

Reinforcement of Paper Documents by Different Starch Modification Processes

Jing Lang *

Paper documents gradually deteriorate during long-term storage, accompanied by acidification and a decline in mechanical strength. To achieve both deacidification and mechanical strengthening, sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) was used as a deacidification agent, and two starch products (enzymatically hydrolyzed starch, quaternary ammonium cationic starch) served as strengthening agents. The documents were treated either by simultaneous deacidification and reinforcement (one-step method), or deacidification followed by reinforcement (two-step method). The effects of different reinforcement treatments on the mechanical properties and pH of the paper were investigated. Accelerated aging tests (dry and wet aging tests) were conducted to evaluate the change of the mechanical performance of paper documents under optimal reinforcement conditions. Deacidification and reinforcement treatments improved the tensile index, tearing index, and folding endurance. The type of starch modification and the different deacidification and reinforcement processes influenced the mechanical strength. The surface pH values of paper documents only modified with different starches remained below 7.0. Accelerated aging tests on paper treated with different starches (both deacidified and reinforced) revealed that under high temperature and humidity conditions, the mechanical properties of paper documents deteriorated more severely. The treated paper exhibited varying degrees of relative improvement in tensile index, tearing index, and folding endurance.

DOI: 10.15376/biores.20.4.8883-8898

Keywords: Paper documents; Reinforcement; Deacidification; Starch; Aging

Contact information: Tianjin University of Science and Technology, Tianjin 300222, China;

**Corresponding authors:* langjing@tust.edu.cn

INTRODUCTION

Paper documents, through various forms such as text and images, record the developmental trajectory of human society and showcase the ideological, cultural, and artistic achievements of different eras. The preservation and research of paper documents have made indelible contributions to the advancement of human society and the development of science and technology. However, the aging of paper documents is an irreversible process over time. Microscopically, this manifests itself as chemical structural changes in the main components of paper, while macroscopically, it appears as yellowing, brittleness, insect damage, fragmentation, and wear (Zhang 2020; Wang 2021; Huang 2022). The aging of paper documents stems from the inherent complexity of paper as a biomass material. Its internal hybrid system and diverse external storage environments can both contribute to aging, which typically results from synergistic interactions between internal and external factors (Fan *et al.* 2020; Zhang 2021a).

The intrinsic factors of paper aging primarily include its composition, papermaking processes, binding materials, and writing media. The main components of paper are cellulose, hemicellulose, and lignin. Cellulose, the predominant component, constitutes the fundamental chemical structure of paper. Under acidic or strongly alkaline environments, high temperatures, oxidizers, ultraviolet radiation, or microbial activity, the 1,4- β -glycosidic bonds in cellulose macromolecules become highly unstable, prone to hydrolysis and oxidation, which would lead to bond cleavage and the formation of ketone, aldehyde, and carboxyl groups, weakening fiber strength and inter-fiber bonding, thereby reducing paper strength (Zhang and Fang 2011; Zhou 2023). Hemicellulose, with lower polymerization degree, chemical stability, and thermal stability compared with cellulose, features more branched structures and higher hygroscopicity, making it more susceptible to acid degradation and oxidations, which would reduce paper strength and generate chromophores such as carbonyl groups. Higher hemicellulose content could accelerate catalytic degradation, diminishing water resistance, mechanical properties, and durability (Yang *et al.* 2013; Yu *et al.* 2020). Lignin side chains contain numerous active groups that oxidize easily to form chromophores, causing paper yellowing (He *et al.* 2019), particularly under higher temperature and humidity conditions that accelerate aging (Małachowska *et al.* 2020). Additionally, acidic sizing agents and precipitants added during papermaking to enhance resistance to water may promote acidic hydrolysis of cellulose and hemicellulose, compromising paper performance (Carter 1996). Bleaching agents such as hydrogen peroxide and sodium hypochlorite used to adjust paper whiteness (Arnold 1997), along with inks and pigments containing acidic substances, transition metal ions ($\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^{+}/\text{Cu}^{2+}$, Mn^{2+}), and oxidizing agents, can catalyze cellulose oxidation through free radical mechanisms, leading to acidification, oxidation, and reduced durability (Simon *et al.* 2007). Paper documents made through acidic sizing processes are more prone to acidification during storage. The acidic sizing process typically uses rosin as the sizing agent and aluminum sulfate as the precipitating agent, respectively. Among them, the aluminum ions in aluminum sulfate are regarded as the source of protons for proton-catalyzed hydrolysis of cellulose, which is because the aluminum ion center has the shortest atomic radius, when present, it can accelerate the hydrolysis of β -1,4 glycosidic bonds; therefore, aluminum ions also act as a catalyst that accelerates cellulose degradation (Baty and Sinnott 2005).

External environmental factors including temperature, humidity, acidic gases, light, microorganisms, and pollutants significantly contribute to paper aging (Zhang *et al.* 2015). Research shows that temperature elevation within certain ranges could accelerate microbial growth and chemical reaction rates between paper components, resulting in brittleness, rigidity, and reduced flexibility and mechanical strength (Feng 2020). Higher humidity (70 to 85%) could disrupt hydrogen bonds between fibers, generate free hydroxyl groups through water absorption and swelling, weaken fiber bonding, and promote microbial growth that could secrete organic acids to accelerate acidification (Wang *et al.* 2012). Conversely, lower humidity could cause dehydration-induced curling and embrittlement (Wu 2015). Light exposure could impact aging through radiation heat, photo-oxidation, and photodegradation (Xu and An 2005). Higher energy UV radiation could break hydrogen bonds and molecular chains (C-C, C-O bonds), reduce polymerization degree, and catalyze lignin oxidation to produce chromophores (Adamo and Magaudda 2003). Paper's organic content could attract insects that physically damage documents and leave harmful residues (Zhang 2021b). Microorganisms (molds, bacteria) secrete cellulases to decompose cellulose/hemicellulose and acidic byproducts that accelerate hydrolysis (Ma

et al. 2020). Moreover, paper's porous structure absorbs airborne pollutants (SO₂, H₂S, O₃, Cl₂, particulates, *etc.*), which could react with moisture to generate acids that hydrolyze cellulose and degrade mechanical properties (Hubbe *et al.* 2017).

