Degree of Polymerization of Fibers from *Wikstroemia* Bark vs. the Durability of Kaihua Paper

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In order to determine the influence of bast fibers isolated from *Wikstroemia* bark on the durability of paper, self-made paper was prepared using bagasse pulp mixed with *Wikstroemia* bark pulp using Kaihua paper manufacturing technology. The durability properties of the paper obtained with different proportions of *Wikstroemia* bark pulp were measured and analyzed. The results showed that *Wikstroemia* bark can lower the acidity, improve the mechanical strength, and delay the aging of paper. The mechanical strength showed an exponential relationship with the amount of *Wikstroemia* bark pulp added to the paper pulp. There was a linear positive correlation between the initial polymerization degree of the paper and the amount of *Wikstroemia* bark pulp, while the molecular fracture rate of the paper with *Wikstroemia* bark pulp was considerably reduced. *Wikstroemia* bark fibers are long fibers with high strength. At the same time, *Wikstroemia* bark fibers differ greatly in length, so the uniformity can meet the requirements. The durability of the paper made from only bagasse pulp was poor, but the overall strength and polymerization degree of the paper improve after being mixed with *Wikstroemia* bark pulp.

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**INTRODUCTION**

According to historical records, Kaihua paper was named after the place it was originally produced, in Kaihua, Zhejiang province of China. Kaihua paper originated in the Tang and Song Dynasties and flourished in the Ming and Qing Dynasties. Due to its aging resistance, long life, and delicate, white, and soft nature, it became popular in the court. It is the best ancient paper in China and the most expensive palace book paper from the Ming and Qing Dynasties. The Si Ku Quan Shu collected in the Forbidden City are made of Kaihua paper. However, for some reason, Kaihua paper manufacturing technology has been lost. Thanks to the efforts of Yang et al. (2018), Kaihua paper manufacturing technology has been rejuvenated to a certain extent, i.e., for paper made with Wikstroemia bark. Now, the Kaihua paper manufacturing technology is listed as a Zhejiang province intangible cultural heritage protection project and a Zhejiang province traditional technology revitalization project (Hu 2019). On May 29, 2019, an intaglio sculpture printed...
on Kaihua paper was displayed at the Stockholm International Stamp Fair in Stockholm, Sweden. This is the first time that Chinese paper making has participated in an international stamp exhibition in the past hundred years (Xu 2020).

During the long-term storage of paper cellulose, hemicellulose, lignins, and other auxiliary chemical components in paper undergo chemical degradation (acid hydrolysis, enzyme hydrolysis, and oxidative degradation) (Yang et al. 2011; Chen et al. 2021), thermal degradation, and radiation degradation (ultraviolet light, visible light, and high-energy radiation). These effects lead to the aging of the paper (Li 2014). It was found that the factors leading to the aging degradation of paper generally included the raw materials and composition of hand-made paper. In general, bast fibers are the most durable because of their toughness and low lignin and heterocyclic content. The durability of wood fiber is less than that of bast fiber. Gramineae fiber has the characteristics of low cellulose content, high lignin content, high impurity cell content, short fiber, and poor interweaving power, leading to poor durability of the paper made by it (Malachowska et al. 2020; Zhang 2019).

Most of the fibers in the transverse section of the trunk of Wikstroemia are round or elliptical, with a large central cavity and uniform cell wall thickness. The average length and diameter of the bark fibers are 3.9 mm and 12.07 μm, respectively. The bast fibers have dense and clear transverse striations, the middle part of the fiber is widened, and the end part is flat and rodlike with additional miscellaneous cells. The fibers of Wikstroemia bark are slenderer compared to the fibers of Pteroceltis and Broussonetia. The calcium oxalate crystals of the Wikstroemia bark are mostly rectangular, with a large number of parenchyma cells between the fibers (Yi et al. 2018). In addition, Wikstroemia contains flavonoids, polysaccharides, acid resin, volatile oil, steroids, saponins, and other components, which are small, toxic, and have antibacterial, antiviral, and antitumor medicinal values (Hu et al. 2000; Wang et al. 2005). Therefore, many places use Wikstroemia bark to make handmade paper, e.g., Kaihua paper in Zhejiang, Dongba paper in Yunnan, Tibetan paper in Tibet, Japanese paper, etc. These papers are characterized by high strength, white color, fineness, uniformity, insect resistance, and durability (Li 2003; Zhao et al. 2020).

