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RESEARCH ARTICLE

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Characterization of Korean handmade papers collected in a *Hanji* reference book

Bin Han^{1,2*} , Léon-Bavi Vilmont², Hyoung-Jin Kim³, Bertrand Lavédrine², Shouji Sakamoto⁴ and Michel Sablier²

Abstract

Korean hand papermaking is a renowned cultural tradition in the Korean peninsula. It is still practiced while scientific analysis of paper itself from a large data set is rare. In this study, a set of more than three hundred Korean handmade papers, collected in a reference collection book *Hanji: Korean handmade paper*, were chemically investigated, and their property data such as colour, pH, grammage, thickness, tensile strength, folding endurance were statistically analysed in order to determine general features for Korean papers. The influence of different paper sheet formation methods (*Heullimtteugi* vs *Gadumtteugi*) were revealed by multivariate data analysis and the chemical profiles of raw materials were studied by pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS). The Korean handmade paper samples display colour gamut in the colour space L^* (69.9–95.9), a^* [(−3)–3], b^* (0–20), most have neutral/alkaline pH values. Paper density, fiber orientation and physical properties are influenced by the sheet formation techniques. For instance, *Gadumtteugi* tends to produce papers with strong fiber orientation while *Heullimtteugi* produces papers with more evenly distribution of fibers. In addition, Py-GC/MS analysis results show that paper mulberry fibers contain less intensity lignin monomers and more terpenic compounds in comparison with gampi and mitsumata fibers. This study provides paper analysis from large sample set, statistics reveal that the material preparing and making craft determined the paper structure which reflected in their physical properties. These properties influenced paper performance and applications in art creations as well as relics conservation and restoration. The characterized paper sample database could be used for handmade paper studies in East Asian region. Consequently, this study contributes to a better understanding of contemporary *Hanji* properties as well as improves knowledge on handmade papers from the Korean peninsula.

Keywords: Korean handmade papers, *Heullimtteugi*, *Gadumtteugi*, Multivariate data analysis, Py-GC/MS, Lignin monomers

Introduction

Crafts of hand papermaking are listed as intangible cultural heritage and handmade papers were commonly used in art creations as well as relics conservation and restoration. Different traditions and crafts explored various plant materials for papermaking through history both chronologically and geographically [1–3]. The variety of material and crafts process in East Asian countries

makes papers that have different properties, such as Chinese *Xuan* paper [4, 5], Japanese *Washi* [6, 7] and Korean *Hanji* [8–11]. Among them, the Korean traditional handmade paper, commonly refers as *Hanji*, is a traditional symbol and heritage treasure from the Korean peninsula [10].

Hanji is primarily used as the writing, painting, and printing substrate and Korean crafters used *Hanji* to repair tears and fill gaps on paper, manuscripts, paintings, and books due to its good properties and durability. Traditional *Hanji* is permanent and it can last for more than 1000 years when preserved in proper conditions [8, 12, 13]. The ancestral *Hanji* craft is renowned due to its

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oriental gracefulness. During its making, bast fiber from paper mulberry (*Broussonetia* spp.) is used as the main raw material while other plant fibers were also used such as gampi and mitsumata. The process of raw material and making methods influenced *Hanji* properties and performance [14–16]. The sheet formation of *Hanji* involves two main methods, *Heullimtteugi* (*Oebal*) and *Gadumtteugi* (*Ssangbal*) which differs in the mould shape and wet formation process [17]. *Heullimtteugi* (single mould) is an original Korean method in which the mould is suspended by a single string. The fiber stock is firstly dipped onto the paper mould and flow away in the forward direction and subsequently repeated several times. The paper stock was scooped again and rhythmically rocked from side to side that enables fiber to accumulate in crisscross layers without dominant fiber orientation [15, 18]. The *Gadumtteugi* (double mould) usually employs a front-water approach that drives the mould forward and then backwards that takes five or six swings until a desired thickness is formed across the mould screen and produced paper with evident fiber orientation [17, 18].

Strong, stable and durable handmade *Hanji* has long been used in book and paper conservation in the Korean peninsula [17]. Moreover, *Hanji* has also gradually drawn attention from art practitioner and conservators worldwide and some European conservators even have established professional links such as Group 130° to test and facilitate the use of *Hanji* as conservation materials [19, 20]. A comprehensive knowledge about the type of paper, the manufacturing techniques and the subsequent physical properties, helps to promote their application in the decoration, art creation as well as in the conservation and restoration process [19]. However, most of *Hanji* characterization studies were based on small set of samples and therefore it is difficult to have an overall knowledge and general cognition of contemporary *Hanji*. And research was still lacking for *Hanji* studies in the areas of observation, analysis, case studies, and status survey [21].

Material characterization can provide useful information on paper composition and conservation state [22–29]. Investigation on traditional East Asian handmade papers employed a variety of material characterisation methods such as physical property measurements [22, 23, 30], microscopy observation [31–33] and chemical composition analysis [34–36]. On-line pyrolysis hyphenated with gas chromatography/mass spectrometry (Py-GC/MS) is among the most frequently used techniques for cellulosic material studies due to simple preparation with minimum quantity required [37–39]. Its practical application on Japanese and Chinese handmade papers was previously explored as a new approach for East Asian handmade paper characterization [3, 40, 41].

In the aim of gaining comprehensive knowledge on *Hanji* properties, we investigated a large set of samples collected in a *Hanji* reference book for an overview features of modern *Hanji*. The influence of making craft on the paper properties were analysed. Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) analysis has been conducted on *Hanji* raw materials of paper mulberry, gampi and mitsumata fibers for their chemical profile characterization. Such material analysis approaches are for the first time investigated with well edited *Hanji* samples in a large quantity.

Materials and methods

Materials

A four-volume reference paper collection book *Hanji, Korean handmade paper* was edited by prof. Hyoung-Jin Kim (Kookmin University, Seoul) [42]. This reference collection provides 309 *Hanji* samples from 26 paper mills across Republic of Korea (Additional file 1: Figure S1; Table S1). It includes valuable information not only on the papermaking process but also provides property information on these papers (Fig. 1; Additional file 1: Table S1). This reference collection forms a well edited reference source that reflects the modern Korean handmade papers. Consequently, the materials used in this investigation consist of 309 *Hanji* samples in this four-volume reference sample book *Hanji, Korean handmade paper*. General data attached in the *Hanji* reference book was listed in table S1 in the supplementary material on the paper samples for which analyses were performed. A reference of Japanese kozo (*Broussonetia kazinoki* Siebold & Zucc.) paper prepared following the Japanese traditional processes was also used in the Py-GC/MS analysis.

Methods

Statistical data analysis

General paper property data on the samples included in the four-volume *Hanji* reference book have been analysed and attached in the reference sample book. The details of certain property data as well as testing conditions are listed in Additional file 1: Table S1. The data on papermaking methods, pH values, mechanical property (e.g., grammage, thickness, tensile strength, folding endurance) and colour information of handmade papers collected in the reference book are statistically analysed using Microsoft Excel, Unscrambler X (Version 10.4) software from CAMO Software AS.

Microscopy observation

Orientation of the fibers in the paper is observed directly under a digital microscope (VHX-1000, Keyence, Japan).



Fig. 1 A The four-volume of reference paper sample collection book *Hanji*, Korean handmade paper in which provides 309 paper samples with making information and property measurements (B)

The samples were placed directly onto the microscope platform in light reflection mode.

