI S-2500C) in magnificence from 150× to 2000×. Sample was examined for the anatomical characteristics of paper structure and it could give also information about fiber destruction. Photographic documentation of characteristic features was made using black-and-white Polaroid film in a camera attached to the SEM.

EDS (Energy Dispersive X-ray Spectroscopy)

EDS apparatus is connected with SEM. This technique can give information about basic composition of chemical elements present in paper pulp.

Results

Light Microscopic Observation

The paper samples (sample 1, 2 and 3) were composed with one kind of fibers, paper mulberry. After staining with Herzberg the fibers were stained with pale purple and reddish brown color (Fig. 2). Condition of paper derived from the wall (sample 1) was weak. Fibers were short and pulp contained high quantity of glue and impurities. The pulp of samples from excavated books (sample 2 and 3) was composed with good quality, long fibers and the paper structure was well preserved. During observation under the microscope with transmitted light each historical paper sample contained fibers with transparent membranes (stained by Herzberg to violet and bluish purple), which were unique

Fig. 4. Transparent membrane separated from paper mulberry fibers in sample 3. The bar represents 100 micrometers.

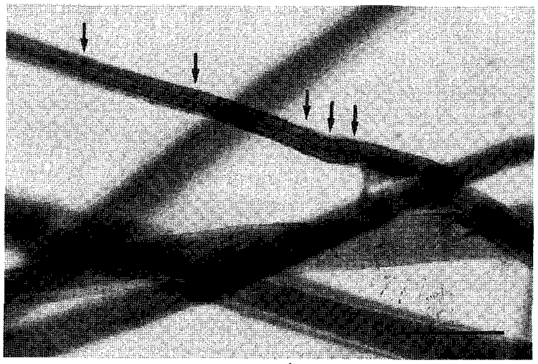

Fig. 5. Morphology of fibers. Irregular lumen and cross-markings (arrows). The bar represents 100 micrometers (sample 2).

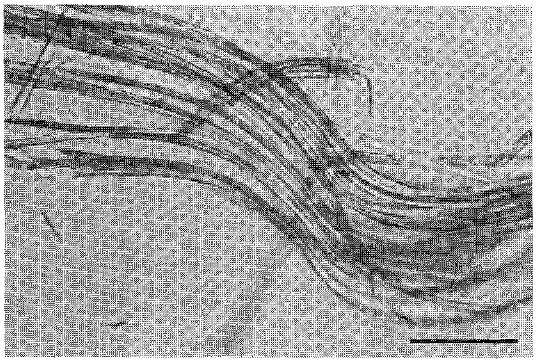

Fig. 6. Bundle of silk fibers. The bar represents 100 micrometers (sample 4).

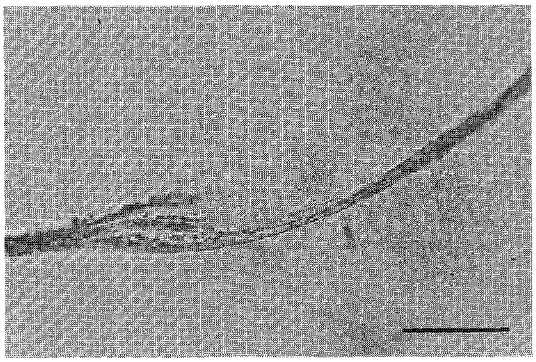

Fig. 7. The fiber without any marks. No reaction with Herzberg stain. The bar represents 50 micrometers (sample 4).

characteristic for paper mulberry fibers. These transparent membranes envelop the fibers in the original plants of paper mulberry. On the sample slides, however, the membrane was mostly destructed and separated from fibers. There was visible the jagged membrane (stained blue to violet) between fibers on the slide in the case of sample 1 (paper from the wall) (Fig. 3). In the case of sample 2 and sample 3 (excavated books), the transparent membrane was mostly separated from

Table 1. Summary of diagnostic features for the identification fiber species in historical papers from Neung-gasa.

No	Origin		Fiber composition	Coloring by Herzberg	Associated cells	Special features	Fiber ends
	Location	Object					
1	Deawung-jun (Main Building)	Notes for monks located on the wall	Paper mulberry	Reddish brown to pale purple	Transparent membrane Short pitted fiber	Membrane is colored by Herzberg on violet to blue-purple	Blunted
2	Cheungwang-mun (Gate for four statues)	Printed book found in a statue. First letters start with "Sari"	Paper mulberry	Reddish brown to pale purple	Transparent membrane Mycelium	Membrane is colored by Herzberg on violet to blue-purple	Blunted
3	Cheungwang-mun (Gate for four statues)	Printing book found in a statue. First letters start with "yookja"	Mainly paper mulberry (one transparent yellow)	Reddish brown to pale purple	Transparent membrane	Membrane is colored by Herzberg on violet to blue-purple	Blunted Pointed
4	Cheungwang-mun (Gate for four statues)	Clothes excavated under chair for a statue "Dong-bangjiguk"	Silk	No coloring	None	Very narrow fiber without any marks	No natural ends

Table 2. Dimensions of fibers in paper pulp of historical papers.

