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ORIGINAL PAPER

Deterioration of ancient cellulose paper, Hanji: evaluation of paper permanence

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Abstract Hanji paper, the paper material traditionally used in Korea, is in the focus of the present aging and mechanistic study. As raw materials and historic recipes for paper making are still available for Hanji today, specimen resembling historical material at the point of production can be prepared. While from that starting point, historical material had taken the path of natural aging, newly prepared samples—prepared according to both historic and current recipes—were artificially aged, and both aging modes can be compared. For the first time, an in-depth chemical and mathematical analysis of the aging processes for Hanji is presented. The aging of Hanji paper, resulting in hydrolysis and oxidation processes, was addressed by means of selective fluorescene labeling of oxidized groups in combination with gel permeation chromatography, providing profiles of carbonyl and carboxyl groups relative to the molar mass distribution. Starting Hanji showed the highest molecular weight (>1,400 kDa) ever reported for paper. We have defined two critical parameters for comparison of the paper samples: half-life DP (the time until every chain is split once on average) and life expectancy (the time until an average DP of failure is reached and no further mechanical stress can be tolerated). The two values were determined to be approximately 500 and 4,000 years, respectively, for the Hanji samples, provided there is no UV radiation. The rate of cellulose chain scission under accelerated aging (80 °C, RH 65 %), was about 600 times faster than under natural conditions. In addition, cellulose degradation of Hanji paper under accelerated aging condition was about 2–3 times slower than that of historical rag paper as those used in medieval Europe.

Keywords Cellulose degradation · Paper permanence · Artificial aging · Degree of polymerization

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Introduction

Korean Hanji paper is traditionally made from bast fibers of one-year-old paper mulberry trees (*Broussonetia kazinoki* Siebold) and is ranked as one of the strongest papers available worldwide. Only cellulose produced by bacteria and very few other celluloses reach comparable strength values. There is a proverb in Korean that says "Silk can stand five hundred years, but paper can stand one thousand". However, there is no scientific evidence on how many years this paper can keep its permanence. Due to its high stability, the long fibers (see Fig. S1) and its natural color tones, Hanji paper is currently growing in appeal to be used as support material in paper conservation, namely in stabilizing historical papers. So far, mainly Japanese *Washi* or *Kozo* paper was used for these purposes. What is missing in that respect is information on the durability and aging behavior of Korean Hanji paper, an sine qua non for use in preservation of valuable art objects.

Scientists and paper conservators have elaborated methods to judge the permanence of paper with various aging tests, usually by applying elevated temperature, humidity, radiation of light and air pollution during the last decades. (Area and Cheradame 2011; Ding and Wang 2007; Forsskåhl 2000: Hotle et al. 2008; Kaminska et al. 2001; Kato and Cameron 1999; Malešič et al. 2005; Porck 2000; Rasch and Scribner 1933; Reilly et al. 2001; Shahani et al. 2001; Strlič et al. 2011; Tétreault et al. 2013; Zou et al. 1996a; Calvini 2014) Since the process of natural aging is too slow, the aging of cellulose has to be accelerated by elevating the temperature to be able to then extrapolate the rate of cellulose scission to room temperature conditions. For this prediction, the rate of degradation at different temperatures is measured and an Arrhenius plot is constructed. The relationship between temperature and rate can be extended from the data at elevated temperature to ambient conditions (Adriaan and Plooy 1981; Zou et al. 1996a, b). The prediction of life expectancy of paper is not straight forward and complicated due to the presence of filling material, hemicelluloses and lignin, to name but a few. Calculating the rate of chain scissions at elevated temperature using the Ekenstam equation and extrapolating from this to room temperature conditions usually leads to limited accuracy and therefore gives rise to high error margins (Kaminska et al. 2001).

In the present study, we compare Hanji paper which has been aging naturally for several hundred years to paper obtained by artificial aging. So far this is a typical approach. What is usually missing is knowledge of the condition of the unaged historical sample material, i.e. the starting point for natural aging, which is typically known for the unaged test samples. This renders impossible a calculation of the numbers of chain scission at cellulose under natural aging conditions. In case of European rag papers, it is practically not viable to get any information on the afore mentioned starting point as rag papers were produced from old worn-out clothing and hence stem from always changing raw materials that were highly dependent on the type and availability of rags in the specific area. With other words, there is no standard rag paper sample as the old cloths used for rag paper production are of ill-defined grade. This is completely different to Korean Hanji paper. Hanji was always produced *de novo* from fresh (one-year old) bast fibers of paper mulberry (*Broussonetia kazinoki*) based on well described recipes. Having been historically handed down, these protocols are still available today. In addition to the bast fibers, a small amount of sunset hibiscus extractives was added to control drainage and to improve sheet formation (Jo et al. 2007). Hence it should be possible to manufacture a proper starting material for an aging study resembling the initial state and to compare this paper to naturally and artificially aged Hanji. Based on these materials the aging kinetics under natural conditions becomes accessible.