Py-GC/MS analyses

Py-GC/MS analyses were performed using a vertical micro-furnace-type pyrolyzer PY-2020iD (Frontier Lab, Fukushima, Japan) directly connected to the injection port of a Shimadzu QP2010 gas chromatograph linked with a Shimadzu QP2010Plus quadrupole mass spectrometer (Shimadzu, Champs-sur-Marne, France). The sample was placed in a stainless steel sample cup. The paper samples were weighted with an XP2U Ultra Micro Balance (Mettler Toledo, Viroflay, France). Typical quantities of paper used in this work were ca. 100 μg weighted with the microbalance. The sample cup was placed on top of the pyrolyzer at near ambient temperature. The sample cup was introduced into the furnace at 500 $^{\circ}\text{C}$, and then the temperature program of the gas chromatograph oven was started. The Py-GC interface was held at 320 $^{\circ}\text{C}$. Chromatographic separation was carried out on a

Frontier Lab DB5-ms 5% phenyl–95% dimethyl polysiloxane fused silica capillary column (30 m length, 0.25 mm inner diameter and coated with a 0.25 μm film thickness). The oven temperature was initially held 3 min at 40 $^{\circ}\text{C}$, and then ramped at 5 $^{\circ}\text{C min}^{-1}$ to 325 $^{\circ}\text{C}$, where it was held for 10 min. The total duration of GC analysis was 70 min. The helium carrier gas Alphagaz 1 (Air Liquide, France) was used in the linear velocity mode (1 mL min^{-1}). The injector was held at 280 $^{\circ}\text{C}$ and used in split mode (1:10 of the total flow). The mass spectrometer was operated at 5000 u s^{-1} , with a scan range from 50 to 500 u , using electron ionization at 70 eV. The interface was kept at 300 $^{\circ}\text{C}$ and the MS source at 200 $^{\circ}\text{C}$. The mass spectra of the pyrolysis products were recorded using the average spectrum + average and subtract spectrum modes in the Shimadzu GCMSsolution software. Identifications were achieved on the basis of EI mass spectra by interpretation of the main fragmentations and using the NIST MS library (2011).

Results and discussion

Overview features

This study investigates a large set of various contemporary Korean handmade papers produced in different workshops [42]. Besides dyed samples using natural or synthetic dyes or pigments for specific calligraphy, fine art or crafts applications, most of the sample are undyed and the $L^*a^*b^*$ colour space (Fig. 2) of *Hanji* without dying process (227 samples) is within a colour gamut of L^* (69.9–95.9), a^* [−3]–3], b^* (0–20). The lightness values range from 69.9 to 95.9 with an average value of 88.2. The colour representation can be classified into groups with L^* value ranging from low, medium and high (Fig. 2). As for a^* and b^* coordinate (Additional file 1: Figure S2), all the papers are located on the $-a^* + b^*$ and $+a^* + b^*$ space with $-a^* + b^*$ space having the majority. The yellowness is the main characteristic with the b^* ranging from 0 to 20: most clustered within 1.6–7.88 and 7.88–14.16 range. For coordinate a^* , the majority clustered in the range −1.43 to 0.04. The distribution in a^*b^* space indicates that most *Hanji* represent more greenness than redness in colour representation. Some samples with less L^* values were also observed which all underwent treatment process such as mix with coloured clay, or black bark. Although practiced conservators can compare colour and colour changes by their experience, the quantified colour space is more convenient to compare colours and to trace colour changes in conservation applications [43]. Furthermore, the paper colour space information could also be used for classification of papers with different origins when obtained large data set [44, 45].

The pH of *Hanji* ranged from 5.3 to 9.8 with 98.3% having pH value above 6. A total of 83.3% were acid-free

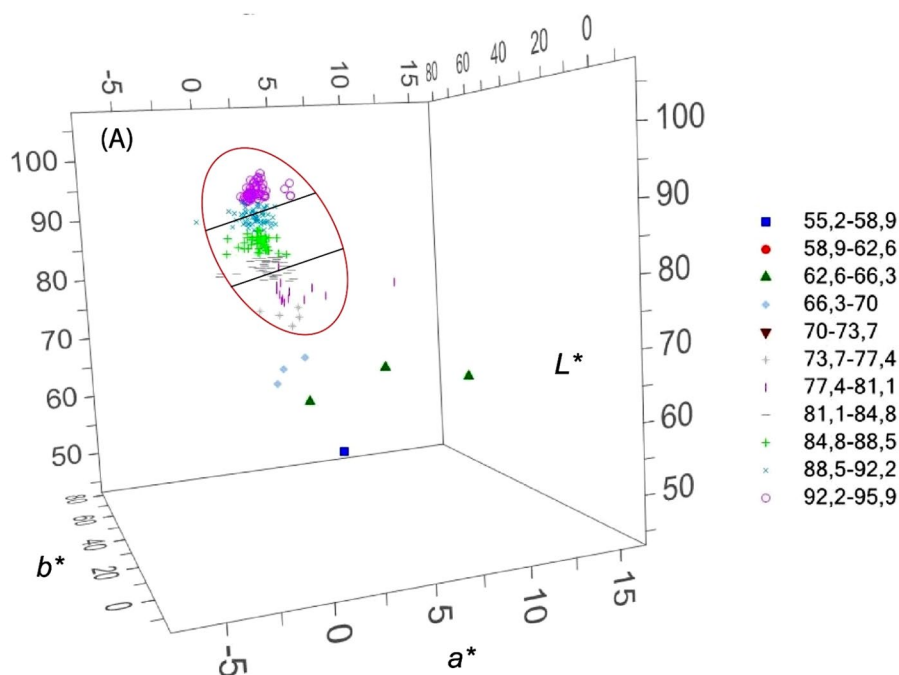


Fig. 2 The L*a*b* colour space of studied modern *Hanji* samples

papers with pH value above 7 (Fig. 3). These general features are likely caused from the treatment process that use plant ash, sodium carbonate (Na_2CO_3) or sodium hydroxide (NaOH) which create alkaline conditions. Plant ash was traditionally utilized to create a mild alkali cooking solution. But nowadays only 13% *Hanji* are still cooked traditionally with plant ash which takes lots of time and energy to maintain, while most are treated with chemical reagents such as sodium carbonate (mild alkali solution that can minimize the damage to the fiber, used to produce high quality *Hanji*) or sodium hydroxide (strong alkali solution, used for lower quality *Hanji*) which helps to shorten the preparation time.

Grammage is an intrinsic physical characteristic of paper which defined as weight in grams per square meter (GSM). Grammage of handmade paper greatly influences the stiffness and the strength of the paper thus

determines different paper applications. It can be seen from Fig. 3 that more than half of *Hanji* samples are with grammage between 20 and 40 GSM while 24.3% are between 40 and 60 GSM. Only 5.8% have grammage more than 80 GSM. As for the thickness, the majority (40.8%) are in the range of 100–150 μm (Fig. 3). Eleven (11) samples have thickness less than 50 μm with 32.5 μm as the minimum value (thin, soft and transparent *Hanji*).

