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Posted Date: 11 October 2024

doi: 10.20944/preprints202410.0838.v1

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Research on the Structure and Properties of Traditional Handmade Bamboo Paper during the Ageing Process

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Abstract: Handmade papers, as carriers of paper-based cultural relics, have played a crucial role in the development of human culture, knowledge, and civilization. Understanding the intricate relationship between the structural properties and degradation mechanisms of handmade papers is essential for the conservation of historical documents. In this work, an artificial dry-heat accelerated ageing method was used to investigate the interplay between the mechanical properties of paper, the degree of polymerization (DP) of cellulose, chemical composition, hydrogen bond strength, crystallinity, and degree of hornification. The results show that the mechanical properties of handmade bamboo paper exhibited a first plateau region, a rapid decline region, and sometimes a second plateau region. A critical point in the mechanical properties of the paper occurs when the cellulose DP decreases to a range of 400-600, signifying a shift from the initial plateau to a sharp decline phase. The strengthening of intermolecular hydrogen bonds and the hornification process help counteract the embrittlement of fibers caused by cellulose chain scission due to DP reduction. A secondary plateau emerges when the DP is smaller than 400, cellulose degradation is slow, and the component content, hydrogen bond strength, crystallinity, and degree of hornification reach a secondary plateau.

Keywords: handmade paper; critical DP; H-bond; hornification

1. Introduction

The saying "Paper lasts for a thousand years, while silk endures for eight hundred" highlights the significance of paper as a crucial medium for the transmission and development of human civilization[1]. Traditional Chinese paper, with a history spanning over 2000 years, has played an irreplaceable role in ancient book printing, calligraphy, painting arts, and other cultural relics[2]. The general manufacturing processes of traditional Chinese paper involve steeping, fermenting, washing, steaming, boiling, natural bleaching, pulping, sheet forming, pressing, and drying, employing mild treatment conditions to minimize adverse effects on plant fibers[2,3]. Throughout the long history of Chinese papermaking, papers can be categorized into bark paper, bamboo paper, straw paper, and mixed fiber paper (i.e. *Xuan* paper), each endowed with distinct characteristics. The prominence of bamboo paper in Chinese history can be attributed to several pivotal factors. Bamboo, as a widely distributed natural resource with rapid growth and ease of acquisition, provided a solid raw material

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foundation for papermaking. The craftsmanship of bamboo paper flourished during the Tang and Song dynasties, particularly in the Song dynasty, where it gained dominance due to its cost-effectiveness and favorable texture. Furthermore, bamboo paper's desirable properties, such as flexibility and water absorption, made it popular in calligraphy and printing. Despite its popularity during the Ming and Qing periods, the manual production of bamboo paper reached its peak, being utilized not only for daily writing but also extensively in the restoration and printing of ancient books, as well as in calligraphy and mounting. However, the relatively short fibers and lower cellulose content of bamboo paper make it less durable compared to papers made from other materials like bark, making it more susceptible to degradation and necessitating specialized conservation and restoration efforts[1]. Therefore, studying bamboo paper's ageing behavior and preservation methods is crucial to prolonging the lifespan of ancient books and manuscripts and gaining insights into their conservation and restoration needs.

During the long-term preservation process, paper can degrade due to a combination of internal and external factors. Internal factors include acidic degradation products and excessive alkali reserves within the paper itself, while external factors consist of light, temperature, humidity, air pollutants in the environment, and the presence of inks, pigments, fillers, insects, and microorganisms on the paper[4–7]. To study the degradation of paper, accelerated ageing experiments are always conducted in laboratories due to the slow degradation rate under natural conditions[8]. These experiments involve severe conditions such as elevated temperatures and humidity levels, intense ultraviolet and visible radiation, and significant pollutant concentrations, which expedite the deterioration of paper. Additionally, environmental factors like high levels of air pollution and adverse meteorological conditions have been shown to exacerbate the degradation process of materials, including paper[9]. In order to gain a deeper understanding of the mechanism behind paper deterioration, researchers often use pure cotton/cotton linter cellulose paper and bleached sulphite softwood/hardwood cellulose paper as model papers[10–12]. Ageing causes a reduction in the adsorption and swelling capacity of the paper, leading to a more compact structure, increased crystallinity, and hornification[13]. It was shown that the dynamic changes in paper properties at different temperatures can be accurately described by the Arrhenius formula within a certain temperature range[14].

Handmade bamboo paper holds great importance in traditional papermaking in China, with a rich history and a wide variety of categories. In 2006, the bamboo paper making process was recognized as the first batch of national intangible cultural heritage in China[15]. It also plays a crucial role in archival and ancient book restoration. A survey indicates that some regions in Fujian, Jiangxi, and Zhejiang provinces still produce bamboo paper suitable for archival and ancient book restoration. However, there are also existing problems, such as the lack of emphasis on bamboo paper, a decline in its quality, a disconnect between production, supply, and marketing, and a lack of successors[16].

Researchers have conducted studies on bamboo paper from various perspectives. Compared to the center of the paper pages, the edges of traditional Chinese bamboo paper pages undergo chemical changes through oxidation and photo-ageing effects[17,18]. Ageing experiments conducted for 72 hours at 105℃ in nitrogen, air, and sealed preservation environments reveal that nitrogen storage exhibits the best anti-ageing properties, followed by air storage, while sealed preservation performs the worst. Sealed storage is not ideal as it inhibits the release of the paper's volatile substances. Therefore, it is recommended to use storage equipment that is breathable to allow for air circulation while protecting the documents[19].