For analyzing hydrolysis and oxidation of the different Hanji papers, molar mass distribution with functional group profiling of carbonyl group and carboxyl group was applied. (Bohrn et al. 2005, 2006; Röhrling et al. 2002a, b).

Based on this data, the papers' life expectancy under natural conditions could be predicted for the first time, enabling the comparison of the rate of chain scission of natural aging conditions on the one hand and artificial ones on the other. This approach brought us a step closer to understanding the overall aging behavior of paper.

Materials and methods

Materials

Bast fibers of paper mulberry (*B. kazinoki*), which were harvested in Korea annually, were used for Hanji making, allowing the production of four types of Hanji paper that could be purchased (supplier in parenthesis): Hanji A (Andong Hanji), B (Gyeongju Hanji), D (Jangjibang), F (Mungyeong Hanji).

Hanji H was prepared by the author according to the historic recipe given below.

The chemicals used were of the highest grade available from commercial suppliers, solvents were of HPLC grade and reagents of p.a. grade. Carbazole-9-carbonyloxy amine (CCOA) and 9H-fluoren-2-yl-diazomethane (FDAM) were not commercially available compounds, and were synthesized according to the literature (Röhrling et al. 2002a; Bohrn et al. 2005).

Preparation of fresh Hanji (Hanji H) according to historic recipes

The making of Hanji was performed in field on full scale. The potash (K_2CO_3) solution required for cooking was obtained from ashes of a stem of barley based on the Korean traditional leaching process: Approximately 3.8 kg of incompletely burned barley ash were placed in a pot and leached with 25 L (60 °C) of groundwater.

After letting the bast fibers swell in water for 2 h, 1.8 kg of bast fibers were boiled in 25 L of potash extracts which had been prepared as described above in a caldron (104 °C) for 2½ h. After cooking, the pulp was washed with streaming groundwater overnight. It was then manually pounded for 4 h using a wooden club. Subsequently, the pulp was suspended in a vat. Mucilaginous material from the root of *Hibiscus Manihot* L., which was squashed, extracted and filtered after swelling in cold water, was added to control drainage and to disperse fibers equally. The sheet was then formed using a traditional Korean mold. After drying the wet sheet on a hot plate (below 80 °C) for 10 min, the basis weight of the obtained paper was between 40 and 45 g/m^2 (Table 1).

Accelerated aging of samples

For aging in an open system, Hanji H was aged with moist heat at 80 °C and RH 65 % for 12 weeks in accordance with ISO 5630-3 “Paper and board–Accelerated ageing”.

For aging in a closed system, 378 ± 2 mg of Hanji F, historical rag paper (1848), two bleached chemical pulps: EN—bleached eucalyptus kraft pulp, paper grade; BZ—bleached beech dissolving pulp, ground wood paper, and Whatman no.1 were placed in separate vials of 134.5 mL. Samples were aged at 80 °C for 17 days after conditioning at 20 °C, RH 54.4 % for 1 day.

Hanji B, D, and F were aged by ultraviolet light in an aging chamber (UV 2000, Atlas, USA) for 30 days. Samples were exposed to a UVA 340 nm lamp with an irradiation level of 0.77 W/m^2/nm at 80 °C.

Fluorescence labeling of functional groups and dissolution of the Hanji paper

The CCOA labeling for carbonyl group profiling was performed according to Röhrling et al. (2002a, b). 25 mg of dry pulp samples were agitated in a mixer for 20 s. The water was then removed by vacuum filtration. The samples were suspended in 4 mL of 20 mM zinc acetate buffer (pH 4.0) with 5.0 mg of CCOA and agitated in a water bath at 40 °C for 7 days.

The FDAM labeling was performed according to Bohrn et al. (2005, 2006). 20 mg of dry pulp were suspended in 0.1 M HCl and agitated in a mixer for 20 s. Then, the pulp was washed with ethanol and *N*,*N*-dimethylacetamide (DMAc) successively, and filtered.

Table 1 Description of traditional handmade papers, Hanji

Condition	Hanji A	Hanji B	Hanji D	Hanji F	Hanji H
Region (Korea) of paper mulberry cultivation	Southeast	Southeast	Central	Southeast	Southeast
Grammage (g/m^2)	24.1	60.7	52.7	40.4	42.3
Density (g/cm^3)	0.27	0.29	0.34	0.35	0.27
Thickness (μm)	88	209	92	129	159
Cooking chemicals	Sodium hydroxide	Sodium hydroxide	Buckwheat ash	Buckwheat ash	Barley ash

After filtration, the pulp was transferred into a 4 mL vial. The pulp was suspended in 3 mL of DMAc, and 1 mL of FDAM solution was added. The final concentration of solution was approximately 0.125 mol/L in DMAc. The suspension was then agitated in a shaking bath at 40 °C for 7 days.