Extensive studies have indicated acidification as the primary cause of paper deterioration. To mitigate aging, deacidification neutralizes free acids through alkaline solutions while maintaining alkaline reserves to prevent β -1,4-glycosidic bond hydrolysis and ensure sustained acid resistance (Ipert *et al.* 2006; Li 2019). The traditional deacidification technologies in museums mainly includes two deacidification systems: aqueous-phase, and organic-phase (Baty *et al.* 2010; Huang *et al.* 2018; Amornkitbamrung *et al.* 2020; Wang 2023b). With in-depth research on the conservation methods of paper documents, an increasing number of deacidifying agents and deacidification treatment methods have emerged. More new technologies have been developed for the deacidification of paper documents, such as plasma technology and supercritical fluid technology, and they have gradually shown application potential (Zhou 2023). However, deacidification alone cannot address brittleness and low strength in aged paper, necessitating subsequent reinforcement. Therefore, paper documents also need to be reinforced and restored. The reinforcement methods for paper documents are mainly divided into physical reinforcement and chemical reinforcement. The physical reinforcement method is generally mounting reinforcement, that is, using lining paper with paste to cover the surface of the paper to be repaired, but this method is labor-intensive. Most of the chemical reinforcement methods use reinforcing agents to treat the paper, endowing paper documents with better strength performance.

Current reinforcement research is mainly focused on the reinforcement materials including natural polymers, synthetic polymers, and their composites. Among them, cellulose, chitosan, starch, *etc.*, with the characteristics of green, safe, and good aging resistance, have been studied for the reinforcement of paper documents (Völkel *et al.* 2017; Zhang 2020; Wang 2023a; Hubbe *et al.* 2023). However, cellulose and chitosan are insoluble in water, and the viscosity of the reinforcing solution prepared from them is generally high, which leads to poor penetration effect inside the paper and affects the reinforcing effect. Therefore, it is generally necessary to select special solvents or carry out modification before reinforcement. Starch-based reinforcing agents have demonstrated unique advantages due to their structural similarity to soluble cellulose derivatives, such as carboxymethyl cellulose, ethyl cellulose, and hydroxypropyl cellulose, but much more cost-effectiveness (Zhou 2023). Xu (2011) developed starch-grafted butyl acrylate/trifluoroethyl methacrylate solutions that improved tensile strength with minimal degradation after aging. Chen *et al.* (2020) modified wheat starch with ammonium zirconium carbonate to create pH-enhanced agents with improved mildew resistance and strength. To address high viscosity limitations, Zhou (2023) employed α -amylase hydrolysis to reduce molecular weight, enhancing starch penetration. Moreover, he found that combined with modified polyethyleneimine (PEI) crosslinkers, the modified starch could improve reinforcement effectiveness, aging resistance, and mildew prevention for paper documents.

This study investigated the effects of different starches including wheat starch, α -amylase hydrolyzed starch, and quaternary ammonium cationic starch, as well as different deacidification and / or reinforcement treatments on the mechanical properties, surface pH values, and aging resistance, aiming to identify optimal starch types and treatment process for paper conservation, thereby providing technical support for paper document preservation.

EXPERIMENTAL

Materials

The paper documents used for the experiment were sourced from the October 1951 Selected Works of Mao Zedong, representing naturally aged paper documents preserved under natural conditions. Prior to treatment, the paper samples were uniformly cut into dimensions of 13 cm × 20 cm and placed in a vacuum drying oven. They were dried at 35 °C for 24 h until completely dry.

Wheat starch (food-grade, molecular weight approximately 570,000) was purchased from Guangzhou Shengtong Trading Co., Ltd. α -Amylase (Bacillus subtilis source, biological reagent, 4000 units/g) was procured from Shanghai Yuanye Bio-Technology Co., Ltd. α -Amylase hydrolyzed starch was prepared according to the research of Zhou (2023), and the molecular weight was approximately 260,000. Quaternary ammonium cationic starch (degree of substitution 0.05 ± 0.01) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd.

Paper Document Treatments

As shown in Table 1, paper documents were subjected to deacidification (Lin *et al.* 2017), reinforcement (Lin *et al.* 2017; Zhou 2023) or the combination of deacidification and reinforcement (Lin *et al.* 2017; Zhou 2023), respectively. The specific experimental conditions were divided into nine groups: T0 to T8, and T0 without any treatment as the control group. The specific experimental methods and groupings are detailed in the following description.

Table 1. Treatment Conditions for Paper Documents

Test group	Deacidifier	Reinforcing agent	Process
T0	--	--	--
T1	Sodium tetraborate	--	Deacidification
T2	--	Wheat starch	Reinforcement
T3	--	Enzymatically hydrolyzed starch	Reinforcement
T4	Sodium tetraborate	Enzymatically hydrolyzed starch	One-step for deacidification and reinforcement
T5	Sodium tetraborate	Enzymatically hydrolyzed starch	Two-steps for deacidification and reinforcement
T6	--	Quaternary ammonium type cationic starch	Reinforcement
T7	Sodium tetraborate	Quaternary ammonium type cationic starch	One-step for deacidification and reinforcement
T8	Sodium tetraborate	Quaternary ammonium type cationic starch	Two-steps for deacidification and reinforcement

Note: -- indicates without treatment.

Deacidification treatment (T1)

The mass of sodium tetraborate (deacidifying agent) was calculated based on a ratio of 0.2 mol per 1 g of paper documents. The sodium tetraborate was dissolved in 500 mL

of an ethanol-water solution (ethanol-to-water ratio of 1:1, v/v) maintained at a constant temperature of 60 °C. The paper was immersed in the sodium tetraborate solution for deacidification. After 60 min of immersion, the paper was removed and placed in a climate-controlled environment at 23 °C and 50% relative humidity for 24 h (Lin *et al.* 2017; Zhou 2023). Subsequently, the paper was subjected to testing and analysis.

Reinforcement treatment (T2, T3, T6)

A total of 10 g each of wheat starch, α -amylase hydrolyzed starch, and cationic etherified starch (absolute dry mass) were weighed and dissolved in 190 g of deionized water. The mixture was magnetically stirred at 95 °C for 15 min to prepare a 5% mass fraction starch paste. The paste was continuously stirred at 70 °C until homogenized. The paper was laid flat on a clean and smooth surface. According to the results of preliminary experiments, a pipette was used to apply the basis weight of 54.5 g/m² of the starch paste onto the paper surface, which was then immediately spread evenly using a wire-wound rod coater. The treated paper was air-dried at room temperature, pressed flat with a book press, and subsequently placed in a climate-controlled chamber (24 °C, 50% relative humidity) for 24 h to equilibrate moisture content.