Different workshops manufactured paper samples with different processes and therefore influenced their features. For instance, most *Hanji* samples from workshop 6 and 11 (Mungyeong Jeontong *Hanji* & Shinhyeonse Jeontong *Hanji*) have high paper strength (Additional file 1: Figure S3). Workshop 8 and 9 (Cheongsong Jeontong *Hanji* & Parkseonghwan Jeontong *Hanji*) produced *Hanji* with low basic weight while workshop 2 and 3 (Wonju

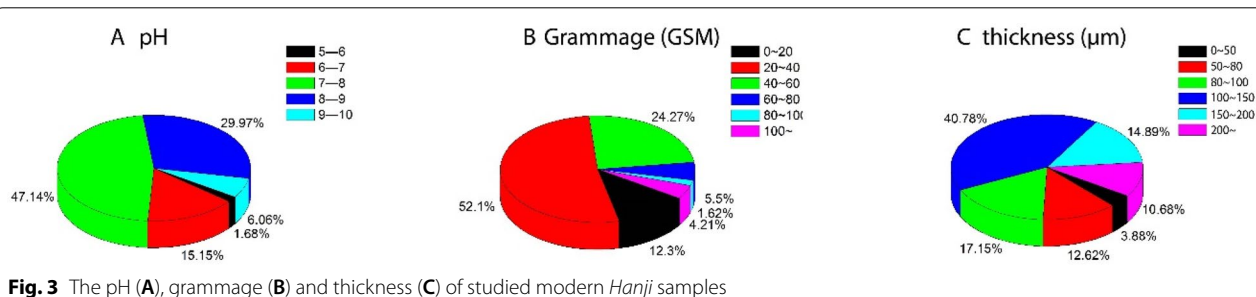


Fig. 3 The pH (A), grammage (B) and thickness (C) of studied modern *Hanji* samples

Hanji & Wonju Jeontong *Hanji*) produced mainly dyed papers (Additional file 1: Figure S3).

Different sheet formation: *Heullimtteugi* vs *Gadumtteugi*

Different sheet formation methods greatly influenced the fiber orientation of handmade papers [46, 47]. As is shown in Fig. 4, the fiber orientation can be clearly observable especially with thin and transparent *Hanji* samples, for instance, Fig. 4A shows a thin *Heullimtteugi Hanji* (thickness 43.6 μm) and the intercross of fibers is clearly depicted: the dense crisscrossed fibers resemble the character ‘#’. Figure 4B shows a thin *Gadumtteugi Hanji* (thickness 34.3 μm) with strong fiber alignment in one direction. *Gadumtteugi* can produce strong fiber orientation papers (Fig. 4B, D) while *Heullimtteugi* produces papers with fiber orientation more evenly distributed (Fig. 4A, C).

The fiber orientation produced with different methods influenced paper physical properties [47]. The tensile strength is mostly in the range of 352.8–3000 N/m (grain-direction) and 183.1–2000 N/m (cross-direction) (Fig. 5A, thick paper board samples not counted). It is

interesting to note that the majority of *Hanji* (75.7%) hold the property that the tensile strength for grain-direction is higher than cross-direction with the reverse ones mostly being *Heullimtteugi Hanji*. The *Heullimtteugi Hanji* showed a proportion of 50% with the ratio of tensile strength grain-direction/cross-direction greater than 1 while this proportion for *Gadumtteugi Hanji* is 95%. The result indicates that the alignment of the fiber direction of *Heullimtteugi Hanji* present more diversity thus gives paper strength in both directions; the *Gadumtteugi Hanji* has more consistency in fiber alignment in one direction that cause different paper strength in grain and cross directions.

The folding endurance varies from several times (minimum 1.2 times) to thousand times (maximum 1681.1 times) (Fig. 5B), 60% of the samples have the folding endurance between 1.2 and 500 times. Almost all the *Gadumtteugi Hanji* were distributed under the diagonal line in Fig. 5B which means the ratio of folding endurance grain-direction/cross-direction is higher than 1. However, the *Heullimtteugi Hanji* presented quite different profiles with 56.7% above and 44.3% under the

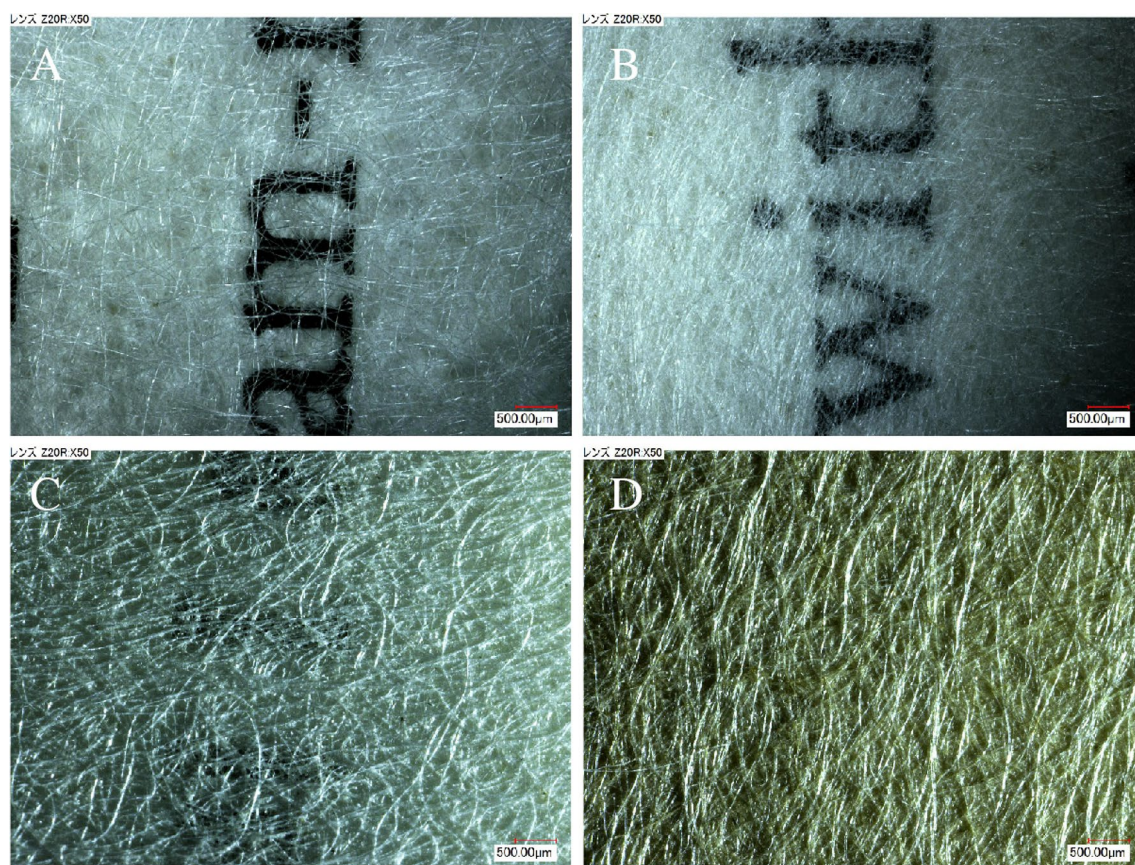
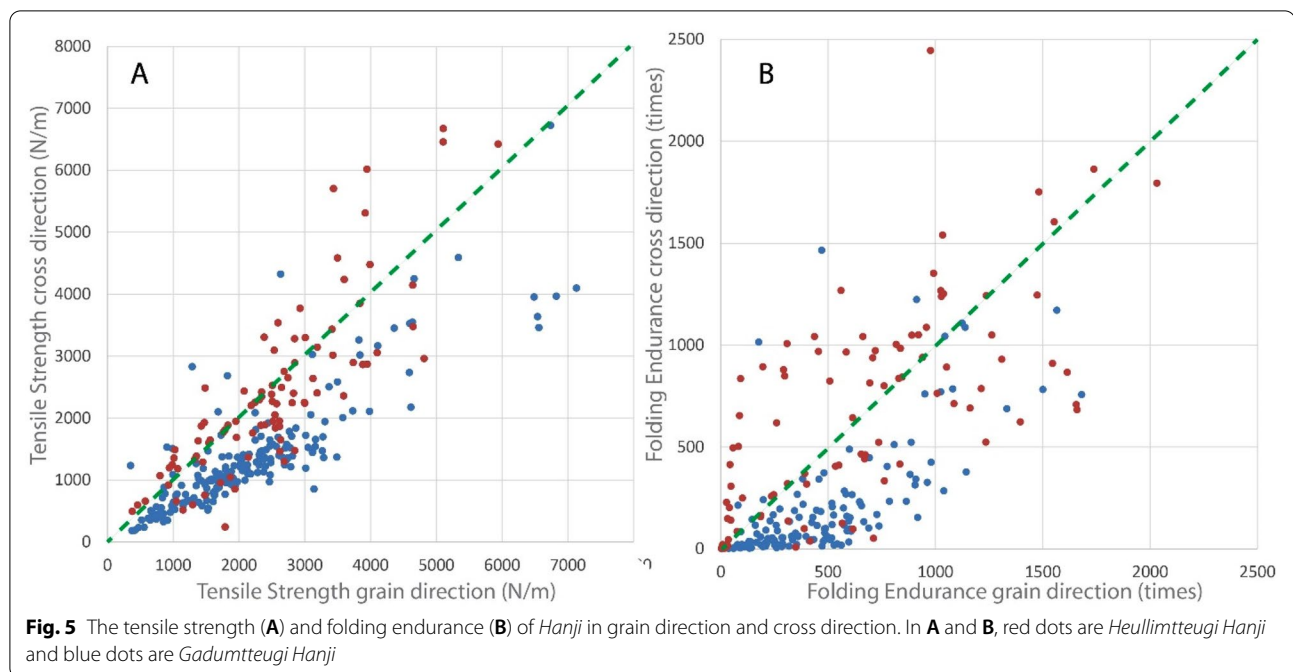