After reacting, the CCOA and FDAM labeled samples were separated by filtration and subsequently activated with DMAc for a day after solvent exchange. The DMAc activated samples were dissolved in 2 mL of DMAc/LiCl (9 %, w/v) at room temperature for 1 day. The solution was diluted with pure DMAc, and filtrated through a 0.45 μm filter.

SEC—MALLS analysis

The molecular weight distribution (MWD), carbonyl and carboxyl content and profiles were analyzed by SEC. The SEC system was modified for the experimental setup as follows (Bohrn et al. 2006; Röhrling et al. 2002a, b).

After filtering through a 0.02 μm filter, DMAc/LiCl (0.9 %, w/v) was used as an eluent. The sample was injected automatically and chromatographed on four serial SEC columns (PL gel mixed AALS, 20 μm, 7.5 × 300 mm). This system was connected with fluorescence (TSP FL2000, CCOA: 290 nm excitation, 340 nm emission, FDAM: 252 nm excitation, 323 nm emission), MALLS (Wyatt Dawn DSP), and RI (Shodex RI-71) detector. A refractive index increment was 0.136 mL/g for cellulose in DMAc/LiCl (0.9 % w/v) at 25 °C and 488 nm. MWD and related polymer-relevant parameters were calculated by ASTRA and GRAMS software programs.

Purely hydrolytic degradation of the cellulose generates novel reducing end-group (REGs) without additional introduction of carbonyls by oxidation. The carbonyl content without reducing ends was calculated from total carbonyl content and REG. REGs can be obtained from the number average molar mass [g/mol].

$$\text{Reducing end-group (REG, μmol/g)} = \frac{1}{M_n} \times 10^6 \quad (1)$$

$$\text{Pure carbonyl content (μmol/g)} = \text{Total carbonyl content} - \text{REG} \quad (2)$$

Crystallinity by ^{13}C-CPMAS

All solid state NMR experiments were performed on a Bruker Avance III HD 400 spectrometer (resonance frequency of ^{1}H of 400.13 MHz, and ^{13}C of 100.61 MHz, respectively), that was equipped with a 4 mm dual broadband CP-MAS probe. Before measurement, the samples were swollen in deionized water over night. ^{13}C spectra were acquired by using the TOSS (total sideband suppression) sequence at ambient temperature with a spinning rate of 5 kHz, a cross-polarization (CP) contact time of 2 ms, a recycle delay of 2 s, SPINAL 64 1H decoupling and an acquisition time of 43 ms. Chemical shifts were referenced externally against the carbonyl signal of glycine with $\delta = 176.03$ ppm. The acquired FIDs were apodized with an exponential function (lb = 1 Hz) prior to Fourier transformation. Peak fitting was performed with the Dmfit program (Massiot et al. 2002).

Results and discussion

In a preliminary study, Korean traditional potashes used as alkali during pulping had been analyzed in more detail by ion chromatography and X-ray fluorescence spectroscopy in order to better understand the ancient pulping. To see the effects of the pulping procedure in the traditional process, the most important parameters have been varied to some extent and the influence of the final paper was addressed (Lee and Mun 1999; Mun 1999; Mun and Lim 1999).

First, the different papers obtained from traditional Hanji producers were compared to those made according to the historic descriptions. The data are given in Fig. 1 and Table 2. Distinct differences are visible in the MWDs, two groups are observed, one of them being composed of Hanji A and B, and the other group consisting of Hanji D, F, and H. MWDs of Hanji A and B show a significantly lower weight average molecular weight (M_w) (393.4 and 317.9 kg/mol, respectively). Both pulps lie within the typical distribution range of wood pulps prepared according to typical pulping methods (Bohrn et al. 2006). The M_w of Hanji D, F and H have the very high molar mass of typical Hanji papers with about 1,500 kDa. The steep curve in the high molar mass region (cf. Fig. 1) is

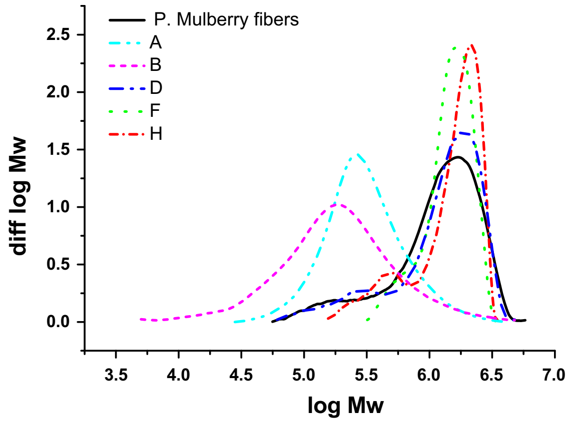

Fig. 1 Molar mass distribution of Hanji papers and bast fiber of paper mulberry

indicative of an already limited separation within the 20 μm columns used in SEC. However, more suitable columns are currently not available on the market for cellulose separation. In any case, the distribution of the cellulose is very narrow with a polydisperisty index (PDI) of 1.30 (F) and 1.37 (H). The second peak in the lower molar mass area, which is not present in papers A and B, results from the mild alkaline pulping which has a somewhat lower molar mass and a high content of carboxyl groups. Table 2 summarizes the statistical moments (MWD data) of all papers, of which Hanji H is prepared from the same paper mulberry used in this study (Table 3).