Deacidification and reinforcement treatment (T4, T5, T7, T8)

The deacidification and reinforcement treatment of paper involved two distinct processes: one-step process (T4, T7) and two-step process (T5, T8). In the one-step process, the deacidifying agent (sodium tetraborate at a dosage of 0.2 mol per 1 g of paper material) was added directly to the starch reinforcement agent, preparing a mutually compatible solution. The solution was thoroughly mixed using a magnetic stirrer at room temperature. The treatment process of the mixture was the same as that in the reinforcement treatment. In the two-step process, the paper was subjected to deacidification followed by reinforcement, respectively.

Determination of Paper Mechanical Properties

In accordance with GB/T 12914 (2018), the tensile strength of paper was measured using an L&W tensile strength tester at a crosshead speed of 20 mm/min. Paper samples were cut into 1 cm × 10 cm strips and clamped in parallel between the tester grips. The test area was free of watermarks, creases, or folds. Ten valid measurements were recorded. The tensile index (Y) was calculated using Eq. 1,

$$Y = \left(\frac{S}{g}\right) \times 1000 \quad (1)$$

where Y is the tensile index (N·m·g⁻¹), S is the tensile strength (kN/m), and g is the basis weight of the paper after reinforcement treatment (g/m²).

Following GB/T 457 (2008), the folding endurance was determined using an S13505 folding endurance tester (double-clamp type). A 1 cm × 10 cm sample, with smooth and parallel edges, was subjected to longitudinal tension and repeatedly folded forward and backward until rupture. At least 10 parallel measurements were performed, and the average value was calculated.

In accordance with GB/T 455 (2002), tear resistance was measured with an L&W tear tester. Ten valid measurements were recorded. The tear index (T) was calculated with Eq. 2,

$$T = \left(\frac{E}{g}\right) \times 1000 \quad (2)$$

where T is the tear index ($\text{N}\cdot\text{m}\cdot\text{g}^{-1}$), E is the tear resistance (kN/m), and g is the basis weight of the paper after reinforcement treatment (g/m^2).

Determination of Paper Surface pH Value

Following GB/T 13528 (2015), five $5\text{ cm} \times 5\text{ cm}$ paper samples before and after aging tests were prepared. Using a dropper, 0.5 mL of deionized water at $20\text{ }^{\circ}\text{C}$ was applied to the paper surface while simultaneously starting a stopwatch. The flat-surface electrode of an HSI-3F pH meter (manufactured by Shanghai Leici Instrument Works) was pressed firmly against the moistened paper area with consistent pressure, and the pH value was recorded after 2 min . This procedure was repeated five times, with the average value calculated as the paper surface pH.

Artificial Accelerated Aging Test for Paper Document

Untreated and treated paper samples subjected to different deacidification and/or reinforcement treatments (Table 1) were carried out dry heat aging test and wet heat aging test, respectively. According to GB/T 464 (2008), the samples were evenly spaced 100 mm apart in a climate-controlled chamber at $105\text{ }^{\circ}\text{C}$ and carried out dry heat aging for 3 d . According to GB/T 22894 (2008), the samples were aged in a climate-controlled chamber at 80°C and 65% relative humidity for 3 d . After aging tests, all samples were equilibrated in a climate-controlled chamber at $24\text{ }^{\circ}\text{C}$ and 50% relative humidity for 24 h to balance the moisture in the paper before testing various properties of the paper. Six replicates in each group.

One-way Analysis of Variance

One-way analysis of variance (ANOVA) was employed to test whether there were significant differences in the effects of different starch modification processes on the mechanical property indices of paper documents, such as tensile index, tearing index, and folding endurance. This was done by comparing the magnitudes of two types of variations: between-group variation and within-group variation. Using SPSS statistical software, the probability P value corresponding to the statistical value F was calculated. A significance level (α) was set at 0.05 (*i.e.*, allowing a 5% probability of making a Type I error). If $P < \alpha$, it was considered that different treatment processes had significant differences in their effects on the mechanical property indices; if $P \geq \alpha$, it was considered that there were no significant effects.

RESULTS AND DISCUSSION

Influence of Different Treatments on Mechanical Strength

Tensile index analysis

Figure 1 shows the percentages of increase of the tensile index of paper documents treated with different starch modifications compared with the original paper document (T0). Compared with the original paper, the tensile index of paper document modified with deacidification and/or reinforcement showed varying degrees of improvement. The paper document treated with deacidification alone (T1) exhibited only a 3.75% increase in tensile index compared with the original paper. This result aligns with the findings of Zhou (2023), who also noted that deacidification treatment alone did not significantly improve the

elongation at breakage of the paper document. Compared with T1, the paper document strengthened with various starch treatments showed a significant improvement in tensile index. Notably, paper document modified with enzymatically hydrolyzed starch demonstrated superior reinforcement effectiveness in comparison to the paper document treated with unmodified starch or quaternary ammonium cationic starch. This was attributed to the fact that α -amylase randomly cleaved the internal α -1,4 glycosidic bonds of wheat starch, breaking the long starch molecular chains and thereby reducing the molecular weight of the starch. The reduction in starch molecular weight could facilitate better penetration of the starch paste into the paper structure. Furthermore, combined approach of both deacidification and reinforcement treatment was more effective in improving the tensile index of the paper document. Among the combined treatments, the two-step method for deacidification and reinforcement (T5, T8) yielded more favorable experimental results under the same type of starch condition. The two-step method involving deacidification followed by enzymatically hydrolyzed starch reinforcement achieved the highest tensile index increase rate, reaching up to 103%.