In their research on bamboo paper ageing, Chen and Ding have found that handmade bamboo paper with minimal processing is more susceptible to yellowing, while excessive treatment can harm the fibers and impact the thermal stability of the paper[20]. They have also developed a quantitative model based on changes in pyrolysis characteristic temperatures to better evaluate the degree of bamboo paper ageing[21]. Additionally, the pyrolysis characteristics of bamboo paper under various dry heat ageing conditions were studied using thermogravimetric analysis, revealing a deterioration in thermal stability. The difference in pyrolysis characteristic temperatures of bamboo paper, $\Delta T0.5$, was proposed as a parameter to evaluate the degree of bamboo paper ageing, with an exponential

 doi:10.20944/preprints202410.0838.v1

relationship established between ΔT0.5 and the retention rate of the tensile index, leading to the development of a quantitative model for assessing bamboo paper ageing[22].

A comparative analysis was conducted to evaluate the properties of uncooked and cooked bamboo paper, with a specific focus on their dimensional stability and durability-related physicochemical indicators [23]. The study revealed that while uncooked bamboo paper exhibited better dimensional stability, cooked bamboo paper demonstrated superior durability, making it more suitable for meeting the quality requirements of paper used in the restoration of ancient books. Samples of uncooked and cooked bamboo papers were obtained from three paper workshops located in *Jiangle*, *Liancheng*, and *Changting* regions of Fujian province. The results indicated that although uncooked paper displayed improved dimensional stability, its durability was inferior to that of cooked paper, thus rendering it a more suitable material for the restoration of ancient books.

Despite the significance of Chinese handmade papers, the understanding of their degradation kinetics and underlying microscopic mechanisms at molecular and supramolecular levels remains limited. The degradation process of handmade papers is inherently complex, further compounded by the diverse range of raw materials used and the intricate handcrafting techniques employed in Chinese papermaking. This study focuses on traditional bamboo paper derived from bitter bamboo, aiming to investigate its ageing behavior and degradation mechanisms at both molecular and supramolecular levels. The findings of this research endeavor seek to enhance our comprehension of the degradation mechanisms of handmade papers across multiple microscopic scales and establish a scientific foundation for the production of long-lasting handmade papers with improved durability.

2. Results

2.1. Mechanical properties

Research on the ageing and degradation of paper is typically approached from two perspectives. The first perspective involves studying changes in paper properties over time [24,25]. While this approach provides a direct reflection of the changes in mechanical properties, it can be challenging to determine the underlying causes due to the influence of fiber bonding strength and the inherent strength of the fibers themselves. Factors such as the bonding strength and inherent strength of fibers are influenced by a multitude of factors, with the degree of polymerization of cellulose playing a significant role in the mechanical properties of paper [26]. Other studies have directly examined the relationship between the reduction of cellulose's degree of polymerization (DP) and the loss of paper's mechanical properties under various conditions, including temperature, humidity, and acidity [11,14,27]. The loss of mechanical properties serves as an indicator of paper degradation; however, it does not always follow a linear function of cellulose degradation. As the DP of cellulose decreases with ageing, the breaking of molecular chains leads to fiber brittleness, whether through oxidation or hydrolytic degradation mechanisms [28]. Additionally, a critical degree of polymerization for cellulose (DPc~750, Mn) has been identified, beyond which the mechanical properties decrease significantly, irrespective of the type of mechanical testing conducted [24]. This study builds upon new insights into the relationship between cellulose DP and the mechanical properties of paper.

Compared to machine-made paper, handmade paper exhibits less variation in fiber orientation during the papermaking process. However, it is possible to control the water flow and reduce fiber orientation through the vibration of the paper screen in manual papermaking. Nevertheless, the water flow still influences the orientation of fibers in the longitudinal and transverse directions, corresponding to the wire and bamboo patterns of the paper mold [2]. This indicates that handmade paper also displays anisotropy in the transverse and longitudinal directions. In this study, the mechanical properties in different directions are referred to as LD (Longitudinal Direction) and TD (Transverse Direction).

Figure 1 depicts the relationship between the tensile, tear, and folding endurance properties of handmade bamboo paper and its DP. The results reveal several key characteristics. Firstly, unaged handmade bamboo paper is primarily oriented in the longitudinal direction, enabling it to bear and transmit more load in this direction. As a result, it exhibits higher tensile index and folding endurance compared to the transverse direction. Due to the ease with which fibers can be pulled out along the paper's longitudinal direction, while those perpendicular to it hinder this process, the transverse tear index is greater than the longitudinal tear index.

The second characteristic is that the strength properties of the paper exhibit different patterns of decline with a reduction in DP caused by the extension of dry heat ageing time. In the early stages of dry heat accelerated ageing (Figure 1a-e), the mechanical properties of the paper in the longitudinal direction show a nearly plateau period. However, in the middle and later stages of ageing, the tensile index-TD (Figure 1c) and tear index-TD experience a significant decline followed by a second plateau period (Figure 1d and e). On the other hand, the tensile index-LD gradually decreases in the middle stage of ageing without a second plateau period (Figure 1b). The trend of energy absorption index changes is consistent with the tensile index in both the longitudinal and transverse directions (Figure 1f and g).

Similar to the phenomena reported by previous study [28], this work also observed a critical degree of polymerization (DP) for the paper. Initially, when the paper's DP is relatively high, there is a plateau period in the paper's properties. At this stage, cellulose degradation does not necessarily result in a loss of mechanical properties [29,30]. However, the mechanical properties of the paper decline after surpassing this critical DP. The DPc for the paper's tensile properties and energy absorption index is estimated to be between 450 and 500 (Figure 1f and g), while for tearing performance, it is approximately between 500 and 600 (Figure 1d and e). Therefore, it can be inferred that the critical DPc for the plateau and decline periods in this study falls within the range of 450 to 600. This differs slightly from the previously reported Mn-750 [28], possibly due to the use of DP obtained from the viscosity-average molecular weight in this study, as well as variations in the raw material content for handmade paper, which lead to different degradation processes and consequently affect the critical degree of polymerization.