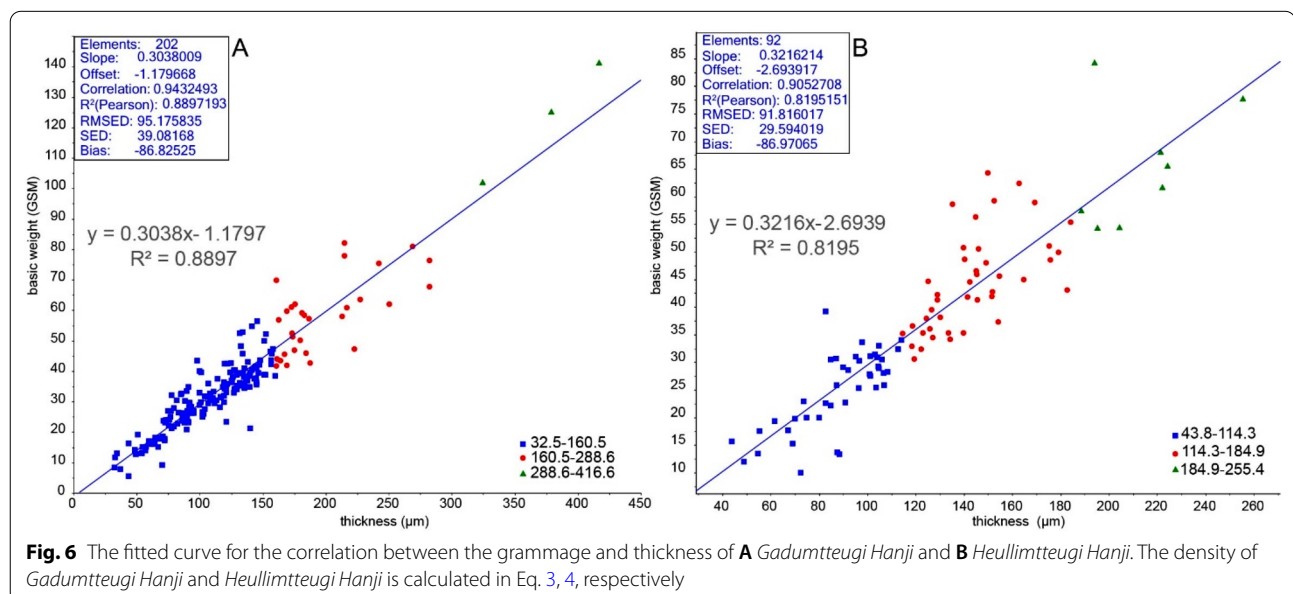
Fig. 4 The microscopy observation of fiber orientations. **A, C** are examples of *Heullimtteugi Hanji* with dense crisscrossed fiber orientation; **B, D** are examples of *Gadumtteugi Hanji* with strong aligned fiber orientation



diagonal line. *Heullimtteugi* sheet formation tend to produce more even dispersed fiber orientation paper which reflected by its tensile strength and folding endurance in both cross and grain directions. This point could be one consideration when choosing *Hanji* for applications requiring frequent folding in both directions. Besides the manufacturing methods, Dochim (calendering) also greatly improves the tensile strength and folding endurance of the papers. For instance, calendered sample 1–15

showed improved strength compared to those papers having similar basic weight and thickness such as sample 10–08, 5–09 and 5–21 (Additional file 1: Table S1).

The density of paper is influenced by the type of fiber and paper treatments. The correlation between grammage and thickness of *Gadumtteugi* and *Heullimtteugi Hanji* was calculated and shown in Fig. 6. From the fitted curve of grammage (w) and thickness (t), the density (ρ) for *Hanji* can be calculated using Eq. 1. The grammage



(w) equals to density (ρ) multiplied by thickness (Eq. 2) which is the slope of the correlation (Fig. 6). The calculated density of *Gadumtteugi Hanji* is 304 kg/m³ while the density for *Heullimtteugi Hanji* is 322 kg/m³ (Fig. 6, Eq. 3 and 4); *Heullimtteugi* sheet formation tend to make denser paper compared to *Gadumtteugi* sheet formation. Further principal component analysis (PCA) of data performed using tensile strength and folding endurance values also showed well separated locations in the score plots, discriminating different type of *Hanji* (Additional file 1: Figure S4).

$$\rho = w/t(\text{kg/m}^3) \quad (1)$$

$$w = \rho t(\text{g/m}^2) \quad (2)$$

$$w = 0.304t - 1.18(\text{Gadumtteugi Hanji}) \quad (3)$$

$$w = 0.322t - 2.69(\text{Heullimtteugi Hanji}) \quad (4)$$

Paper property data analysis showed that the sheet formation methods (*Heullimtteugi* vs *Gadumtteugi*) influenced the fiber orientation, tensile strength, folding endurance and density of *Hanji*. The fiber orientation of *Heullimtteugi Hanji* is more evenly distributed than that of *Gadumtteugi Hanji*, which gives paper strength in both directions. For instance, *Heullimtteugi Hanji* shows profiles of more evenness, better folding endurance and even tensile strength in all fibre direction and consequently *Heullimtteugi Hanji* is a better choice for applications that requires good folding endurance or even strength in both directions; meanwhile, *Gadumtteugi Hanji* with strong fiber orientation is more suitable for conservation or strengthening of book spine which requires frequent folding in one direction. In practice, however, it is noted that 212 out of 309 samples (69%) were made by *Gadumtteugi* while only 97 samples (31%) by *Heullimtteugi* which showed that the tradition of *Heullimtteugi* is less practiced since it requires intensive labor and virtuosity.

The chemical profiles of raw fibers

Most modern Korean handmade papers collected in the reference sample book were made of paper mulberry (Korean name *Dak*) fibers while bark fibers from other plants such as gampi and mutsumata have also been used in *Hanji* making. Their chemical profiles were analysed by Py-GC/MS. They are mainly composed of cellulose that resulted in numerous peaks generated from the thermal carbohydrate backbone degradation. Levoglucosan, a six-carbon oxygenate, is the most abundant primary

product from cellulose pyrolysis, a characteristic feature of cellulosic material pyrolysis that has been previously elaborated (Fig. 7A) [3, 40, 48, 49].