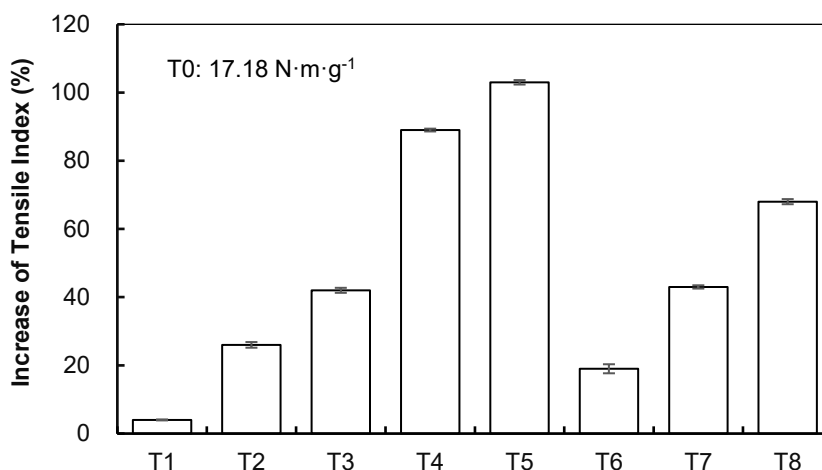


Fig. 1. Effect of different starch modification processes on the increase of tensile index of paper documents. Note: Increase was calculated based on the value of the control group (T0).

As can be seen from Table 2, a significant level of $p < 0.05$ was obtained, indicating significant inter-group differences in the mean tensile index among T0-T8. In other words, significant differences in the enhancement of tensile index were observed among paper documents modified with different starch modifications.

Table 2. One-way Analysis of Variance for Tensile Index of Paper Documents

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F - Statistic	p - value
Between Groups	1878.79	8	234.848869	369.690185	0.00
Within Groups	28.59	45	0.635259	-	-
Total	1907.38	53	-	-	-

Folding endurance analysis

Figure 2 shows the increase rates of paper documents treated with different starch modifications compared with the original paper. Compared with the original paper, the

folding endurance of paper modified with deacidification and/or reinforcement showed varying degrees of improvement. The paper document treated with strengthening agents alone (T2, T3, T6) exhibited a significantly higher folding endurance improvements than those subjected to other treatments. The paper document modified with enzymatically hydrolyzed starch achieved the highest improvement percentage of 42.1%. In contrast, the paper document modified with cationic quaternary ammonium starch showed a folding endurance increase similar to that of paper treated with unmodified starch, both at 27.5%. The paper document treated solely with deacidification showed the lowest folding endurance improvement, at 18.4%. Overall, paper documents with different treatments did not show a significant increase in folding endurance, as indicated by the one-way analysis of variance shown in Table 3 ($p > 0.05$). This may be related to the inherently low initial folding endurance of the paper documents themselves.

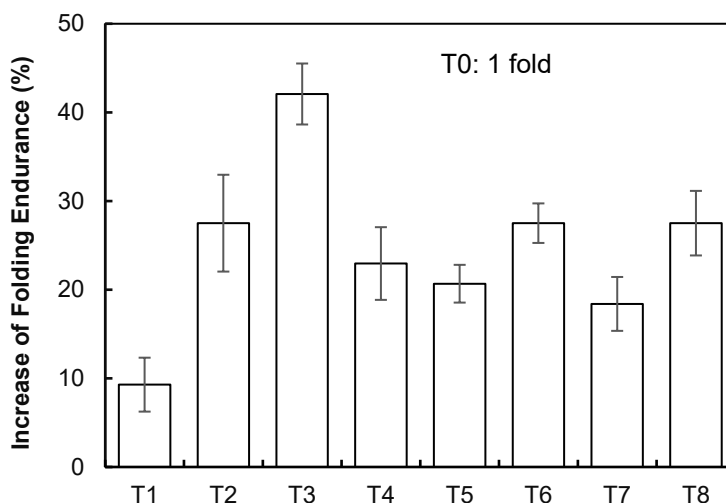


Fig. 2. Effect of different starch modification processes on the increase rates of folding endurance of paper documents. Note: Increase was calculated based on the value of the control group (T0).

Table 3. One-way Analysis of Variance for Folding Endurance of Paper Documents

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F - Statistic	p - value
Between Groups	2.33	8	0.29	0.83	0.58
Within Groups	15.77	45	0.35	-	-
Total	18.10	53	-	-	-

Tearing index analysis

Figure 3 shows the increase rate of tearing index of paper documents treated with different starch modifications. Compared with the original paper, the tearing index of paper documents modified with deacidification and/or reinforcement showed varying degrees of improvement. The paper document treated solely with deacidification (T1) showed the lowest tearing index increase compared with the original paper (T0), at only 7.60%.

Unlike the folding endurance improvement results, paper treated only with different starch strengthening agents showed a significantly lower tearing index increase than those treated with the combination of deacidification and reinforcement either through the one-step or two-step process. Comparing the one-step process with the two-step processes, the latter—deacidification first followed by reinforcement (T5, T8)—yielded paper document

with a higher tearing index increase. The samples in the group of T8 treated with quaternary ammonium cationic starch achieved a higher tearing index increase (20.5%) than those in the group of T5 treated with enzymatically hydrolyzed starch (15.2%). This was likely because the positively charged quaternary ammonium cationic starch strengthening agent could adsorb between cellulose molecules, enhancing the bonding force between paper cellulose fibers (Lin *et al.* 2017).

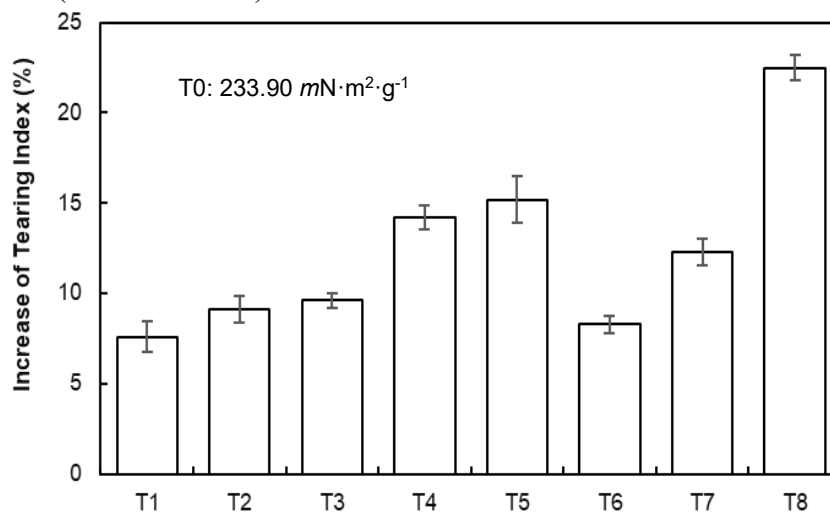


Fig. 3. Effect of different starch modification processes on the increase of tearing index for paper documents. Note: Increase was calculated based on the value of the control group (T0).