One consequence of cellulose polymer chain degradation, as the primary component of paper fibers, is an increase in paper brittleness during ageing. This property could be assessed through folding endurance, expressed as the number of double folds [27]. The folding endurance in the longitudinal direction (folding endurance-LD) exhibits a slight decline in the early stages of ageing, with the DPc appearing at 500, after which a significant decline is observed (Figure 1a), consistent with previous findings [24]. On the other hand, the change in folding endurance in the transverse direction (folding endurance-TD) is not significant, remaining below 10 overall and dropping to 0 once the DP falls below 600. The folding endurance-TD is lower than 10 due to the paper's thinness and weaker transverse binding force, coupled with the decrease in fiber strength. In the longitudinal direction, where fibers have certain bonds, the folding endurance-LD gradually decreases along with the weakening of fiber strength. It sharply declines once the DP exceeds 500 and completely disappears when the DP falls below 350. The decline in folding endurance is mainly influenced by fiber brittleness caused by oxidation and cross-linking in the initial stage of ageing [26]. It is evident that oxidative degradation dominates due to the significant decline in DP [28], leading to the speculation that fiber embrittlement may play a more significant role in the first plateau region than the deterioration of fiber-fiber bonds. However, this research suggests that although fiber degradation results in brittleness during the initial plateau phase, there is a notable reduction in the degree of polymerization (DP). Interestingly, this brittleness does not significantly impair the mechanical properties of the paper. This resilience is likely attributed to the predominant influence of fiber bonding. Nevertheless, obtaining conclusive evidence of cross-linking remains a challenge.

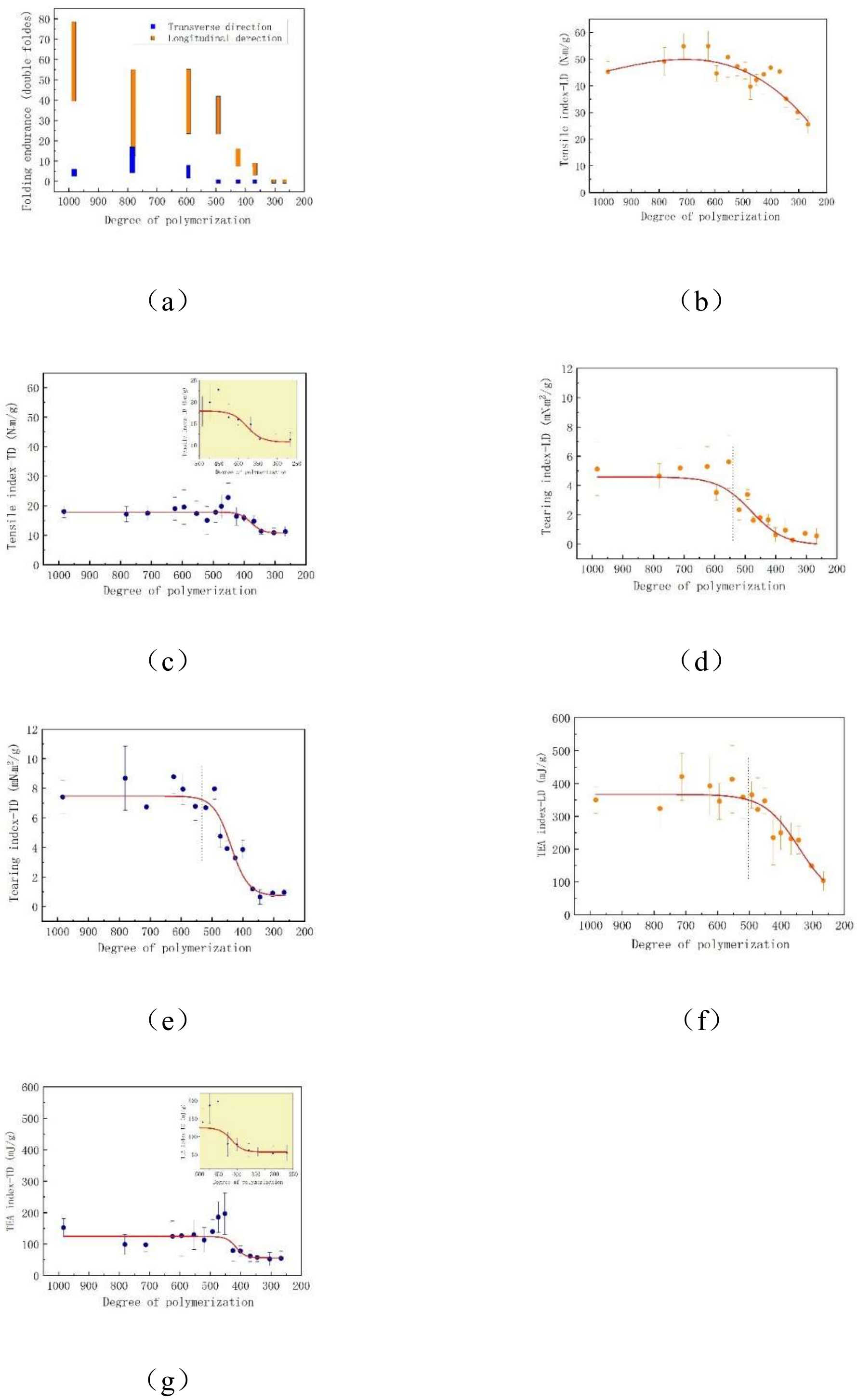

Figure 1. Evolution of mechanical properties with the decrease of degree of polymerization, as measured by folding, tearing and tensile tests for the bamboo paper in the longitudinal and transverse directions under 105 ℃ accelerated dry heating treatment. LD-Longitudinal Direction and TD-Transverse Direction. The vertical dot line indicates the value of critical DP.