Alongside the chemical disintegration process of the fibers, the geographical origin of the tree plays a certain role. As mentioned above, the bast fibers of Hanji paper are always taken from one-year old paper mulberry trees. As a matter of fact, the respective morphology of the bast fibers may slightly vary depending on the area where the trees are grown. Choi et al. (2007) compared the fiber length of paper mulberry from 39 different locations in South Korea. The average fiber length was 6.8 ± 0.4 mm (N = 39). No significant differences were found concerning the area of cultivation. The fiber length from paper mulberry trees in the southeastern regions of Korea were slightly longer compared to other locations. Hanji A, B, F and H used in this study were harvested in the southeast. Therefore, the morphological differences due to different cultivation places cannot be made responsible for the large differences observed in the two groups.

The small amounts of additives, exopolysaccharide from *H. manihot* L. of which an M_w of approximately 2,500 kDa was reported by Han et al. (2005), added during the stock preparation (Jo et al. 2007) are well separated in sample activation, labelling and SEC and do not influence the molar mass of cellulose.

What is obvious from the molar mass distribution is the strong influence of the cooking chemicals. If the stronger sodium hydroxide solution is used, the Hanji cellulose strongly degrades during pulping. The historically used Korean potash is less alkaline and therefore preserves the high molar mass of cellulose. Korean traditional potashes, which are obtained from ashes of a stem of barley based on a special traditional leaching process (for details see Materials and methods part), have a pH around 11. The respective potashes contain mainly potassium carbonate (details of the inorganic composition are given in Tables S1 and S2) which is much less aggressive to cellulose in terms of molar mass loss than sodium hydroxide. As a

Table 2 Molecular mass and carbonyl/carboxyl data of of Hanji paper and bast fibers of paper mulberry

Parameter	Original mulberry bast fibers	Hanji A	Hanji B	Hanji D	Hanji F	Hanji H
M_n (kg/mol)	585	233	103	771	1,123	1,139
M_w (kg/mol)	1,325	393	318	1,458	1,456	1,566
M_z (kg/mol)	1,838	714	927	1,874	1,707	1,836
PDI	2.26	1.69	3.10	1.89	1.30	1.37
REG	1.71	4.29	9.76	1.30	0.89	0.88
Total carbonyl group content (μmol/g)		7.2	12.9	12.4	29.4	24.3
Pure carbonyl group content (μmol/g)		2.9	3.2	11.1	28.5	23.4
Carboxyl group content (μmol/g)	20.5	–	40.7	36.7	79.9	67.2
Crystallinity (^{13}C-CPMAS) crystalline : amorphous		1:0.67	1:0.82	1:0.76	1:0.77	1:0.73

Table 3 M_w and pure carbonyl and carboxyl group content of Hanji paper under UV radiation (80 °C)

Parameter	Aging					
	Un-aged (control)			30 days		
	Hanji B	Hanji D	Hanji F	Hanji B	Hanji D	Hanji F
M_n (kg/mol)	102.5	771.0	1,123	33.0	36.9	24.5
M_w (kg/mol)	317.9	1,458	1,456	198.5	332.2	265.6
PDI	3.10	1.89	1.30	6.02	8.99	10.84
REG	9.8	1.3	0.89	30.3	27.1	40.8
Total carbonyl group content (μmol/g)	12.9	12.4	29.4	35.7	31.9	69.1
Pure carbonyl group content (μmol/g)	3.2	11.1	28.5	5.3	4.8	28.3
Carboxyl group content	40.7	36.7	79.9	44.0	32.8	62.4

result, the sugar composition is similar for both pulping methods, and a significant portion of lignin still remained in the Hanji pulps after pulping (ref. Table S3), which is higher in the traditional technique. The data indicate that Korean traditional potashes are much less detrimental than sodium hydroxide towards the cellulosic material, mainly due to the milder, less alkaline cooking condition.

The M_w of the extracted Hanji fibers by Korean potash pulping is even slightly higher when compared to the original bast fibers. This is caused by the partial dissolution of accompanying polysaccharides and extractives which causes a slight shift in the MWD and an apparently higher M_w.

Average molar mass of traditionally cooked Hanji papers (Hanji D, F, and H) was determined to be 1,493 ± 80 (5.4 %) kDa ranging from 1,401 to 1,584 kDa within the 95 % confidence interval. Considering the minor degradation caused by Korean potash pulping and the similar M_w range of Hanji D, F and H, it can be expected that most Hanji cooked according to the Korean traditional recipes may have molar masses within the above average range.