As can be seen from Table 4, the level of $p < 0.05$, indicating significant inter-group differences in the mean tearing index among T0-T8. That is, there were significant differences in the enhancement of tearing index among paper documents modified with different starch modifications.

Table 4. One-way Analysis of Variance for Tearing Index of Paper Documents

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F - Statistic	p - value
Between Groups	10256.49	8	1282.06	27.72	0.0
Within Groups	2081.51	45	46.26	-	-
Total	12337.99	53	-	-	-

Influence of Different Treatments on the Surface pH Values

Table 5 shows the pH values on the surface of paper documents treated with different starch modifications. The untreated paper document had a surface pH of 5.7, indicating acidity. The acidic substances in the paper document could promote cellulose hydrolysis, leading to paper aging, deterioration, and reduced strength (Rousset *et al.* 2004), which was detrimental to the long-term preservation of paper documents. After different modification treatments, the surface pH values of the paper document were increased to varying degrees, which indicated that both deacidification agents and strengthening agents could remove some acidic substances from the paper, reducing its acidity. However, using only starch strengthening treatment had a limited effect on improving the acidic conditions of the paper surface. As shown in Table 5, the surface pH values of paper documents modified with different starches (T2, T3, T6) remained below 7.0, indicating that the paper surface was still acidic, which suggested that relying solely on starch strengthening agents

could not reduce the acidic substances in paper documents to a sufficiently low level. In contrast, paper documents treated with deacidification could achieve a surface pH of 7.5, placing the paper in a pH condition more favorable for preservation. Therefore, deacidification treatment was essential for paper documents for long-term preservation. The increase in surface pH of paper documents treated with the one-step method (simultaneous deacidification and strengthening) was significantly greater than those treated with the two-step method (sequential deacidification and strengthening). Among them, the one-step enzymatic starch modification treatment and cationic starch modification treatment (T4, T7), as well as the two-step cationic starch modification treatment (T8), could all raise the surface pH of paper documents above 7.0, which demonstrated that combined deacidification and strengthening treatments were more effective in enhancing the long-term preservation of paper documents.

Table 5. Effects of Different Treatments on Paper Surface pH Value

Test group	T0	T1	T2	T3	T4	T5	T6	T7	T8
pH value	5.7	7.5	6.7	6.0	7.5	6.8	6.5	7.7	7.3

Mechanical Strength Analysis of Paper Documents after Aging Tests

The paper documents were subjected to one-step and two-step deacidification and reinforcement treatments using enzymatically hydrolyzed starch and quaternary ammonium cationic starch, respectively. Untreated paper documents (T0) were used as the control group. The effects of different starch treatments on the tensile index, tearing index, and folding endurance of the paper documents after dry and wet aging tests were evaluated, and the results are shown in Figs. 4, 5, and 6, respectively. As shown in Fig. 4, after deacidification and reinforcement treatment, the tensile index of the paper document treated with different starches was higher than that of the untreated paper under both dry and wet aging conditions. The tensile index after dry aging test was generally higher than that after wet aging test, while the decline rates of tensile index showed the opposite trend. This may be because, under high-humidity conditions, hydrogen bonds between cellulose fibers were disrupted, generating a large number of free hydroxyl groups. The water-absorbing and swelling effect of these hydroxyl groups loosened the fibers, weakening the bonding force between them (Wu 2015).

Zhou *et al.* (2024) also pointed out such effects. Moreover, moisture continuously disrupts the molecular packing within fibers, causing severe swelling and weakening. The water molecules can destroy the hydrogen bond network between cellulose fibers in paper, leading to dimensional instability and thereby affecting properties such as paper strength. Based on this finding, they developed a sustainable hyperbranched wet strength agent OA-PI to enhance the multidirectional cross-linking strength of cellulose paper under humid conditions and improve the cross-linking strength. Additionally, under high temperature and humidity, the chemical reaction rates between components in the paper document had been accelerated, leading to increased brittleness, hardening, and a reduction in flexibility and mechanical strength (Feng 2020). In comparison, the one-step treated paper exhibited a lower rate of decrease in tensile index during aging than the two-step treated paper document. Notably, the cationic starch modified paper document treated with the one-step method showed the most gradual decline in tensile index. Compared with T0, in which the tensile index was $16.0 \text{ N} \cdot \text{m} \cdot \text{g}^{-1}$ after dry aging test and $11.3 \text{ N} \cdot \text{m} \cdot \text{g}^{-1}$ after wet aging test, the tensile index of paper documents with promising treatment could be increased by more

than 50% after dry aging test, and could be increased by 93.9% with promising treatment after wet aging test.

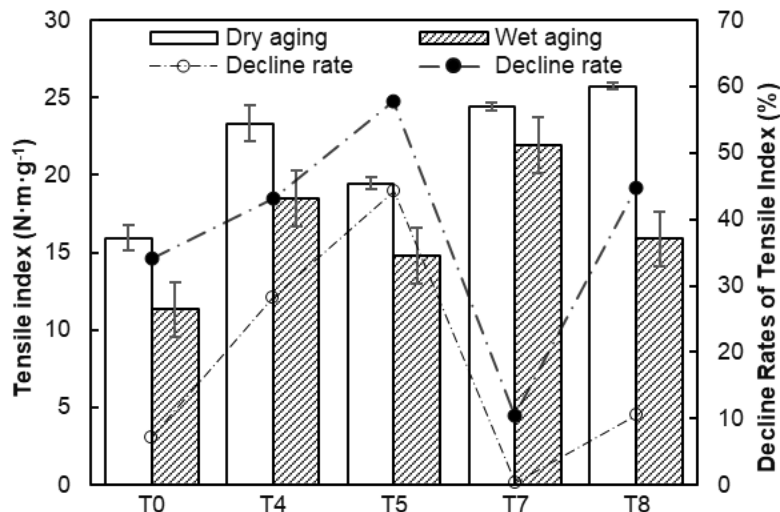


Fig. 4. Effect of different starch modification processes on the tensile index of paper documents after dry and wet aging tests

As shown in Fig. 5, under high-temperature and high-humidity aging conditions, untreated paper documents exhibited a significantly lower tearing index than papers that had undergone deacidification and reinforcement treatments.