2.2. DP and Component Contents

The degree of polymerization (DP) is a crucial factor in evaluating the performance and longevity of paper [1,31,32]. Accelerated dry heat ageing can significantly decrease the DP of cellulose in paper, a process typically divided into three stages (Figure 2a). The initial stage occurs within 30 days, during which the DP of the paper decreases by nearly 40%. Subsequently, as ageing progresses to 50 days, the DP further drops by 10% to around 500. While the DP continues to decline in this phase, the rate slows down. The sharp decline in DP results in extensive breakage of cellulose molecular chains, a decrease in fiber strength, and a notable reduction in folding endurance. However, it may not impact the bonding strength between fibers, thus maintaining tensile and tear strength, corresponding to the first plateau region. From 50 days onwards, as the paper continues ageing up to 200 days, the DP decreases at a slower rate. Research has indicated that cotton fibers take approximately 850 days for the DP to decrease from 300 to 280, suggesting a slow decrease in molecular weight in the later stages of cellulose degradation[24]. Throughout the ageing process from 50 to 200 days, there is a significant decline in the mechanical properties of the paper but a slow degradation of cellulose.

It is often overlooked that during the ageing process, the composition of the main components in the paper, namely cellulose, hemicellulose, and lignin, undergoes constant changes. As depicted in Figure 2b, the lignin content shows a gradual slight downward trend, particularly in the later stages of ageing, where the content remains relatively stable when the DP is below 600. It is widely acknowledged that lignin negatively impacts paper durability [11]. The prevailing view has been that lignin accelerates the ageing of paper produced in acidic environments, with conservators attributing the yellowing of papers to high lignin content [33]. Recent studies have indicated that the lignin content does not affect the ageing rate of paper produced at a neutral pH [34]. This is likely due to the crosslinking between lignin and carbohydrate effectively preventing the formation of hydrogen bonding in the fibers, both internally and externally, and reducing irreversible hornification [35].

It is important to note that the cellulose and hemicellulose content exhibits a similar trend to mechanical properties when comparing Figure 1 with Figure 2. In Figure 2b, a clear plateau region is evident for the cellulose and hemicellulose content before the degree of polymerization exceeds 600, with a slight downward trend. Between a degree of polymerization of 400 and 600, a significant decrease is observed. Specifically, the cellulose content decreases from 60% to 50%, and the hemicellulose content drops from 18% to 12%. Once the DP falls below 400, the cellulose decrease rate slows down, while hemicellulose shows a plateau. Additionally, the paper's pH value declines gradually from an initial 7.25 to 6.8 when the degree of polymerization is above 600. Subsequently, as the cellulose DP and content decrease, the pH value exhibits a linear downward trend (Figure 2c). The decrease in hemicellulose content indicates ongoing degradation, likely contributing to the pH value decrease. Figure 2b illustrates that cellulose and hemicellulose are the main components undergoing degradation, leading to an increase in acidic degradation products. This accelerates autocatalytic hydrolysis and increases the number of chromophoric groups, such as double bonds, in the degradation products, gradually altering the paper's color (Figure 2c). During natural ageing, paper undergoes color changes and becomes brittle primarily due to cellulose degradation, the primary component of paper fibers [26]. Although lignin content does not decrease significantly, it may play a role in these processes through changes in its functional groups. Understanding how the slowly changing cellulose, hemicellulose, and lignin content maintains mechanical stability when the DP exceeds 600, i.e., the first plateau region, warrants further investigation.

However, there is limited literature explaining the critical degree of polymerization (DPc) for cellulose [28]. This polymerization threshold is observed in traditional semi-crystalline polymers [36], ensuring a minimum amorphous phase thickness that influences the plastic deformation mechanism. The complexity of cellulose's microstructure adds to this issue [28,36]. The appearance of this plateau period seems uncommon in ageing studies of pure cellulose samples but emerges when the DP reaches a certain value and the paper includes other components [29].

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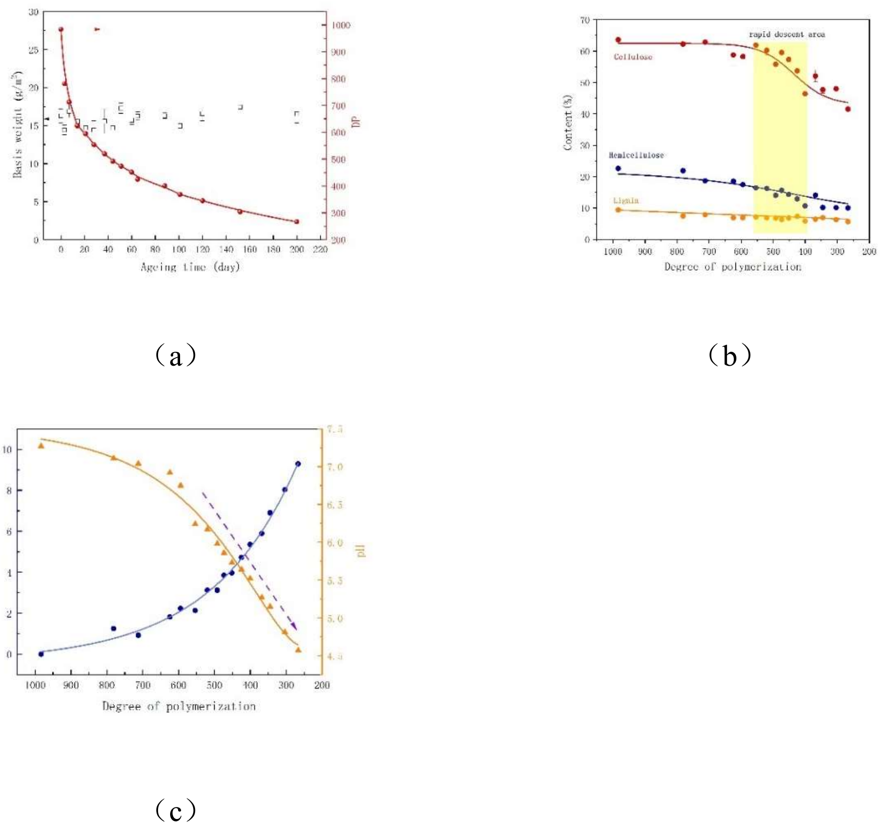

Figure 1. Variation of basic weight and DP as a function of ageing time for bamboo paper(a); variation of chemical composition (b) and △E-pH (c) with the decrease DP under 105 ℃ accelerated dry heating treatment.