In usual papermaking processes, chemical additives are added to improve the pulp performance, e.g., reinforcing agents, sizing agents, bactericides, defoamers, cleaning agents, etc. (Hubbe et al. 2018). For example, magnesium-containing compounds and calcium-containing compounds can remove acidic substances from paper, while quaternary ammonium guar gum has certain application prospects in the reinforcement of paper documents (Fan et al. 2022). Additives are often discharged together with papermaking water, which causes pollution (Zeng 2010). Since papermaking with Wikstroemia bark has good performance, and Wikstroemia has various useful components, the addition of Wikstroemia bark pulp to bagasse pulp may also improve the paper performance. In order to study the effect of the addition of Wikstroemia bark pulp on the durability of paper, the method of Yao et al. (2021) was used to prepare Wikstroemia bark pulp in this study. The resulting Wikstroemia bark pulp was mixed with bagasse pulp purchased in the market to prepare paper by Kaihua paper manufacturing technology. Then, the paper samples with different mixing ratios of Wikstroemia bark pulp, were subjected to wet-heat aging experiments. Afterwards, the physical properties of the samples before and after aging were measured, respectively, and their properties were analyzed. The molecular weight and changes of cellulose were analyzed via the viscosity method, and the degradation kinetic equations of the different handmade papers were established. In addition, the degradation
rate and durability of the different handmade papers prepared by addition of *Wikstroemia* bark pulp were compared.

### EXPERIMENTAL

**Materials**

Bagasse pulp (Guangxi Nongken Group, 85% ISO brightness) was used. *Wikstroemia* bark, provided by the Traditional Skills Research Center of Kaihua Paper, was *Wikstroemia monnula* Hance. The cooking agent used was CaO, which was purchased from Chron chemicals Co. Ltd. (Chengdu, China). Bleaching agent used was K$_2$CO$_3$, which was AR grade and purchased from Chron chemicals Co. Ltd. (Chengdu, China).

**Experimental Methods**

*Pulping process*

First, the *Wikstroemia* bark was cut into 15 to 20 cm segments and then soaked in water until the bark became soft, but no fermentation odor was produced. Next, the outer black bark was scraped off and dried at a low temperature for later use. Then, the white bark was placed into a high-pressure cooking pot, to which 1.5 L of water was added, followed by 50 g of cooking agent (CaO). The mixture was heated at 110 °C under high pressure for 12 h. After cooking, the white bark was wrapped in gauze, rinsed with running water, and wrung dry. Then, the above steps were repeated. Next, the boiled white bark was placed into a hydraulic pulper, 3 L of clear water was added, and then beat until it was completely broken. Finally, the bleaching process with K$_2$CO$_3$ was performed for 15 d (as shown in Fig. 1).

![Diagram](image)

**Fig. 1.** Schematic diagram of the pulping process: the white bark and cooked bark were treated *Wikstroemia* bark; the virgin pulp and bleached pulp were *Wikstroemia* bark pulp

*Mixed papermaking*

A paper with a quantification of 30 g/m$^2$ was prepared by mixing *Wikstroemia* bark pulp and bagasse pulp in various proportions.
Table 1. Paper Composition Design

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wikstroemia Bark Pulp Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>75</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
</tr>
</tbody>
</table>

Artificial wet-heat aging treatment

According to GB/T standard 22894-2008 (2008), the above five kinds of paper were subjected to humidity and heat aging experiments at a temperature of 80 °C and a relative humidity (RH) of 65% in a constant temperature and humidity box. In the aging test, it is generally considered that 3 d of aging in the laboratory is equivalent to 18 years to 25 years of aging under natural conditions (Wilson et al. 1980). Therefore, a group of paper samples was taken out every 3 d in the experiment, and five groups (0 d, 3 d, 6 d, 9 d, and 12 days) were taken from each paper sample according to different aging days.

Methods of Measurement

Scanning electron microscopy (SEM) analysis

The morphologies of the Wikstroemia bark fibers were examined by a scanning electron microscope (SEM SU1510, Hitachi, Tokyo, Japan) operating at an accelerating voltage of 15 kV. Before observation, the samples were coated with gold using a vacuum sputter-coater (MSP-2S/MSP-Mini; IXRF, Inc., Travis County, TX).

Whiteness measurement

The whiteness was measured with a whiteness tester according to GB/T standard 22879-2008 (2008) (YQ-Z-47B, Qingtong & Boke, Hangzhou, China). This experiment was performed 3 times.

Surface pH test

According to GB/T standard 13528-2015 (2015), the paper was placed on a mat, and a drop of deionized water was added to the surface of the paper. Then, the test electrode of the pH meter was placed into the water drop, and the pH value was read after the reading was stable (PGSJ-4F, Rex, Shanghai, China). This experiment was carried out 3 times.

Mechanical strength test

The tensile strength of paper was tested according to GB/T standard 12914-2008 (2008). A paper sample with a width of 15 mm was cut, the chuck was adjusted to make the test length 150 mm; and the tensile speed was 15 mm/min ± 3.75 mm/min (ZB-L300A, Zhibang, Hangzhou, China). There were three replications of this experiment.