Besides those cellulose pyrolysis products, other components such as lignin monomers and terpenic compounds were characterized in *Hanji* raw fibers. Lignin is a polyphenol produced by oxidative condensation of three phenylpropanoid monomers, namely p-coumaryl, coniferyl and sinapyl alcohols. The phenyl moieties of such compounds differ in the hydroxy and methoxy substituents and classified as hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units [50]. Within the same region, lignin markers of phenolic compounds of different types were identified that mainly composed of G and S moieties (Fig. 7B; Table 1). It is noted that *Hanji* made from bast fibers of gampi (H1-05) and mitsumata (H1-06) present much higher intensity of lignin pyrolysis products especially for compound 12 (demonstrated by m/z 180 in Fig. 7C), compound 13, 15, 19 (demonstrated by m/z 180 in Fig. 7C) and compound 14, 18 (demonstrated by m/z 196 in Fig. 7C). While these lignin monomers were less intensive in *Hanji* made from paper mulberry fiber. The use of strong alkali solution NaOH during cooking process damaged the fiber and reduce much of lignin component as can be observed from sample *Hanji* H1-08 that shows almost complete removal of the lignin monomers (Fig. 7C) (the paper treatment conditions can be found at Table 2 as well as Additional file 1: Table S1).

Terpenic compounds with the characteristic ions of m/z at 218, 203, 189 was identified and characterized in the pyrolysis of *Hanji* that are in accord to papermaking fibers from the *Moraceae* family [40, 41, 51, 52]. It can be seen from the total ion chromatogram (TIC) that these terpenic compounds elute in the plant marker region (defined as region of interest, ROI) at a comparatively high temperature (Fig. 7A). The dominant structures obtained from the pyrolysis of *Hanji* identified in this region consist of triterpene of oleanane and ursane structures (Table 1). As can be seen from its extracted ion chromatograms (EIC) in Additional file 1: Figure S5, the distribution of the terpene compounds with the selected ions (m/z at 218, 203 and 189) constitute the main compounds in the plant marker region (Table 2).

A general behaviour observed during the pyrolysis of *Hanji* with different fiber sources showed that paper mulberry fiber presented high concentrations of terpene compounds while gampi and mitsumata fiber mainly generated compounds of phytosterols in the defined ROI (Additional file 1: Figure S6). The characterization of paper mulberry fibers from those of gampi and mitsumata fibers in Japanese handmade papers by Py-GC/MS was previously studies with similar observations in compound distributions compared to Korean handmade

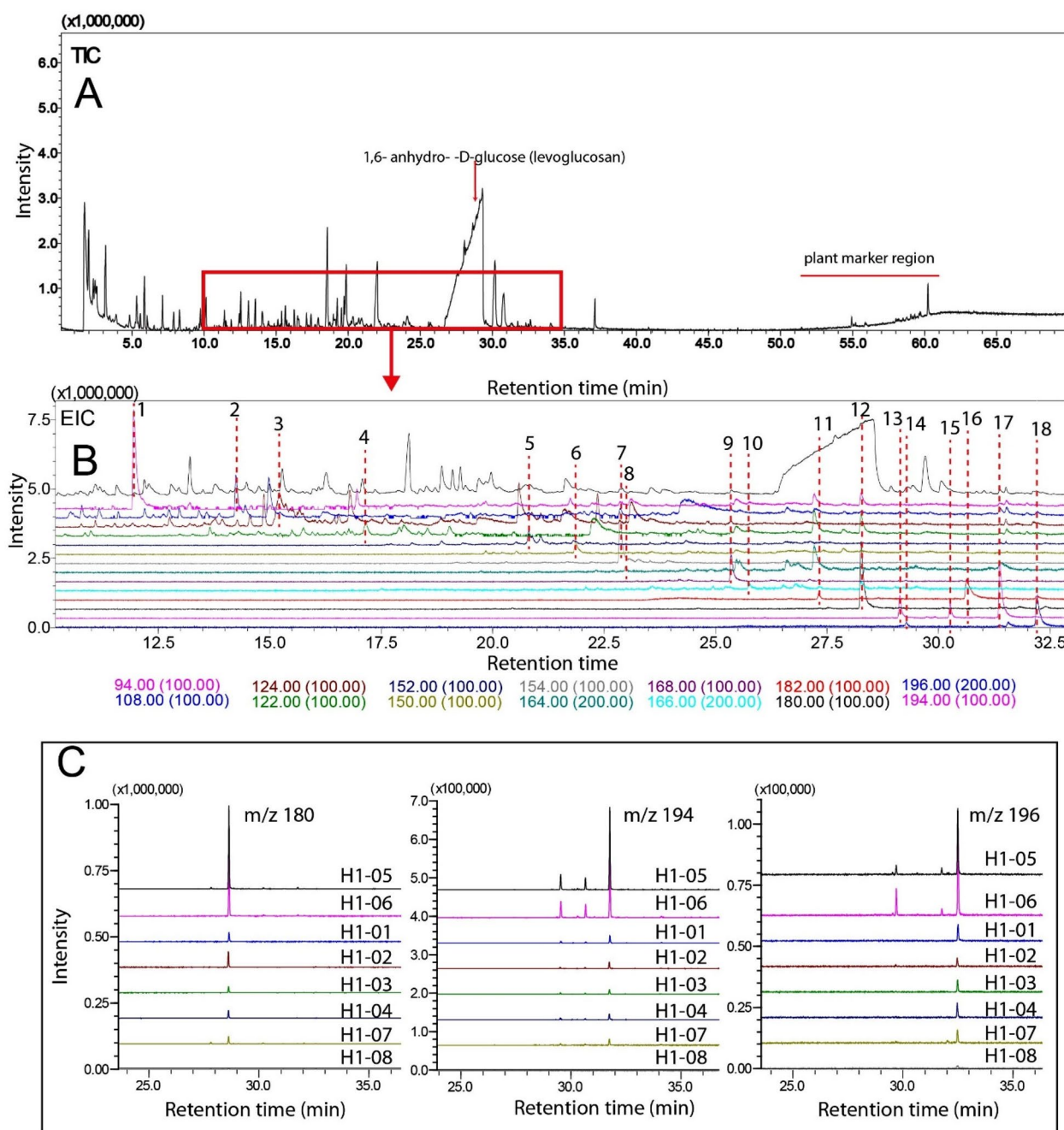


Fig. 7 The TIC chromatogram of *Hanji* pyrolysis products (**A**), the TIC/EIC chromatogram of lignin monomers (**B**) and EIC chromatogram of lignin monomers (**C**). For compound assignments, see Table 1. Detailed information of sample H1-01 to H1-08 is listed in Table 2

papers [3, 40]. Furthermore, the *Hanji* pyrolysis component of lignin monomers has been characterized which also showed different distributions between paper mulberry fiber and gampi, mitsumata fibers (Fig. 7C). The difference of lignin monomers increased the dimension of the data that can be used for handmade paper fiber

identification and discrimination [3]. The lignin monomer content may also provide information to estimate handmade paper treatment process (e.g., mild alkali treatment or modern strong alkali agent treatment) that can be used in study and identification of ancient handmade papers.