2.3. Microstructures

The primary constituent of Chinese handmade paper is cellulose, which is a polymer consisting of linear chains of hundreds to thousands of D-glucose units linked by β-(1,4)-glycosidic bonds [37,38]. The hydroxyl groups present in cellulose participate in numerous intra- and intermolecular hydrogen bonds, resulting in various ordered crystalline arrangements [39]. These hydrogen bonds play a crucial role in the mechanical properties of paper by forming inter-fiber connections through interactions between the hydroxyl (-OH) groups in cellulose molecules [40]. The strength and quantity of hydrogen bonds can impact the interlayer spacing and elastic modulus of paper. Moreover, the presence of hydrogen bonds provides paper with a self-healing capability, as these bonds can dynamically reform under certain conditions, repairing the microstructure of the paper. Some studies suggest that cellulose degradation at the supramolecular level leads to changes in the intensity of hydrogen bonds and the crystallinity of cellulose macromolecules [41,42].

Figure 3 depicts the alterations in hydrogen bond lengths and energies between and within cellulose molecules during the paper ageing process. As shown in Figures 3a and b, both intramolecular and intermolecular hydrogen bond energies increase throughout the ageing process, with intermolecular hydrogen bonds displaying a more pronounced change. In the initial 40 days of ageing, the bond length of intermolecular hydrogen bonds gradually decreases, indicating a potential movement of cellulose molecular chains towards each other. Subsequently, the bond length increases and stabilizes, fluctuating within a narrow range until day 200. The decrease in intramolecular hydrogen bond length and increase in bond energy suggest possible contraction or distortion of cellulose molecular chains due to prolonged dry heat treatment. Conversely, the intermolecular hydrogen bonds exhibit a significant decline followed by recovery, suggesting a potential rearrangement process of hydrogen bonds [43] that accompanies the decrease in paper cellulose DP.

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In the first plateau region of paper mechanical properties, despite the sharp decrease in DP, the increased hydrogen bond energy may strengthen the bonding between fibers, thereby mitigating the decay of mechanical properties. In other words, while the cellulose molecular chains may experience breakage and make the fibers brittle, the enhanced strength of hydrogen bonds within the internal fiber network of the paper reinforces the binding between fibers and may lead to irreversible hornification.

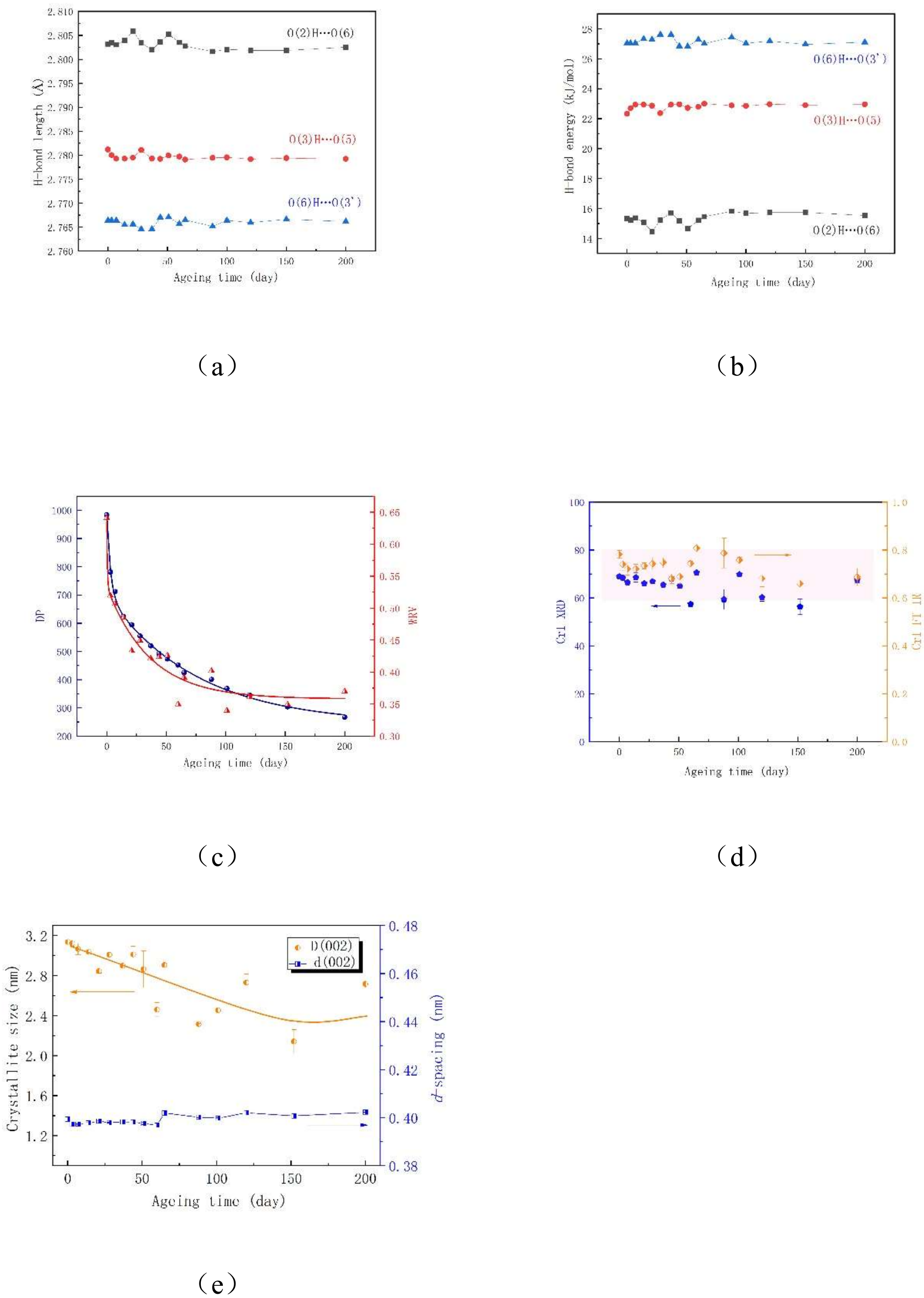

Figure 3. Variation of H-bond length (a), H-bond energy (b), DP and WRV (c), CrI-XRD and CrI-FTIR (d), crystallite size and d-spacing (e) as a function of ageing time for bamboo paper.