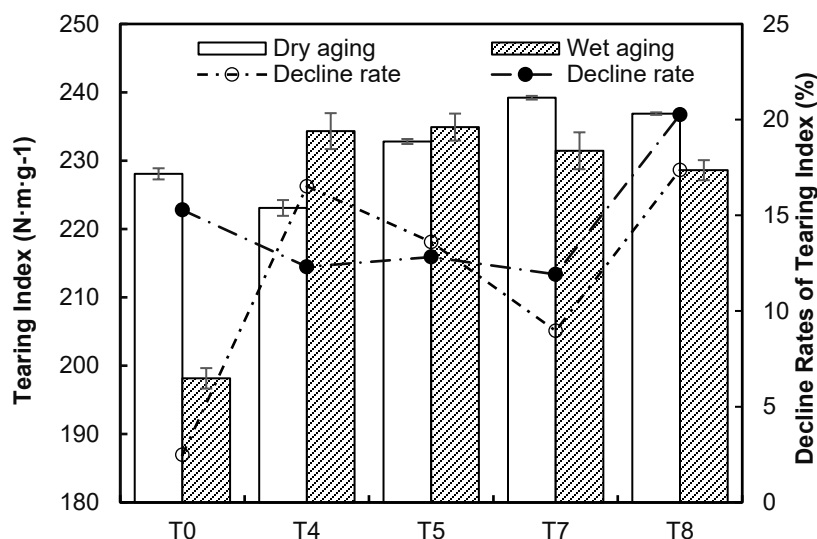


Fig. 5. Effect of different starch modification processes on the tearing index of paper documents after dry and wet aging tests

The decline percentages of the tearing index were also much higher than those observed under drying aging conditions. This further indicated that wet aging accelerated the oxidation and acid hydrolysis reactions of cellulose within the paper document, with high temperature and humidity being key factors in the deterioration of paper's mechanical strength. However, the effects of different starch modification processes on paper during dry and wet aging tests varied considerably. For paper modified with enzymatically hydrolyzed starch, the tearing index during humid aging was higher than that under dry

aging and surpassed the tearing index of paper modified with quaternary ammonium cationic starch. In contrast, paper modified with quaternary ammonium cationic starch exhibited the opposite trend, demonstrating superior aging resistance during dry aging test. The differences in aging performance among papers modified with different types of starch may be attributed to variations in their aging reaction processes under high-temperature and/or high-humidity conditions. From the decline results for the tearing index, it was evident that different starch modifications, deacidification methods, and reinforcement techniques all influenced the experimental results to some extent. Overall, papers treated with combined deacidification and reinforcement processes exhibited better anti-aging effects. Compared with T0, in which the tearing index was $228 \text{ N} \cdot \text{m} \cdot \text{g}^{-1}$ after dry aging test and $198 \text{ N} \cdot \text{m} \cdot \text{g}^{-1}$ after wet aging test, the tearing index of paper documents was not increased obviously after drying aging test, but it could be increased by 18.6% with promising treatment after wetting aging test.

As shown in Fig. 6, except for the T8 group, which showed little difference in folding endurance between dry and wet aging tests, the folding endurance of other modified papers decreased drastically during wet aging test, with a significantly higher decline rate than the dry aging test. Compared with the original paper, the modified starch-treated paper documents exhibited a notable improvement in folding endurance and a reduced decline. Overall, after aging tests, the quaternary ammonium cationic starch modified paper documents demonstrated better folding endurance than those modified with enzymatically hydrolyzed starch. In the dry aging test, papers treated with the one-step deacidification and reinforcement process showed higher folding endurance than those treated with the two-step method. Conversely, in the wet aging test, the two-step deacidification and reinforcement process resulted in significantly higher folding endurance than the one-step approach. Compared with T0, in which the folding cycle was 0.88 fold after dry aging test and 0.31 after wet aging test, the folding cycles of paper documents could be increased obviously by 128.57% after dry aging test, and it could be increased by 520% with promising treatment after wet aging test.

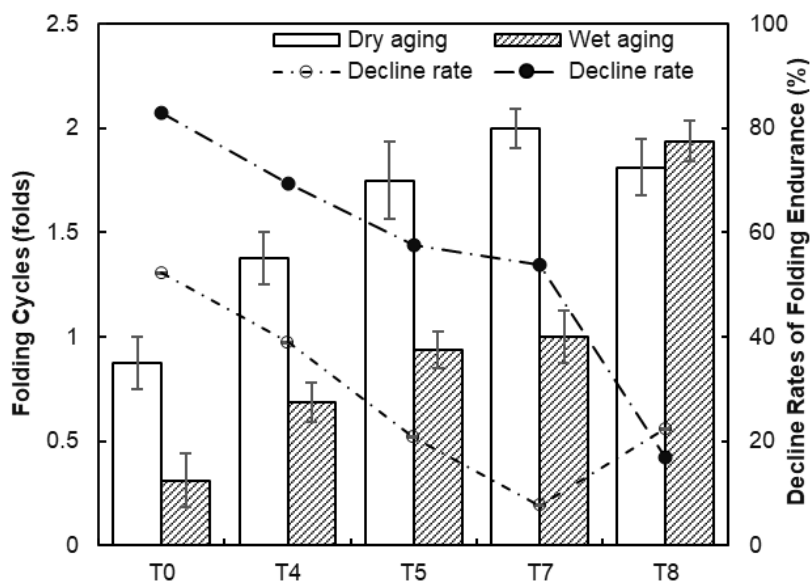


Fig. 6. Effect of different starch modification processes on the folding endurance of paper documents after dry and wet aging tests