	Width			Length		
	Min.-Max.	Median	Mean	Min.-Max.	Median	Mean
SAMPLE 1	12-27 μm	17 μm	16 μm	2-11 mm	6 mm	7 mm
SAMPLE 2	13-21 μm	14 μm	15 μm	5-12.5 mm	8.5 mm	8 mm
SAMPLE 3	9-25 μm	14.5 μm	16 μm	5-15 mm	9 mm	8 mm

fibers (Fig. 4). The degree of deterioration of this two samples (sample 2 and 3) were similar each other. Morphological properties of the end of natural fibers enclose blunted and pointed fiber ends. Natural ends of were not found due to broken fibers. The lumen could be visible but was not continuous. Cross-markings, the characteristic of paper mulberry, were clearly seen but the distance between separate marks were different (Fig. 5). Overall results of observations enable to identify fibers of sample 1, 2 and 3 as paper mulberry.

The sample of cloth (sample 4) was composed with one kind of fibers (Fig. 6). Fibers were very narrow without any marks. Fiber had not got any color after staining with Herzberg (Fig. 7). Results of observations enable to identify fibers as a silk. The light microscopic characteristic of the samples is summarized in Table 1.

Image Analysis

Most fibers were collapsed and cut, so results of measurements can tell us only something about techniques of papermaking and degradation. Comparison with reference material should be done very carefully with attention to changes of morphology. The results of fiber measurements are given in Table 2. The range of obtained values corresponds with the results published by Choi and Cho.[2]

Fig. 8. Glue and impurities on the surface of fibers (sample 1).

Sem

The pulp was composed with long fibers but the paper structure of sample 1 is not well preserved. Paper pulp was highly sized (Fig. 8). Glue and impurities covered the surface of fibers. After glue separation (by boiling in water) the morphology of fibers was visible. In the case of next two samples, most fibers appeared to be well preserved (Fig. 9), but also significant quantity of fibers was broken. Degree of deterioration is much higher in sample 1 ("Notes for monks") than others (sample 2 and 3). Morphology of the

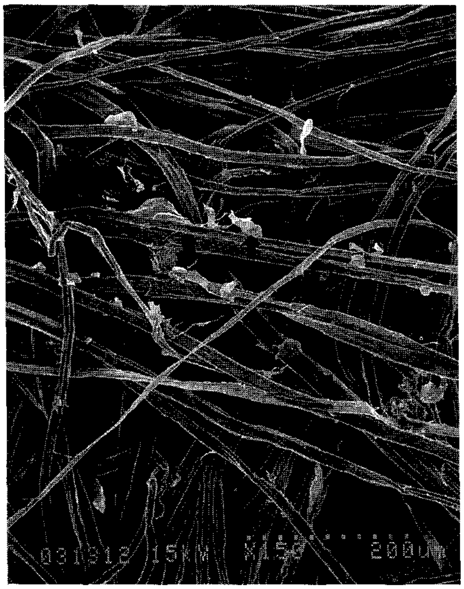

Fig. 9. Condition of paper mulberry fibers in paper structures (sample 3). Transparent membrane on the fiber surface (arrows).

fibers in each case was cleared and confirmed by the results of light microscopic observation.

Fibers in the cloth did not have any lumens, cross-marks and any other marks on the surface. The cross-section of fiber appeared to the triangle. Cloth is composed with alternate bundles of very narrow fibers.[3]

EDS

Sample 1

Analysis of crystals appeared on the surface of fiber indicates the presence of four chemical elements in paper pulp (Table 3).

Sample 2

Three crystals, which appeared on the fiber surface, were chosen randomly from two extreme margins and from the middle of paper sample. EDS measurements indicate the presence of six elements as components of crystals in the paper pulp (Table 4).

Table 3. Percentages of trace elements in paper pulp of sample 1 (EDS analysis).

Trace elements found in the pulp	Crystal (weight %)
Al	12.38
Si	28.60
Ca	57.11
Fe	1.91

Table 4. Percentage of trace elenents in three crystals found in paper pulp of sample 2 (EDS analysis).