We also analyzed the extent of oxidation for different Hanji papers. For this purpose, pure carbonyl contents (not considering naturally present reducing end groups) are determined by the CCOA method. All Hanji papers have pure carbonyl contents between 3 and 30 μmol/g. These values are in the typical range of chemical pulps as reported by Röhrling et al. (2002a). The pure carbonyl contents of Hanji cooked with Korean traditional potash (traditional Hanji (D, F, H)) were higher than those of Hanji cooked with sodium hydroxide (Hanji-NaOH (A, B)). It can be assumed that, compared to Korean potash, sodium hydroxide leads to a stronger removal of accompanying materials in the bast fibers which carry carbonyl groups. In addition, the pure carbonyl content shows a certain variation within traditional pulped Hanji papers in spite of a similar Mw.

Carboxyl contents analyzed by the FDAM protocol, which covers mainly uronic acids, do not relate to the pulping method. The content of uronic acid groups is mainly influenced by the mucopolysaccharide additive which contains a large amount of sugar acids alongside the hemicelluloses present. Hence, the acid content is significantly higher in samples of Hanji B–H and about 2–4 times higher than in the bast fiber itself.

Artificial aging of Hanji paper

Hanji paper was aged with moist-heat (see Materials and methods part), which causes an almost exclusive hydrolytic cleavage of the cellulose. As expected, the cellulose DP decreased proportional to aging time. The content of pure carbonyls as a typical sign of oxidation was not increased (Fig. 2). This clearly indicates that accelerated aging of Hanji under elevated temperature is dominated by hydrolysis. Similar results are obtained with other paper types which also show pure hydrolytic damage under these aging conditions (Ahn et al. 2011). To some extent, at early stages of aging, the pure carbonyl content decreased slightly. Rather than to a real effect affiliated to the actual aging process, the phenomenon may be related to the removal of some degraded mucopolysaccharides during sample preparation for SEC.

The rate of cellulose chain scission was calculated applying the Ekenstam equation (Fig. 3) and is

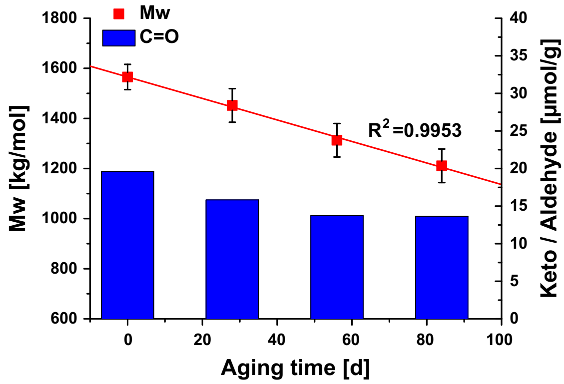

Fig. 2 M_w and pure carbonyl content of Hanji H after moist-heat accelerated aging (80 °C, 65 % RH)

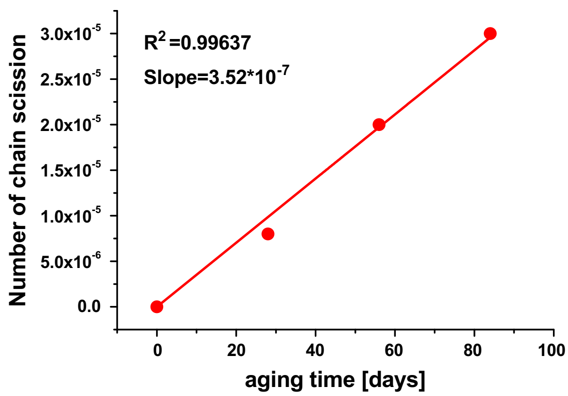

Fig. 3 The rate of cellulose chain scission (K_t, number of chain scission per anhydroglucose unit (AGU)) as a function of aging time (80 °C, RH 65 %)

directly proportional to the time of aging. The rates of chain scission per day (K_{1day}), i.e. the number of chain scission per anhydroglucose unit for 1 day, was 3.52×10^{-7}. Hence, the calculated half-life DP at these aging conditions (80 °C, RH 65 %, Hanji H) is 294 days.