CONCLUSIONS

1. Starch modification was able to improve the mechanical properties of paper documents. Compared with untreated samples (T0), samples modified with deacidification and enzymatically hydrolyzed starch by the two-step method (T5) achieved the highest tensile index increase (103%), while samples modified with cationic quaternary ammonium starch and deacidification with the two-step method had the highest tearing index improvement (20.5%). The improvement of folding endurance was not as obvious as those of tensile index and tearing index.
2. Deacidification could make the surface pH of document increase from 5.7 to 7.5, while the strengthening treatments with different types of starches (T2, T3 and T6) still made the surface pH of document below 7.0. The combined deacidification and strengthening treatments were more effective in enhancing the long-term preservation of paper documents, especially for the one-step method (simultaneous deacidification and strengthening)
3. Compared with untreated samples (T0), after dry aging test, the tensile index of paper documents with promising treatment was increased by over 50%, folding endurance was significantly improved by 129%, and the tearing index did not show a notable increase. After the aging test, the tensile index was increased by 93.9%, folding endurance was increased by 520%, and the tearing index could be increased by 18.6% for the most promising treatment system relative to the control specimens.
4. This work confirmed that the combination of starch and deacidification can significantly improve the mechanical properties and durability of paper documents. This is consistent with the “principle of minimal intervention” and “material compatibility standards” emphasized by the International Centre for the Study of the Preservation and Restoration of Cultural Property (ICCR).
5. Future research can further align with the Guidelines for the Preservation of Paper Archives issued by the Preservation and Access to Archives and Special Collections Section of the International Council on Archives (ICA-PAG). It should focus on verifying the safety of starch-modified paper documents, and formulate treatment parameter tables for different types of paper documents (such as acidic newspapers and ancient rice paper) with reference to ICA-PAG's requirements for “process standardization”. This research can be applied to the treatment of endangered documents with extremely poor mechanical strength to quickly alleviate the problem of paper embrittlement; for documents that need to take tear strength into account (such as the covers of ancient books), the treatment of cationic quaternary ammonium starch combined with deacidification is more targeted.

ACKNOWLEDGEMENTS

The authors are grateful for the financial support of the Research Program of Long-term Biological Protection Technology for Mildew-proof Paper-based Materials (2500170018) and the Research Program of Branding Shaping of Corporate Internal Journal Editing and Fusion Innovation of Nanomaterial Anti-Counterfeiting Technology for Publications (2025120021000712).

REFERENCES CITED

- Adamo, M., and Magaudda, G. (2003). "Susceptibility of printed paper to attack of chewing insects after gamma irradiation and ageing," *Restaurator* 24(2), 95-105. DOI: 10.1515/REST.2003.95
- Arnold, R. B. (1997). "The preservation of paper: How long will the page you are reading last," *Serials Review* 23(4), 15-26. DOI: 10.1080/00987913.1997.10764407
- Amornkitbamrung, L., Brac̆ic, D., Brac̆ic, M., Hribernik, S., Malešič, J., Vesel, A., Kleinschek, K. S., Kargi, R., and Mohan, T. (2020). "Comparison of trimethylsilyl cellulose stabilized carbonate and hydroxide nanoparticles for deacidification and strengthening of cellulose-based cultural heritage," *ACS Omega* 5(45), 29243-29256. DOI: 10.1021/acsomega.0c03997
- Baty, J. W., and Sinnott, M. L. (2005). "The kinetics of the spontaneous, proton- and Al^{III} catalysed hydrolysis of 1,5-anhydrocellobiitol – Models for cellulose depolymerization in paper aging and alkaline pulping, and a benchmark for cellulase efficiency," *Canadian Journal of Chemistry* 83(9), 1516-1524. DOI: 10.1139/v05-168
- Baty, J. W., Maitland, C. L., Minter, W., Hubbe, M. A., and Jordan-Mowery, S. K. (2010). "Deacidification for the conservation and preservation of paper-based works: A review," *BioResources* 5(3), 1955-2023. DOI: 10.15376/biores.5.3.1955-2023
- Carter, H. A. (1996). "The chemistry of paper preservation: Part 1. The aging of paper and conservation techniques," *Journal of Chemical Education* 73(5), article 417. DOI: 10.1021/ed073p417
- Chen, X. L., Yun, Y., Zhang, N., Chen, Q., and He, K. X. (2020). "Research on modified adhesives for paper cultural relics," *China Adhesives* 29(10), 37-40.
- Fan, H. M., Guo, M. F., Mou, H. Y., Liu, J., and Li, J. (2020). "Extending the durability of old books by atomized deacidification and reinforcement treatments," *BioResources* 15(1), 276-289. DOI: 10.15376/biores.15.1.276-289
- Feng, Z. Z. (2020). *Study on Reinforcement of Paper Cultural Relics with Cellulose Solution*, Master's Thesis, Zhengzhou University, Zhengzhou.
- GB/T 455 (2002). "Paper and board – Determination of tearing resistance," Standardization Administration of China, Beijing.
- GB/T 457 (2008). "Paper and board – Determination of folding endurance," Standardization Administration of China, Beijing.
- GB/T 464 (2008). "Accelerated aging (dry heat treatment) of paper and board," Standardization Administration of China, Beijing.
- GB/T 12914 (2018). "Paper and board – Determination of tensile properties -- Constant rate of elongation method (20 mm/min)," Standardization Administration of China, Beijing.
- GB/T 13528 (2015). "Paper and board – Determination of surface pH," Standardization Administration of China, Beijing.
- GB/T 22894 (2008). "Paper and board – Accelerated ageing -- Moist heat treatment at 80 Celsius and 65% relative humidity," Standardization Administration of China, Beijing.
- Huang, S. S. (2022). *Study on Strengthening of Literature Paper with In-situ Grafting of Aminoalkylalkoxysilane*, Master's Thesis, South China University of Technology, Guangzhou.
- He, B., Xu, G., Fan H. M., and Ren, J. L. (2019). "Research progress on deacidification