Table 1 Assignment of Pyrolysis of *Hanji* plant markers

No.	Ret. time (min)	MW	Main ions	Attribution	Type
1	11.97	94	94, 66, 55, 58	Phenol	L-H
2	14.23	108	108, 107, 79, 85	2-Methylphenol	L-H
3	15.19	124	124, 109, 81, 95	Guaiacol	L-G
4	17.17	122	122, 107, 91, 77	2,6-Dimethylphenol	L-H
5	20.82	152	152, 137, 122, 128	4-Ethylguaiacol	L-G
6	21.86	150	150, 135, 107, 77	4-Vinylguaiacol	L-G
7	22.86	154	154, 139, 111, 93	2,6-Dimethoxyphenol	L-G
8	22.93	164	164, 149, 103, 121	Eugenol	L-G
9	25.36	168	168, 153, 125, 107	2,6-Dimethoxy-4-methyl-phenyl	L-S
10	25.77	166	166, 137, 122, 94	Homovanillin	L-G
11	27.33	182	182, 167, 122, 136	4-Ethyl-2,6-dimethoxypheno	L-S
12	28.28	180	180, 165, 137, 91	2,6-Dimethoxy-4-vinylphenol	L-S
13	29.12	194	194, 91, 119, 131	4-Allyl-2,6-dimethoxyphenol	L-S
14	29.22	196	196, 167, 110, 103	2,6-Dimethoxy-4-propylphenol	L-S
15	30.26	194	194, 179, 151, 119	cis-2,6-Dimethoxy-4-propenyl-phen	L-S
16	30.62	182	182, 181, 167, 91	Syringaldehyde	L-S
17	31.38	194	194, 179, 119, 91	trans-2,6-Dimethoxy-4-propenylphe	L-S
18	32.22	196	196, 181, 153, 123	Acetosyringone	L-S
19	54.37	408	218, 203, 189, 119	Oleanane-2,12-diene	T-O
20	54.96	408	218, 189, 119, 95	Urs-2,12-diene	T-U
21	54.92	412	135, 143, 394, 81	Stigmasta-4,6-dien-3-ol	S
22	55.05	–	218, 189, 95, 119	Ursane structure NA	T-U
23	55.19	396	145, 81, 396, 275	stigmasta-3,5-diene NA	S
24	55.27	–	218, 189, 203, 95	Ursane structure NA	T-U
25	55.90	408	218, 107, 119, 105	Ursane structure NA	T-U
26	58.20	424	218, 203, 95, 119	Oleanane-12-en-3-one	T-O
27	58.49	426	218, 203, 189, 95	Oleanane-12-en-3-ol	T-O
28	58.75	424	218, 95, 109, 107	Urs-12-en-3-one	T-U
29	59.05	426	218, 95, 107, 121	Urs-12-en-3-ol	T-U
30	59.17	410	174, 410, 159, 161	Stigmasta-3,5-dien-7-one	S
31	59.70	468	218, 203, 189, 95	Oleanane-12-ene-3-acetate	T-O
32	60.22	468	218, 189, 95, 135	Urs-12-ene-3-acetate	T-U

L lignin; H hydroxyphenyl; G: guaiacyl; (L)-S syringyl; T terpene; O oleanane; U ursane; S stigmasta

Table 2 The fiber composition, making method of the test samples from H1-01 to H1-08

No.	Fiber composition	Cooking condition	Mucilage	Method	Bleaching	Beating	pH	Use
H1-01	100% <i>Dak</i>	<i>Yukjae</i>	<i>Dakpul</i>	<i>G</i>	<i>Non</i>	<i>K</i>	8.7	Conservation
H1-02	96% <i>Dak</i> + 4% <i>Anpi</i>	<i>Yukjae</i>	<i>Dakpul</i>	<i>H</i>	<i>Non</i>	<i>K</i>	9.8	Conservation, art work
H1-03	96% <i>Dak</i> + 4% <i>Anpi</i>	<i>Yukjae</i>	<i>Dakpul</i>	<i>H</i>	<i>Non</i>	<i>K</i>	5.8	Conservation
H1-04	96% <i>Dak</i> + 4% <i>Anpi</i>	<i>Yukjae</i>	<i>Dakpul</i>	<i>H</i>	<i>Non</i>	<i>K</i>	8.1	Conservation
H1-05	100% <i>Anpi</i>	Na ₂ CO ₃	<i>Dakpul</i>	<i>G</i>	NaClO	<i>N</i>	7.4	Printmaking
H1-06	100% <i>Samjidak</i>	Na ₂ CO ₃	<i>Dakpul</i>	<i>G</i>	<i>Non</i>	<i>N</i>	6.5	Calligraphy
H1-07	100% <i>Dak</i>	Na ₂ CO ₃	<i>Dakpul</i>	<i>G</i>	NaClO	<i>K</i>	7.5	Crafts
H1-08	100% <i>Dak</i>	NaOH	PAM	<i>G</i>	NaClO	<i>K</i>	5.8	Paintings

Dak paper mulberry; *anpi* gampi; *samjidak* mitsumata; *yukjae* natural plant ash; *dakpul* natural formation aid from Hibiscus manihot; PAM Polyacrylamide; *G* Gadumtteugi; *H* Heullimtteugi; *K* knife beater; *N* niagara beater

In East Asia, the inner bark of paper mulberry has been widely used as raw material for hand papermaking. For instance, paper mulberry fiber has been used in Korean handmade papers (*Hanji*) and Japanese handmade papers (*Washi*). Since they are made from quite similar species, no difference was clearly evidenced by microscopic observation to distinguish papers from these two areas. The pyrolysis profiles of *Hanji* are also quite similar in chemical compositions to those of *Washi* as both of them use fibres from the species in *Broussonetia* genus [3]. The similarity can also be observed from their similar compound distribution patterns in the ROI demonstrated in Additional file 1: Figure S7. Nevertheless, a difference in the intensity ratio of compound X1 (sterol compound tentatively identified as lanosta-8,24-dien-3-ol, acetate) and compound T1 (oleanane-12-ene-3-acetate, No.31 in Table 1) has been noticed with *Hanji* having relative higher ratio when both compounds were detected (Additional file 1: Figure S8).

Conclusion

This study reports the characterization of Korean handmade papers constituted in a well edited *Hanji* reference book. It was observed that the difference in material preparing and paper making craft lead to different paper structure which is statistically reflected in their physical properties. The structure differences determine paper performance and applications as a general connection between the crafting, measured data and potential significance. The chemical composition of *Hanji* raw fiber materials of paper mulberry, gampi and mitsumata has been analysed by Py-GC/MS that showed different profiles of lignin monomers and terpenic compounds. The use of strong alkali solution was observed to greatly eliminate the lignin component. The difference of *Hanji* and *Washi* from a relative intensity ratio of two compounds in the plant marker region is observed in their pyrolysis results which could be used in ancient paper samples differentiation with further proper method development. These quantified data analysis and descriptions serves as a way to retrieve paper crafting information as well as providing potential significance on their applications which are useful to get acquainted with modern Korean handmade papers for different applications.

This report is the first study on well-defined *Hanji* samples in large quantities, forming a base for further study and comparison of handmade papers in East Asian region. It also contributes to a better understanding of *Hanji* properties for cultural relics applications, as well as improves knowledge on handmade papers from the Korean peninsula. In a general sense for handmade paper study, this investigation pointed out what benefit can be

derived from protocol well-defined handmade papers in large quantities as well as stressed a situation where these samples are currently rare and lacking in scientific research on handmade papers.

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s40494-021-00570-9>.