Trace elements	Crystal 1 (weight %)	Crystal 2 (weight %)	Crystal 3 (weight %)
Al	25.68	18.80	24.45
Si	57.52	61.61	20.27
K	14.67	5.26	5.19
Ca	1.80	11.73	33.75
Fe	0.32	2.61	11.96
Cl	-	-	4.38

Table 5. Percentage of trace elenents in three crystals found in paper pulp of sample 3 (EDS analysis).

Trace elements	Crystal 1 (weight %)	Crystal 2 (weight %)	Crystal 3 (weight %)
Si	99.42	64.25	91.69
Al	-	23.71	7.38
Ca	0.58	2.10	0.43
K	-	8.62	-
Fe	-	1.32	0.50

Sample 3

Three crystals, which appeared on the fiber surface, were chosen randomly from two extreme margins and from the middle of sample 2. EDS measurements indicate the presence of five elements as components of crystals in the paper pulp (Table 5).

Table 6. Percentages of trace elements in paper pulp of sample 4 (EDS analysis).

Trace elements found in the pulp	Crystal (weight %)
Al	12.40
Si	79.85
K	4.03
Ca	1.07
Fe	2.65

All results of EDS analysis for four samples are compared in Figure 10.

Sample 4

Analysis of crystals appeared on the surface of fiber indicates presence of five elements in paper pulp (Table 6).

Discussion

The paper samples (first three, i.e., sample 1, 2 and 3) from Neunggasa temple were analyzed for fiber composition. Results of microscopic examination demonstrate that paper samples contained paper mulberry fibers. There were transparent membranes on the fibers. Condition of fibers and membrane depends upon used technique and quality of fiber material. First sample (sample 1) seems to be beaten more highly than others during papermaking process and the degree of deterioration was higher. The condition of fibers in different samples of artifacts was related to the environments where they stored or used. No morphological properties could be used to recognize the origin of artifact, i.e., country.

Generally, paper mulberry pulp was composed with good quality of long fibers and it had kept good condition of paper structure. Samples of pure paper mulberry showed much better condition than others, what was possible to observe by SEM. All samples except sample 1 presented good condition and it should correspond with real condition of artifact. Sometimes the bad condition of art object had come from non-chemical factors (readers activity- tears, folds etc.), that did not have significant influences to general paper structure. SEM method also confirmed the fiber composition results. For each sample EDS test was performed. During process of papermaking some crystals can get into the paper pulp. There are many ways for the input of these basic elements into pulp.[4] That can originated from water, soil, fillers and other chemicals used during pulp and papermaking process. Chemical elements could be also introduced to the paper during conservation and restoration processes; for example, by deacidificating compounds or bleaching chemicals. It was possible to obtain chemical element's composition of crystals found in

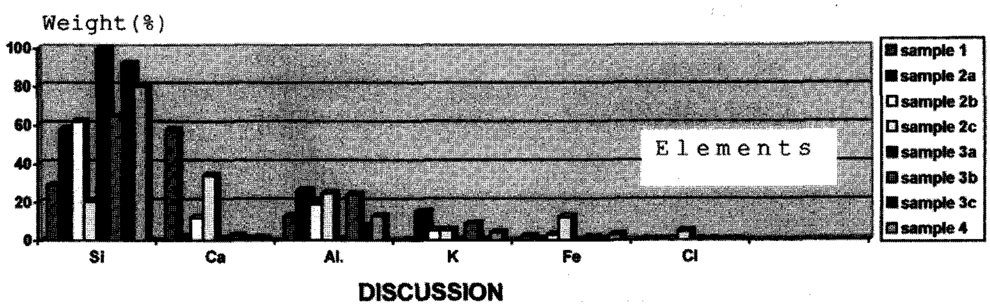

Fig. 10. Percentage of trace components of crystals found in pulp of all samples from Neunggasa temple (EDS analysis).

paper pulp, Some researches suggested that chemical composition of trace elements would be used to separate the origin (country) of paper mulberry.[4] The samples in this study contained various contents of silica, calcium, potassium and aluminum, so it was very difficult to recognize their origins of production.

The samples from Neunggasa temple contained mainly Si, Ca, K, Al and Fe. The content of silica was higher than content of other elements. High content of silica may result from the contacts of paper with muddy wall (sample 1) or with ground soil (sample 2 and 3).

The alkaline buffer protects the paper against the further formation of acids and environmental poisons like SO_2 and NO_2. Therefore the value of the alkaline buffer is very important for the further aging durability of the paper.[5] Content of calcium compounds in the paper can protect paper against acidity.[6] It means that the papers from Neunggasa are not so good protected and probably need deacidification treatment. In such case the pH-test is recommended. Influence of other factors, for example, the degree of sizing, should be also taken into consideration. From a conservation point of view, the presence of iron and chlorine is harmful. Contents of these elements in papers from Neunggasa are traceable, but should be paid attention to.

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