- and reinforcement of ancient books,” *China Pulp and Paper* 38(8), 73-81.
- Huang, J., Liang, G. Z., Lu, G., and Zhang, J.-P. (2018). “Conservation of acidic papers using a dispersion of oleic acid-modified MgO nanoparticles in a non-polar solvent,” *Journal of Cultural Heritage* 34, 61-68. DOI: 10.1016/j.culher.2018.04.018
- Hubbe, M. A., Smith, R. D., Zou, X., Katuscak, S., Potthast, A., and Ahn, K. (2017). “Deacidification of acidic books and paper by means of non-aqueous dispersions of alkaline particles: A review focusing on completeness of the reaction,” *BioResources* 12(2), 4410-4477. DOI: 10.15376/biores.12.2.Hubbe
- Hubbe, M. A., Maitland, C., Nanjiba, M., Horst, T., Ahn, K., and Potthast, A. (2023). “Archival performance of paper as affected by chemical components: A Review,” *BioResources* 18(3), 6430-6498. DOI: 10.15376/biores.18.3.Hubbe
- Ipert, S., Dupont, A., Lavedrine, B., Begin, P., Rousset, E., and Cheradame, H. (2006). “Mass deacidification of papers and books. IV-A study of papers treated with aminoalkylalkoxysilanes and their resistance to ageing,” *Polymer Degradation & Stability* 91(12), 3448-3455. DOI: 10.1016/j.polymdegradstab.2006.04.033
- Li, J. (2019). *Research on Deacidification and Restoration of Paper Cultural Relics based on Ultrasonic Atomization Method*, Master’s Thesis, South China University of Technology, Guangzhou.
- Lin, Y. T., Tan, W., Xu, B., Wu, T., and Fang, Y. X. (2017). “Development of deacidification and reinforcement agent for the paper documents and its application,” *Chemical Research and Application* 29, 3, 435-440.
- Ma, X., Tian, S., Li, X., Fan, H., and Fu, S. (2021). “Combined polyhexamethylene guanidine and nanocellulose for the conservation and enhancement of ancient paper,” *Cellulose* 28, 8027-8042. DOI: 10.1007/s10570-021-03989-2
- Ma, Y. Y., Zhang, F. Y., and Pan, J. (2020). “Analysis of the composition of the golden scriptures in the Tibetan Tripitaka and microorganisms on the paper,” *Sciences of Conservation and Archaeology* 32(6), 78-86.
- Małachowska, E., Dubowik, M., Boruszewski, P., Ojewska, J., and Przybyszcz, P. (2020). “Influence of lignin content in cellulose pulp on paper durability,” *Scientific Reports* 10(1), article 19998. DOI: 10.1038/s41598-020-77101-2
- Rousset, E., Ipert, S., and Cheradame, H. (2004). “Mass deacidification of paper and books, II: Deacidification in the liquid phase using aminosilanes,” *Restaurator* 25(2), 104-118. DOI: 10.1515/REST.2004.104
- Simon, A. V., Strlič, M., Kolar, and Pihlar, J. B. (2007). “The role of transition metals in oxidative degradation of cellulose,” *Polymer Degradation and Stability* 92(8), 1476-1481. DOI: 10.1016/j.polymdegradstab.2007.05.006
- ISO/CIE 11664-6 (E) (2022). “Colorimetry-part 6: CIEDE2000 colour-difference formula,” International Organization for Standardization, London, England.
- Völkel, L., Ahn, K., Hähner, U., Gindl-Altmutter, W., and Potthast, A. (2017). “Nano meets the sheet: Adhesive-free application of nanocellulosic suspensions in paper conservation,” *Heritage Science* 5, 23. DOI: 10.1186/s40494-017-0134-5
- Wang, Z. (2021). “Analysis of the acidification characteristics of Dowling paper in Republic of China Archives,” *Archives Science Bulletin* 1, 89-95.
- Wang, J., Yiu, B., Obermeyer, J., Filipe, C. D. M., Brennan, J. D., and Pelton, R. (2012). “Effects of temperature and relative humidity stability of paper-immobilized antibodies,” *Biomacromolecules* 13(2), 559-564. DOI: 10.1021/bm201740576
- Wang, J. (2023a). “Protective measures and scientific management of paper books in libraries: A case study of the library of Qiannan Normal University for nationalities,”

- Paper Equipment and Materials* 52(10), 181-183.
- Wang, H. H. (2023b). *Study on the Application of Water-soluble Chitosan in the Protection of Paper Literature*, Master's Thesis, South China University of Technology, Guangzhou.
- Wu, H. (2015). "Influence of relative humidity on the moisture content of paper," *Science and Wealth* 7, 373-374.
- Xu, L. L. (2011). *Experimental Research on the Protection of Paper Cultural Relics with Modified Natural Materials*, Master's Thesis, Nanjing University of Aeronautics and Astronautics, Nanjing.
- Xu, T., and An, Q. K. (2005). "Application of chitosan in the papermaking industry," *Jiangsu Papermaking* 4, 37-39.
- Yang, D., Zhong, L. X., Yuan, T. Q., Peng, X. W., and Sun, R. C. (2013). "Studies on the structural characterization of lignin, hemicelluloses and cellulose fractionated by ionic liquid followed by alkaline extraction from bamboo," *Industrial Crops and Products* 43, 141-149. DOI: 10.1016/j.indcrop.2012.07.02423
- Yu, Y. F., Shen, Y. F., Hou, A. Q., Li, Y., and Feng, Z. Z. (2020). "Study on the reinforcement of deteriorated rice paper with nanocellulose," *China Adhesives* 29(1), 55-58.
- Zhang, J. L., and Fang, Y. X. (2011). "Acidification of ancient books and modern restoration techniques," *Journal of Library Science* 33(8), 23-25.
- Zhang, H., Zhang, J. P., and Zhu, Q. G. (2015). "Research on the influence of molds on the chemical properties of paper," *China Pulp & Paper* 34(3), 31-34.
- Zhang, Y. F. (2020). *Research on Deacidification Protection of Modern Paper Documents by Nano MgO*, Master's Thesis, Southeast University, Nanjing.
- Zhang, Y. L. (2021). *Study on the Protection of Paper Documents by Bifunctional Polyamidoamines*, Master's Thesis, South China University of Technology, Guangzhou.
- Zhang, X. (2021b). *Study on the Protection of Sodium Carboxymethyl Cellulose as Reinforcement for the Paper Documents of the Republic of China*, Master's Thesis, Shandong University, Jinan.
- Zhou, Z. Y. (2023). *Research on the Starch in the Reinforcement of Paper Documents*, Master's Thesis, South China University of Technology, Guangzhou.
- Zhou, Y. X., Huang, Q. B., Wang, W. L., and Wang, X. H. (2024). "Enhancing cross-linking network for superior wet strength of paper by sustainable hyperbranched polyimines," *ACS Applied Materials & Interfaces* 16(12), 15383-15393. DOI: 10.1021/acsami.4c01403

Article submitted: July 7, 2025; Peer review completed: August 1, 2025; Revised version received: August 3, 2025; Accepted: August 4, 2025; Published: August 18, 2025.
DOI: 10.15376/biores.20.4.8883-8898