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Hornification refers to the irreversible changes that occur in paper during the water removal process, either at room temperature or high temperatures. These changes result in alterations in the paper's water absorption behavior, including reduced flexibility, decreased water retention capacity, and increased brittleness [13,44]. This phenomenon is attributed to the formation of irreversible hydrogen bonds between microfibrils within the fibers, which are typically associated with the durability and stability of paper. The water retention value (WRV) serves as a significant indicator of fiber hornification in paper. The findings presented in Figure 3c demonstrate that, similar to DP, the change in WRV can be divided into three stages. However, when DP > 600, there is a clear overall correlation with WRV, which gradually decreases as DP decreases. After 50 days of ageing, DP experiences a slow decline, while WRV exhibits a relatively stable fluctuation trend. Thus, it can be inferred that hornification displays an initial increasing trend followed by a leveling off throughout the entire ageing process.

During the hornification process, the formation of hydrogen bonds between cellulose molecular chains plays a central role. These hydrogen bonds, which are formed by free hydroxyl groups, create strong bonds within the fibers that are, to some extent, irreversible. The resulting multiple hydrogen bond structures are highly stable and not easily disrupted [45]. Additionally, the formation of ester bridges between cellulose molecular chains, which are covalent bonds and irreversible in water, contributes to hornification [46]. These various mechanisms may all contribute to the hornification process and potentially interact with each other. For instance, functional groups within the cellulose chains may engage in hydrogen bonds, ester bonds, ether bonds, and other types of bonding interactions. Recent research findings also confirm that while hydrogen bonds play a crucial role in hornification, they are not the sole influencing factor. It is important to note that hornification is not entirely detrimental. This study suggests that moderate hornification can by strengthened by the hydrogen bonds between cellulose molecules, thereby enhancing the binding between fibers and helping to preserve the mechanical properties of paper, preventing a sharp decline in the initial stage.

Cellulose co-crystallization, which involves hydrogen bonds, hydrophobic interactions, and van der Waals forces within the fibers, was not observed. Studies have shown that lignin and hemicellulose inhibit the hornification of paper cellulose, preventing the enlargement of crystalline particles and the aggregation of cellulose microfibrils [47]. However, hemicellulose and lignin may contribute to bonding and maintaining the stability of the fiber structure, despite the decrease in cellulose DP. Xylan and glucomannan are important types of hemicellulose that have been found to reduce hornification [48,49]. Additionally, hemicellulose and lignin provide structural support to the fibers. During dry heat ageing, the fibers gradually shrink from their initial cylindrical shape, with significant collapse and surface wrinkles observed by day 28 (Figure 4 a-b). Subsequently, the shrinkage slows down, but the overall fiber morphology remains stable (Figure 4 c-f). Most fiber shrinkage is likely to occur within the first few hours of the drying process[48], which aligns with the trend reflected by the Water Retention Value (WRV). As the fiber structure contracts during the early stages of ageing, water absorption decreases. Once a certain level of contraction is reached, the fiber morphology remains almost unchanged, while water absorption performance undergoes irreversible hornification.

Research has also indicated a correlation between mechanical properties and crystalline structure during paper ageing [17,50]. The supramolecular structure of cellulose affects the degradation of the cellulose molecular structure, with a higher supramolecular order hindering degradation [42,51]. The changes in paper crystallinity over time during ageing are shown in Figure 3d. The infrared OKI crystallinity index demonstrates a significant decrease in the first 3 days, followed by a stable period (3-40 days), an increase, and then a decrease after 100 days, eventually leveling off within a certain range. XRD results show an initially stable period, followed by regular fluctuations after 50 days. The main interplanar distances, especially for the 002 plane, remain generally stable. However, the crystal grain size gradually decreases from 8 layers to 5-7 layers in the later stages (Figure 3e). This change is likely attributed to the hornification effect caused by cellulose microfibrils during the drying process. In the later stages of paper ageing, although thermal ageing leads to fiber contraction or collapse, the amorphous regions of cellulose may have degraded

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significantly. Nevertheless, the barrier formed by hemicellulose and lignin effectively supports and isolates the crystalline regions of cellulose, resulting in stabilized hydrogen bond lengths and energy changes. This hornification effect plays a crucial protective role in the final plateau stage of paper ageing, maintaining certain properties of the paper despite significant decreases in polymerization degree (DP) and increased fiber brittleness.