Additional file 1: Figure S1. A map of *Hanji* workshop locations in Korea. The map was according to the *Hanji* making workshop information in the four-volume of reference handmade paper sample collection book *Hanji, Korean handmade paper* [42]. **Figure S2.** (B) and (C) are projections in a* and b* space of colour gamut from the studied *Hanji* samples. **Figure S3.** Scores plot and loadings plots in PCA analysis of the general property data in Table S1. The variation factors of FC, CC, FM, SFM, BL, BM, DY, Do has been digitalized as input number of 1,2,3... And the weightings of the variables were using 1/STD, where STD stands for standard deviation, for principal component analysis. **Figure S4.** Scores plot in PCA analysis of the mechanical property of *Hanji* with mappings of tensile strength value in grain-direction (A) and cross-direction (B), folding endurance value in grain-direction (C) and cross-direction (D). PCA was performed with tensile strength and folding endurance data values without normalization. In general, the *Gadumtteugi* (G) and *Heulimtteugi* (H) *Hanji* were clustered into two parts with *Heulimtteugi Hanji* locate in the positive PC2 coordinate while *Gadumtteugi Hanji* situated in the negative PC2 coordinate: Mapping with the tensile strength value (grain direction), within each type, they can be classified into three groups with the tensile strength ranging from low, medium and high (A); while mapping with the cross direction value (B), *Heulimtteugi Hanji* can still be classified into three groups meanwhile the *Gadumtteugi Hanji* is divided either low or high types; mapping with the folding endurance value (grain direction) (C), the low and medium value were clustered together; while mapping with cross direction value showed that *Gadumtteugi Hanji* has weak values in the cross direction folding endurance (D). **Figure S5.** The total ion chromatogram (TIC) of *Hanji* sample made with paper mulberry fibers (A) and the extracted ion chromatogram (EIC) of pyrolysis products of terpenic compounds distribution pattern exemplified with paper mulberry as raw material (B). For compound assignment, see Table 1. **Figure S6.** The total ion chromatogram (TIC) of *Hanji* sample made with paper mulberry fibers (H1-01), gampi fibers (H1-05) and mitsumata fibers (H1-06). **Figure S7.** (A) is the TIC chromatogram while (B) is the EIC m/z at 218. In (A) and (B), (I) is *Hanji* and (II) is *Washi*. (C) is the enlarged demonstration of the region in (B), (D) is the mass spectra of compound X1 after background subtraction and (E) is the NIST library search results with high match factor. **Figure S8.** The ration of the EIC (m/z at 218) area of X1/T1 (in percentage). The data are from 12 test of *Hanji* papers and 12 test of *Washi* papers that have signals of X1 and T1 at EIC m/z at 218 and respective retention time at 59.6 min and 59.7 min, respectively. **Table S1.** Some general property data of the handmade paper samples attached in the four-volume *Hanji* reference book that data analyses have been performed in this study.

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Authors' contributions

Conceptualization: BH, L-BV; methodology: BH, H-JK, SS, MS; investigation: BH, L-BV, H-JK, BL, SS, MS; funding acquisition: BH; writing—original draft: BH; writing—review and editing: BH, L-BV, H-JK, BL, SS, MS. All authors read and approved the final manuscript.

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Availability of data and materials

The data used in the study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare no competing interests.

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References

- Tsien T-H. Raw materials for old papermaking in China. *J Am Orient Soc*. 1973;93:510–9. <https://doi.org/10.2307/600169>.
- Shi JL, Li T. Technical investigation of 15th and 19th century Chinese paper currencies: fiber use and pigment identification. *J Raman Spectrosc*. 2013;44(6):892–8. <https://doi.org/10.1002/jrs.4297>.
- Han B, Vial J, Sakamoto S, Sablier M. Identification of traditional East Asian handmade papers through the multivariate data analysis of pyrolysis-GC/MS data. *Analyst*. 2019;144(4):1230–44. <https://doi.org/10.1039/C8AN01898G>.
- Luo Y, Cigić IK, Wei Q, Strlič M. Characterisation and durability of contemporary unsized Xuan paper. *Cellulose*. 2021;28(2):1011–23. <https://doi.org/10.1007/s10570-020-03554-3>.
- Chen G, Katsumata KS, Inaba M. Traditional Chinese papers, their properties and permanence. *Restaurator Int J Preserv Libr Arch Mater*. 2003;24(3):135–144. <https://doi.org/10.1515/REST.2003.135>.
- Lee K, Enomae T, Inaba M. Comparison of degradation behaviour of the painting paper in Japanese scrolls for moist heat and sealed tube ageing methods. *Stud Conserv*. 2021. <https://doi.org/10.1080/00393630.2020.1846931>.
- Masuda K. Japanese paper and Hyōgu. *Paper Conserv*. 1985;9(1):32–41. <https://doi.org/10.1080/03094227.1985.9638467>.
- Jeong M-J, Kang K-Y, Bacher M, Kim H-J, Jo B-M, Potthast A. Deterioration of ancient cellulose paper, Hanji: evaluation of paper permanence. *Cellulose*. 2014;21(6):4621–32. <https://doi.org/10.1007/s10570-014-0455-4>.
- Song M, Munn J. Permanence, durability and unique properties of Hanji. In: *The book and paper group annual* (2004). Princeton: Citeseer; 2005. p. 127–36.
- Yum H. Traditional Korean papermaking: history, techniques and materials. Newcastle upon Tyne: Northumbria University; 2008.
- Park Y-S. a history of Korean Paper. *Study of Washi Culture*. 2004;12:32–48.
- Choi J-I, Chung YJ, Lee KS, Lee J-W. Effect of radiation on disinfection and mechanical properties of Korean traditional paper. *Hanji Radiat Phys Chem*. 2012;81(8):1051–4. <https://doi.org/10.1016/j.radphyschem.2011.11.019>.
- Jeong M-J, Bogolitsyna A, Jo B-M, Kang K-Y, Rosenau T, Potthast A. Deterioration of ancient Korean paper (Hanji), treated with beeswax: a mechanistic study. *Carbohydr Polym*. 2014;101:1249–54. <https://doi.org/10.1016/j.carbpol.2013.10.033>.
- Jeon C. The effect of paper making methods and dochim of handmade Korean paper (Hanji) on the strength. *J Korean Wood Sci Technol*. 2002;30(2):134–43.
- Kim HJ, Jo BM, Lee YM. The quality evaluation of Korean traditional Hanji by different sheet-making processes. *J Korea Tech Assoc Pulp Paper Ind*. 2004;36(5):44–52.
- Cho J-H, Kim K-J, Park S-B, Eom T-J. Comparison of the functional properties of Hanji depending on the different manufacturing process. *J Korea Tech Assoc Pulp Paper Ind*. 2009;41(3):42–8.
- Lee S-Ch. Hanji: everything you need to know about traditional Korean paper. Republic of Korea: Hyeonamsa Publishing Co., Ltd.; 2012.
- Cheon C, Kim S-J, Jin Y-M. Properties of indigenous Korean paper (Hanji)-Classification of Oebal (single frame) papermaking methods. *J Korean Wood Sci Technol*. 1999;27(1):88–104.
- Paolo F, Calvini CF, Poggi CDPAN. Use of the Korean mulberry paper Hanji in book and paper conservation: when a traditional material meets new techniques. In: *Adapt & evolve 2015: East Asian materials and techniques in western conservation*. Proceedings from the International Conference of the Icon Book & Paper Group, London 8–10 April 2015. The Institute of Conservation; 2017: London; 2015. p. 110–7.
- Jacobi E. Workshop Hanji papier maken: een verslag. Amsterdam: Au Courant-Restauratoren Nederland; 2016. p. 26–33.
- Go IH, Jo AH, Ye JH, Jeong SH. Analysis of domestic research trends on Korean paper Hanji. *J Conserv Sci*. 2017;33(6):457–66. <https://doi.org/10.12654/JCS.2017.33.6.05>.
- Brown N, Lichtblau D, Fearn T, Strlič M. Characterisation of 19th and 20th century Chinese paper. *Herit Sci*. 2017;5(1):1–14. <https://doi.org/10.1186/s40494-017-0158-x>.
- Brown N, Coppola F, Modelli A, Amicucci F, Lichtblau D, Strlič M. Non-destructive collection survey of the historical Classense Library. Part I Paper Characterisation *Herit Sci*. 2020;8(1):1–11. <https://doi.org/10.1186/s40494-020-00432-w>.
- Dragojević A, Gregor-Sveteć D, Tomažič JV, Lozo B. Characterization of seventeenth century papers from Valvasor's collection of the Zagreb Archdiocese. *Herit Sci*. 2021;9(1):1–20. <https://doi.org/10.1186/s40494-021-00507-2>.
- Jang KJ, Heo TY, Jeong SH. Classification option for Korean traditional paper based on type of raw materials, using near-infrared spectroscopy and multivariate statistical methods. *BioResources*. 2020;15(4):9045–58. <https://doi.org/10.15376/biores.15.4.9045-9058>.
- Di Turo F, Mai C, Haba-Martínez A, Doménech-Carbó A. Discrimination of papers used in conservation and restoration by the means of the voltammetry of immobilized microparticles technique. *Anal Methods*. 2019;11(35):4431–9. <https://doi.org/10.1039/C9AY00998A>.
- Vetter W, Frühmann B, Cappa F, Schreiner M. Materials and techniques used for the "Vienna Moamin": multianalytical investigation of a book about hunting with falcons from the thirteenth century. *Herit Sci*. 2021;9(1):1–17. <https://doi.org/10.1186/s40494-021-00553-w>.
- Li HM, Severini L, Titubante M, Gong DC, Micheli L, Mazzuca C, Gong YX. Gellan gum hydrogel as an aqueous treatment method for Xuan paper. *Restaurator Int J Preserv Libr Arch Mater*. 2021;42(1):37–54. <https://doi.org/10.1515/res-2020-0010>.
- Horst TH, Smith RD, Potthast A, Hubbe MA. Accelerated aging of deacidified and untreated book paper in 1967 compared with 52 years of natural aging. *Restaurator Int J Preserv Libr Arch Mater*. 2020;41(3):131–52. <https://doi.org/10.1515/res-2020-0006>.
- Luo Y, Zhang X. Effects of yellow natural dyes on handmade Daqian paper. *Herit Sci*. 2021;9(1):1–10. <https://doi.org/10.1186/s40494-021-00560-x>.
- Collings T, Milner D. The identification of oriental paper-making fibres. *Paper Conserv*. 1978;3(1):51–79. <https://doi.org/10.1080/03094227.1978.9638509>.
- Carr D, Cruthers N, Smith C, Myers T. Identification of selected vegetable textile fibres. *Stud Conserv*. 2008;53(sup2):75–87. <https://doi.org/10.1179/sic.2008.53.Supplement-2.75>.
- Haugen E, Holst B. Flax look-alikes: pitfalls of ancient plant fibre identification. *Archaeometry*. 2014;56(6):951–60. <https://doi.org/10.1111/arcm.12054>.
- Han B, Niang J, Rao H, Lyu N, Oda H, Sakamoto S, Yang Y, Sablier M. Paper fragments from the Tibetan Samye Monastery: clues for an unusual sizing recipe implying wheat starch and milk in early Tibetan papermaking. *J Archaeol Sci Rep*. 2021;36:102793. <https://doi.org/10.1016/j.jasrep.2021.102793>.
- Go IH, Jo AH, Jeong L, Heo TY, Cho K, Choi TH. Predictive model of geographical origin discrimination of paper mulberry and handmade paper using ICP-AES/MS and multivariate statistical analysis. *J Cult Herit*. 2021;49:222–8. <https://doi.org/10.1016/j.culher.2020.12.004>.