To elucidate the permanence of Hanji paper, the rate of cellulose chain scission of Hanji papers and other papers was compared based on exactly identical accelerated aging conditions in closed reaction vessels at elevated temperature (80 °C, Hanji F). Based on that comparison (Fig. 4), the rate of cellulose chain scission of Hanji paper is found to be almost two times slower, contrary to the otherwise rather stable cotton or rag papers. Chemical pulp showed a similar stability as rag paper while the dissolving pulp was significantly less stable. The least stable paper was

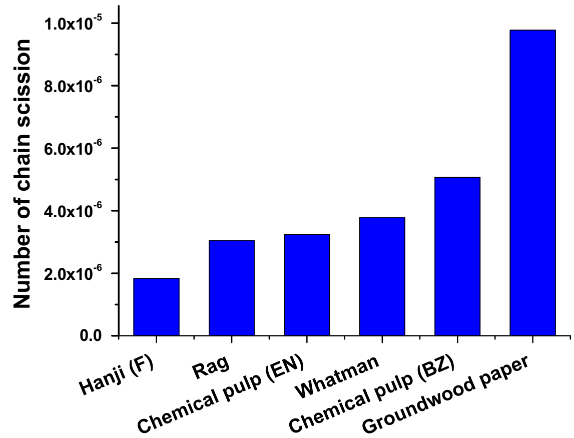

Fig. 4 The rate of cellulose chain scission (K_{1day}), number of chain scission per AGU for a day in the closed reaction vessel (80 °C)

groundwood pulp which degraded about five times faster than Hanji. The calculated half-life DP at these aging conditions (80 °C) for groundwood paper was only 34 days, compared to beech sulfite pulp (66 days) < Whatman no.1 (88 days) < bleached kraft paper pulp (103 days) < rag paper (110 days) < Hanji F (182 days), which definitely demonstrates the excellent stability and permanence of Hanji paper.

Cellulose can also be degraded by the absorption of UV radiation which can induce the formation of free radicals. As a result, cellulose is oxidized and may further be degraded (Fengel and Wegener 1984). For the sample prepared with NaOH as a pulping base (Hanji B), the already small molar mass was further decreased by UV radiation to about 60 % of the original value. Pure carbonyl and carboxyl contents of Hanji B were increased slightly. Hanji D and F, cooked with Korean traditional potash, showed no significant oxidation upon UV radiation. After subtracting the amount of reducing ends, the actual degree of oxidation was not increased. Lower amounts for pure carbonyls and also changing values for uronic acid groups, as seen for Hanji D, are usually caused by dissolution of carboxyl and carbonyl containing low M_w material after UV radiation during sample preparation (activation step). However, the molar mass was affected rather dramatically with a loss of about 80 % in the original value. A possible reason for this significantly different behavior of the NaOH cooked pulp on the one hand and the potash treated pulp on the other during UV irradiation is the residual lignin content (cf. Table S3). In addition to the presence or absence of lignin, also the structure of lignin has an influence on whether it acts as antioxidant protecting cellulose (Schmidt et al. 1995; Potthast et al. 2004) or as the exact opposite–a pro-oxidant. The result obtained from this study corresponds to a previous investigation on UV radiation and cellulose oxidation in the presence of residual lignin. For pulps cooked under alkaline conditions (unbleached kraft pulp), a similar behavior as for the NaOH cooked Hanji paper was observed, namely cellulose was oxidized in the presence of kraft lignin (Potthast et al. 2004). The lignin structure of the potash cooked mulberry fibers largely preserved the cellulose from oxidation and acted as a sacrificial substrate during irradiation.

Naturally aged Hanji paper

In a recent paper, we have reported the molar mass distribution and also the profiles for oxidized functionalities for naturally aged Hanji paper dating from 1473 to 1665 AD (Jeong et al. 2014). With the data available, it is not possible to determine the half-life DP using the rate of cellulose chain scission of these papers since the original values of M_w are usually not known.

The latter is a typical dilemma unique to almost all historical samples as we never know the condition of the fresh un-aged material, as has been discussed in the introduction. In that respect, Hanji papers, being produced from fresh material, have a large advantage.

If these fresh Hanji are compared to the well preserved naturally aged materials, there is only a small difference in the MWD, and hence the DP between Hanji papers after 500 years of natural aging and fresh Hanji papers prepared according to historic recipes is observed. Therefore, it should be allowed to propose that the DP of the historical paper before natural aging lies within the fresh-made traditional Hanji paper, on average DP = 9,216 ± 494 (5.4 % of standard deviation).

Actually, even if the original DP is available, it is still not easy to predict and extrapolate cellulose degradation over time, as degradation during aging usually comprises different processes at a time, as for example hydrolysis and oxidation. In particular oxidation, generating carbonyls and carboxyl groups, changes the reactivity towards hydrolysis and also complicates the degradation pathways (Henniges et al. 2006a, b; Potthast et al. 2003; Röhrling et al. 2002a, b).