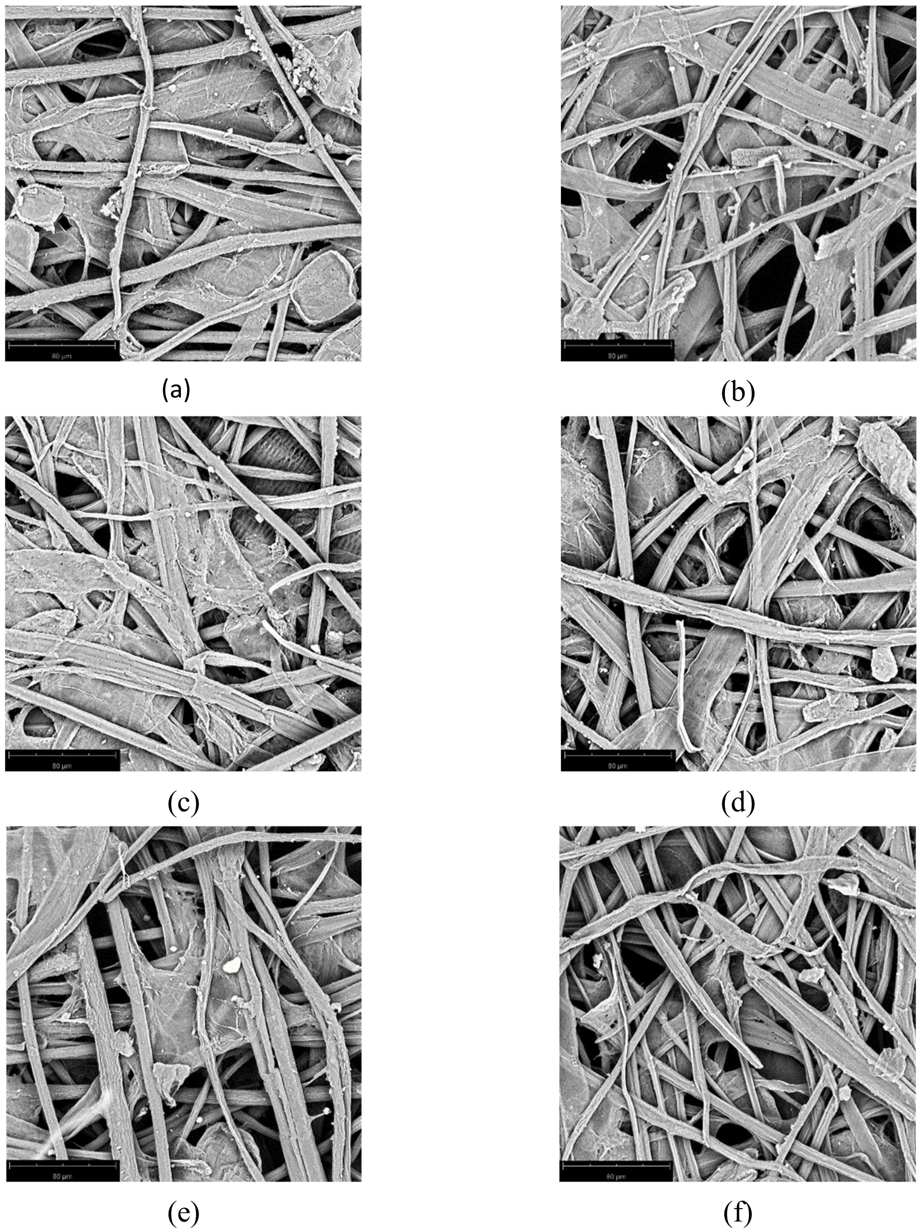

Figure 4. Morphological changes of bamboo paper during accelerated ageing (a)0D, (b)28D, (c)50D, (d)100D, (e)150D, (f)200D.

3. Materials and Methods

3.1. Materials

The bamboo paper used in this study is made from bitter bamboo, crafted by hand using traditional craftsmanship. According to the "*Fenghua* City Chronicles," *Tang'ao* bamboo paper was first recorded in historical books in the ninth year of the *Zhengde* period of the Ming Dynasty (1514

 doi:10.20944/preprints202410.0838.v1

AD), and it has a history of nearly 500 years. It can be used for the restoration of ancient books, with a thickness of 0.08mm.

Copper ethylenediamine (CED) solution (Bis(ethylenediamine)copper(II) hydroxide solution (1 M in H_2O) was purchased from Sigma-Aldrich.

3.2. Accelerated Ageing

The handmade papers were artificially aged at 105 ℃ for 200 days. Sample collection is carried out according to the predetermined number of ageing days. Sampling intervals are shorter in the early stages of ageing and longer in the later stages.

3.3 Analysis of Chemical Components

The standard method of the United States Department of Energy was applied to quantitatively analyze cellulose, hemicellulose and lignin in materials. The types and content of sugars in the hydrolyzed products were determined by HPLC.

3.4. Viscosity Determination

The DP value of paper cellulose was measured. using the viscosity method according to the report[1]. Paper samples were weighed and added into a plastic bottle with10 mL of deionized water. After shaking for 30 min, 10 mL of CED (1 M in H_2O)solution was added. The plastic bottle was shaken evenly for 1 h at 25 ℃ until the paper specimen was dissolved completely. Then the obtained solutions were transferred into a capillary viscometer, and the time of solution declining from the top to the bottom was recorded. Martin empirical equation was used to calculate the DP of paper samples (Eq. 1-3).

$$\eta_r = h_n * t_n \quad (1)$$

$$[\eta] = \eta_r / \rho \quad (2)$$

$$DP^{0.905} = 0.75[\eta] \quad (3)$$

where η_r is the relative viscosity of paper cellulose; h_n is the constant of viscosimeter (0.0703 s^{-1}); t_n is the recorded time (s); $[\eta]$ is the intrinsic viscosity of paper cellulose; ρ is the concentration of paper solution (g mL^{-1}).

3.5. Mechanical Properties Tests

The tensile strength was measured according to GB/T 12914-2008 at a constant elongation rate of 20 mm/min by a tensile strength tester (ZB-WLQ, Hangzhou Zhibang Automation Technology Co., Ltd., Hangzhou, China). The folding endurance was measured according to GB/T 475-2008 by an MIT folding endurance tester (ZB-NZ135A, Hangzhou Zhibang Automation Technology Co., Ltd., Hangzhou, China). The tearing strength was performed according to GB/T 455-2002 by a tearing strength tester (ZB-SL, Hangzhou Zhibang Automation Technology Co., Ltd., Hangzhou, China).