36. Li T, Liu C, Wang D. Applying micro-computed tomography (micro-CT) and Raman spectroscopy for non-invasive characterization of coating and coating pigments on ancient Chinese papers. *Herit Sci*. 2020;8(1):1–16. <https://doi.org/10.1186/s40494-020-00366-3>.
37. Keheyen Y, Eliazan G, Engel P, Rittmeier B. Py/GC/MS characterisation of naturally and artificially aged inks and papers. *J Anal Appl Pyrol*. 2009;86(1):192–9. <https://doi.org/10.1016/j.jaap.2009.06.004>.
38. Ohtani H, Komura T, Sonoda N, Taguchi Y. Evaluation of acidic paper deterioration in library materials by pyrolysis-gas chromatography. *J Anal Appl Pyrol*. 2009;85(1–2):460–4. <https://doi.org/10.1016/j.jaap.2008.11.037>.
39. Imn SY, Ji AY, Lee JS, Jeong HW. Material analysis and conservation treatment of sangryangmun in Jinnamgwon. *Yeosu J Conserv Sci*. 2020;36(3):213–24. <https://doi.org/10.12654/JCS.2020.36.3.06>.
40. Avataneo C, Sablier M. New criteria for the characterization of traditional East Asian papers. *Environ Sci Pollut Res*. 2017;24(3):2166–81. <https://doi.org/10.1007/s11356-016-6545-0>.
41. Han B, Vial J, Inaba M, Sablier M. Analytical characterization of East Asian handmade papers: a combined approach using Py-GC/MS and multivariate analysis. *J Anal Appl Pyrol*. 2017;127:150–8. <https://doi.org/10.1016/j.jaap.2017.08.013>.
42. Kim H-J. Hanji, Korean handmade paper. Parkes: National Library of Australia; 2010.
43. Tsai FW, Van der Reyden D. Analysis of modern Chinese paper and treatment of a Chinese woodblock print. *Paper Conserv*. 1997;21(1):48–62. <https://doi.org/10.1080/03094227.1997.9638598>.
44. Sakamoto S, Okada Y. Paper analysis and database of papers of the pelliott collection, Dunhuang manuscripts. In: International Conference on culture and computing (culture computing). Kyoto Japan: IEEE; 2015. <https://doi.org/10.1109/Culture.and.Computing.2015.24>.
45. Han B, Yimin Y, Huanhuan W, Changsui W. Prospects of technical authentication of bogus traditional Chinese paintings. *China Cult Herit Sci Res*. 2014;4:17.
46. Masuda K. The findings from the survey of ancient document papers in the Shosoin treasure house and the present papers made by various hand sheet forming technique. *Bull Off Shosoin Treasure House*. 2010;32:85–95.
47. Han Y-H, Enomae T, Isogai A, Yamamoto H, Hasegawa S, Song J-J, Jang S-W. Traditional papermaking techniques revealed by fibre orientation in historical papers. *Stud Conserv*. 2006;51(4):267–76. <https://doi.org/10.1179/sic.2006.51.4.267>.
48. Yao N, Wei S. Characterization and identification of traditional Chinese handmade paper via pyrolysis-gas chromatography-mass spectrometry. *BioResources*. 2021;16(2):3942. <https://doi.org/10.15376/biores.16.2.3942-3951>.
49. Zhang X, Yang W, Dong C. Levoglucosan formation mechanisms during cellulose pyrolysis. *J Anal Appl Pyrol*. 2013;104:19–27. <https://doi.org/10.1016/j.jaap.2013.09.015>.
50. Galletti GC, Bocchini P. Pyrolysis/gas chromatography/mass spectrometry of lignocellulose. *Rapid Commun Mass Spectrom*. 1995;9(9):815–26. <https://doi.org/10.1002/rcm.1290090920>.
51. Han B, Daheur G, Sablier M. Py-GC/MS in cultural heritage studies: an illustration through analytical characterization of traditional East Asian handmade papers. *J Anal Appl Pyrol*. 2016;122:458–67. <https://doi.org/10.1016/j.jaap.2016.10.018>.
52. Han B, Lob S, Sablier M. Benefit of the use of GC/MS profiles for 1D GC/MS data treatment illustrated by the analysis of pyrolysis products from east Asian handmade papers. *J Am Soc Mass Spectrom*. 2018;29(8):1582–93. <https://doi.org/10.1007/s13361-018-1953-7>.

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