Fortunately, the Annals of the Joseon Dynasty dating back to 1665 AD, which have already been analyzed, did not show signs of oxidation. The number of reducing end groups measured corresponded to the number of celluloses chains; no significant additional oxidation was observed. Only specific volumes which suffered from additional damage (forming fine powder or severe discoloration) displayed minor oxidative alterations (Jeong et al. 2014). This is in accord with the behavior of fresh Hanji paper prepared according to the historic recipes. As the Annals are comprised of large format books made of Hanji paper and printed on with non-aggressive inks (Oriental inks), risk for oxidative degradation is minor. In addition, the historical materials have been stored in wooden boxes to prevent degradation by UV radiation, insects and moisture variation. Hence, these prerequisites create a very rare case which paves the way for comparing freshly prepared material and its aging behavior, allowing to get a unique insight into natural aging, i.e. the hydrolytic degradation of cellulose during several hundred years.

We based our kinetic approach on the Ekenstam equation, $1/DP-1/DP_0 = k_t$ which is well suited to study polymer degradation. Cellulose as a polymer sometimes shows a deviating performance from classic polymer behavior. When the Ekenstam equation is applied to cellulose hydrolysis, the error increases for a zero- or first order kinetic modeling if the DP approaches lower values, i.e. close to the leveling-off degree of polymerization (Emsley and Stevens 1994; Heywood et al. 1999). In order to correct this deviation, Emsley et al. (1997) proposed a modified Ekenstam equation using at least two different rates for cellulose chain scission as a function of aging time between the initial and the latter period. An alternative approach is followed by Calvini et al. (2008). He and his coworkers proposed to distinguish between amorphous and crystalline regions in cellulose (Calvini et al. 2008). Ding and Wang (2007, 2008) used the time–temperature superposition method (Ding and Wang 2007) and the percentage DP loss (Ding and Wang 2008) as a measure for anticipating the degree of degradation. There is still an ongoing discussion on how to properly treat kinetic data and how to correctly model the processes on a mathematical bases, which was clarified by Calvini in a recent

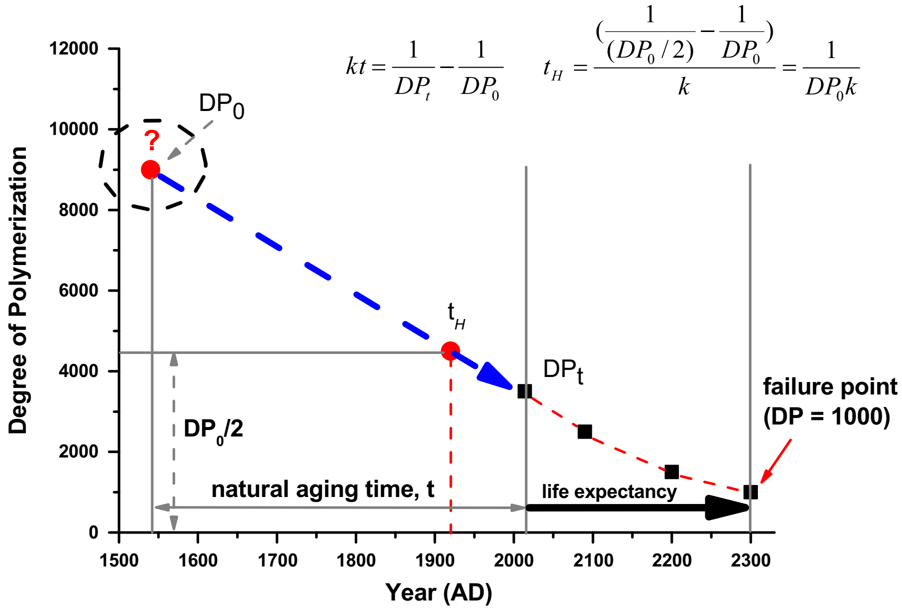

Fig. 5 Scheme illustrating the calculation of Half-life DP, rate of cellulose scission and life expectancy (k = the rate of chain scission per year, t = natural aging time (years), DP_{ts} = DP of naturally aged Hanji for time (t), DP_0 = DP of fresh Hanji paper, t_H = the time to reach the half-life DP (years))

paper (2014). It depends on crystallinity, degree of oxidation, chemical additives, and morphology, to name but a few, when the level-off DP for cellulose in paper is eventually reached and when a critical level for failure is attained.

To simplify these rather complex problems, this study focused on determination of the half-life DP. The half-life DP can be defined as the time needed to decrease the average molar mass M_w (based on SEC-light scattering data) to half the original value. This allows also for a comparison of different paper types or cellulosic materials. If no special damage pattern is observed, even in the aged form (more than 300 years of natural aging) the Hanji papers are far from close to the leveling-off DP, which should minimize errors.

The rate of chain scission and half-life DP, in other words the number of one chain scission, was first calculated from fresh Hanji and its naturally aged counter piece according to equations in Fig. 5.