3.6. Infrared Analysis

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectrum of paper sample was taken on Spectrum Two Spectrometer (PerkinElmer) equipped with a diamond ATR detector. The scan scope was 4000-400 cm^{-1}. The original spectra were calibrated to eliminate the effect of radiation wavelength on the intensities of absorption bands.

The hydrogen bond energy (E_H) was calculated by Eq.4[52].

$$E_H = \frac{1}{k}\left[\frac{v_0 - v}{v_0}\right] \quad (4)$$

where 1/k = 2.625 × 10^2 kJ, v_0 is the frequency of standard free hydroxyl group (3650 cm^{-1}), and v is the frequency of the hydroxyl group calculated.

The hydrogen bond length (R) was calculated by the Sederholm equation (Eq. 5).

$$v_0 - v = 4.43 \times 10^3 (2.84 - R) \quad (5)$$

where v_0 is the stretching vibration frequency of single hydroxyl group (3600 cm^{-1}), and v is the frequency of the hydroxyl group calculated.

3.7 Water Retention Value Measurement

The water retention value of the sample is tested as follows: 2g of the sample is immersed in distilled water for 3h, then removed and placed within the water retention value tester to centrifuge for 30 minutes. The weight of the sample post-centrifugation, denoted as M_1. After that, the sample is transferred into an oven and dried at 105 °C for 4 hours. After cooling, the weight of the sample, M_2, is measured, and the formula for calculating water retention value is as follows:

$$WRV = \frac{M_1 - M_2}{M_2} \quad (6)$$

3.8 Chromaticity test

The chromaticity of the paper was determined with an automatic colorimeter. To ensure accuracy and minimize potential errors, each sample was measured six times at different locations. The change in chromaticity △E was calculated via the following equation:

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (7)$$

where, L, a and b represent three different colorimetric coordinates values, respectively. △L, △a and △b are the differences between corresponding values of different samples.

3.9 X-ray Diffraction measurement

The X-rays from a Cu tube operating at 30 kV and 10 mA were collected by the energy dispersive detector that is able to resolve the Cu-Kα line (λ=0.154184 nm). The X-ray source was a copper target bombarded with electrons. Scans were obtained from 5 to 40° 2θ using a step size of 0.05°.

To calculate the CrI of cellulose from the XRD spectra. CrI was calculated from the height ratio between the intensity of the crystalline peak and total intensity as the following equation:

$$CrI = \frac{I_{200} - I_{AM}}{I_{200}} \times 100\% \quad (8)$$

where I_{200} and I_{AM} are the scattering intensities from the diffraction intensity of (200) lattice plane and the height of the minimum value between the (200) and the (110) peaks, respectively.

The *d*-spacing were calculated using the Bragg's Equation [9] and the crystallite sizes were calculated using the Scherrer Equation [10]:

$$n\lambda = 2dsin\theta \quad (9)$$

$$L = 0.9\lambda/(\beta sin\theta) \quad (10)$$

where n is an integer; λ is the wavelength of incident wave length; d is the spacing between the planes in the atomic lattice; θ is the angle between the incident ray and the scattering planes; L is the crystallite size perpendicular to the plane and β is the full width at half-maximum (FWHM) in radians.

4. Conclusions

This study delves into the structural and performance alterations of traditional Chinese bamboo paper during the process of dry heat ageing degradation. The research reveals that the degree of polymerization (DP) of cellulose experiences an initial sharp decline followed by a gradual slowing down throughout the ageing process. Concurrently, the mechanical properties of the paper, including tensile strength, tear resistance, and folding endurance, display an initial plateau phase followed by a subsequent decline, with some properties exhibiting a second plateau phase in the later stages of degradation. The content variations of cellulose, hemicellulose, and lignin in the paper occur

 doi:10.20944/preprints202410.0838.v1

in tandem, with lignin content remaining relatively stable while cellulose and hemicellulose content decreases, aligning with the decline in mechanical properties. A critical performance threshold is observed when the DP ranges from 400 to 600, marking a shift from a balanced or slightly decreasing trend in the initial plateau phase to a sharp decline. The rapid decrease in cellulose DP in the first plateau phase does not immediately result in a proportional decline in mechanical strength. Despite the reduction in DP suggesting the weakening of cellulose chains and inherent fiber strength, mechanical performance is offset by the shortening of intermolecular hydrogen bonds, increased bond energy, and resultant irreversible hornification. Beyond the critical DP point, the continuous brittleness stemming from reduced DP and cellulose/hemicellulose content exerts a more significant influence on mechanical properties than hydrogen bonds and hornification, leading to a rapid decline. Subsequently, a second plateau phase emerges when the DP is lower, cellulose degradation slows down, and the content of components, strength of hydrogen bonds, crystallinity, and hornification degree stabilize. While there are limitations in the study, obtaining detailed insights into hydrogen bond rearrangements and chemical group bonding would enhance explanations from a chemical structural perspective, providing a deeper comprehension of the bamboo paper degradation mechanism. Nevertheless, this research explores the structural and performance changes of traditional Chinese bamboo paper during dry heat ageing degradation, offering valuable insights for traditional papermaking practices and the preservation of ancient books.

Author Contributions: Conceptualization, X.J. and P.L.; methodology, Z.Z., K.Z., Y.W., Y.Z., P.L.; validation, Z.Z., K.Z., Y.X. Z.L.; formal analysis, X.J.; investigation, Z.Z., K.Z., Y.X., Z.L., Y.W.,Y.Z., X.J. and P.L.; resources, X.J. and P.L.; data curation, Z.Z., K.Z. Y.W.; writing—original draft preparation, Z.Z., K.Z.; writing—review and editing, Z.Z., K.Z., X.J. and P.L.; All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Foundation of Shanghai, China (21ZR1405100), Foundation of State Key Laboratory of Biobased Material and Green Papermaking, Qilu University of Technology, Shandong Academy of Sciences, China (GZKF202210), Humanities and Social Sciences Foundation of the Ministry of Education of China (21YJCZH089).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.
Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflicts of interest.

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