The results are summarized in Table 4 and Fig. 6. For Hanji paper without a special damage pattern the half-life DP amounted to the impressive figure of 514 years (±147 years). In order to estimate the life expectancy to reach the condition of failure, we need to know at which DP this point is reached. Usually a DP 200 is considered as the point when cellulose loses all its mechanical strength. Interestingly this seems to be different for Hanji papers. From a previous study (Jeong et al. 2014) we have access to beeswax-coated paper samples with brown stains from the volumes of the Annals of King Sejong. This Hanji paper had almost lost all mechanical strength and had to be handled with extreme care. The M_w of this paper was 158,600 g/mol which corresponds to a DP of 979. With these data available we defined the DP of failure with approximately DP 1,000 instead of the much lower DP 200 used for European papers and pulps.

Hence, the life expectancy of traditional Hanji papers is approximately 4,000 years, which supports its excellent permanence.

The rate of chain scission of beeswax-coated papers with or without stains, which suffered from increased hydrolysis, is about 3.4 and 5.1 times faster, respectively, compared to papers without any contact to beeswax (Jeong et al. 2014). Hence, it is expected that the beeswax-coated papers have a life expectancy of approximately 700 years from now on.

Conversion index: natural aging versus accelerated aging

From these data, it is also possible to compare natural aging with artificial aging and in further consequence to get some more information on artificial aging in general. The accelerated aging for 1 day at 80 °C and RH 65 % corresponds to 603 days under natural aging conditions in Korean climate, which, based on the

Table 4 The average values of rate of cellulose chain scission, half-life DP, and life expectancy to reach DP 979 of Korean traditional Hanji papers (the Annals of King Sejong), errors based on standard deviation

Type of Hanji paper	Beeswax coated		Without beeswax
	No stain	Brown stains	
Year printed	1,473	1,473	1,665
DP	2,031 ± 198	1,457 ± 401	5,536 ± 685
K_t	3.86×10^{-4}	6.22×10^{-4}	7.41×10^{-5}
$K_{t1\ year}$	7.22×10^{-7}	1.16×10^{-6}	2.17×10^{-7}
$K_{1\ day}$	1.98×10^{-9}	3.19×10^{-9}	5.94×10^{-10}
Half-life DP (years)	151 ± 19	100 ± 33	514 ± 147
Life expectancy to reach point of failure (years)[a]	1,272 ± 141		4,212 ± 1,087

[a] Defined as DP 979 based on an aged Hanji paper without mechanical strength, time calculated from the year of printing

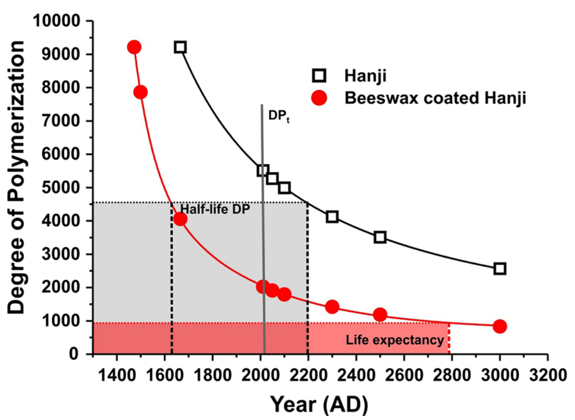

Fig. 6 Illustration of the extrapolated DP, the year to reach the half-life DP and failure point (DP 1,000) of Korean traditional Hanji papers (the Annals of King Sejong) as a function of the natural aging time (years)

Köppen-Geiger climate classification (Kottek 2006), is classified as hot summer continental climate.

Conclusions

First, we have investigated different methods of Hanji paper making. The materials obtained were compared to the virgin bast fibers from paper mulberry tree which serves as raw material for Hanji papers. Hanji papers, obtained from cooking of bast fibers with Korean traditional potash according to historic recipes had not degraded significantly during the whole pulping process. Comparison to well preserved historical papers confirms that they resemble historical Hanji paper. Pulping with sodium hydroxide as a base causes severe degradation and completely different cellulose characteristics. The obtained Hanji paper served as a starting point for an aging study and a comparison to naturally aged Hanji, which is now available to evaluate the life expectancy of paper. Provided there is no serious UV radiation, the dominant pathway for degradation during natural aging of Hanji is hydrolysis.

The half-life DP, i.e. the time until every cellulose chain is split once, and therefore the overall DP is half of the original value was estimated to be 500 years. Hence, the life expectancy to reach a DP of 1,000 is approximately 4,000 years, a time span significantly higher compared to other papers tested (kraft pulp, groundwood pulp, Whatman or rag paper). DP 1,000 was estimated as the point of failure based on analysis of strongly degraded Hanji papers. This result supports superior permanence of Hanji paper and for the first time provides a reasonable base of data. Additional treatments of Hanji paper such as beeswax coating can strongly accelerate paper degradation (Jeong et al. 2014).

In addition, this study also provides a conversion index from accelerated aging to natural aging. The accelerated aging under moist-heat, 80 °C (RH 65 %), for 1 day corresponds to 1.65 years (603 days) under natural aging conditions. This study will be continually updated to other accelerated aging settings.

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