Viscosity method to measure degree of polymerization

The intrinsic viscosity of the pulp was determined in a copper ethylenediamine (CED) solution according to GB/T standard 1548-2016 (2016). The formula for calculating the degree of polymerization (DP) is shown in Eq. 1,

\[ DP^{0.905} = 0.75 \frac{[\eta] \times \rho}{\rho} \]  \hspace{1cm} (1)
where $\rho$ is the concentration of pulp in dilute solution (0.5 mol/L CED solution). The product $[\eta] \times \rho$ was calculated using $\eta_{\text{ratin}}$. As seen from Table B.1 of GB/T standard 1548-2016 (2016), the calculation formula of $\eta_{\text{ratin}}$ is given by Eq. 2,

$$\eta_{\text{ratin}} = \frac{f}{t_s} \times t$$

(2)

where $f$ is the viscometer constant, and $t_s$ is the outflow time of dilute solution (0.5 mol/L of CED solution) in the calibration viscometer. Then, $\rho$ can be calculated using Eq. 3,

$$\rho = \frac{m}{50}$$

(3)

where $m$ is the absolute dry weight of pulp.

RESULTS AND DISCUSSION

Microstructure Analysis (Scanning Electron Microscopy)

Scanning electron microscopy was used to analyze the surface morphology of fibers, and to evaluate whether the fiber surface was rough, split, or damaged. For bark raw materials used for papermaking, long fibers provide strength and short fibers provide evenness. Generally, greater difference in fiber diameter leads to better evenness of the paper produced. At the same time, longer and thinner fiber results in higher strength of the paper. As shown in Fig. 2, the fiber content of the Wikstroemia bark was high, and the fibers were slender, less twisted, smoother, and less damaged than general bark fiber, with dense transverse streaks and mixed crystal blocks. There were differences in the fiber morphology of the Wikstroemia bark. The samples taken from dry Wikstroemia bark included both coarse fibers wrapped by parenchyma cells and bare fine fibers. According to the study of Qin and Qiu (2010), the greater the difference in fiber diameter, the better the uniformity of the paper, and the longer the fiber, the higher the strength of the paper. Hence, these characteristics indicated that Wikstroemia bark has good evenness and strength.

Fig. 2. SEM micrographs of Wikstroemia bark fibers (Note: magnification: (A) 800X; and B) 3000X)
Whiteness of samples

The reaction of phenolic compounds to capture free radicals and produce quinones is crucial for the termination of the free radical chain reaction for cellulose degradation. The amount of free radical reaction in the surrounding environment determines the decrease in paper strength. The yellowing of paper is an inevitable consequence of the antioxidant properties of lignins (Li et al. 2013). Therefore, color change is the most intuitive index to judge the degree of paper aging.

As can be seen in Fig. 3, the whiteness of the paper using only bagasse pulp was higher at the beginning, but it rapidly decreased with the aging process. Although the whiteness of the paper using pure *Wikstroemia* bark pulp was not as good as that of bagasse pulp paper at the beginning, it exceeded that of the bagasse pulp paper after 6 d of aging due to the small change in whiteness. The whiteness of *Wikstroemia* bark pulp paper was less than that of bagasse pulp paper, but *Wikstroemia* bark pulp paper had better durability and a slower rate of whiteness decline. According to the results of this experiment, the whiteness of the paper was the best when the mixing ratio of bagasse pulp and *Wikstroemia* bark pulp was 1 to 1. A high proportion of *Wikstroemia* bark pulp led to a low initial whiteness, while a high proportion of bagasse pulp led to a low post-aging whiteness.

![Graph showing whiteness of samples](image)

**Fig. 3.** Whiteness of the paper with different *Wikstroemia* bark pulp ratios and the changes with aging time (Note: proportions of *Wikstroemia* bark pulp: (1) 0%; (2) 25%; (3) 50%; (4) 75%; and (5) 100%)

Surface pH

Cellulose is a polymer containing glucose groups linked by β-1, 4-glycosidic bonds. The glycosidic bond has low stability to acid and is easily broken in acidic environments. Although the glycosidic bond of cellulose may be broken via alkaline hydrolysis, it is generally stable to alkali (Yan et al. 2018). Therefore, it is believed that a neutral or weakly alkaline surface pH of paper is more conducive to long-term preservation. Paper acidification usually occurs because the lignins in paper are easily oxidized into acidic substances, and there are acidic gases in the air, as well as organic acids produced by
microbial metabolism. The acidification rate of paper is related to the lignin content of the paper. The surface pH of the paper can be maintained at a higher state by adding weakly alkaline substances during the papermaking process (Hubbe et al. 2017; He et al. 2019).

As can be seen in Fig. 4, the surface pH of the paper with bagasse pulp was always below 6, while the initial surface pH of the paper with pure Wikstroemia bark pulp was 8.78, showing moderate and weak alkalinity, respectively. Both papers gradually became weakly acidic after 12 d of aging. Adding a small amount of Wikstroemia bark pulp into bagasse pulp had little effect on the pH. When the mixing ratio of Wikstroemia bark pulp to bagasse pulp was increased to 1:1, the paper was initially alkaline, so it was more resistant to aging and more conducive to long-term preservation. However, after 9 d of aging, the surface pH of the paper with a mixing ratio of 1 to 1 was not much different from that of the paper with a mixing ratio of 3 to 1. All the samples aged for 12 d showed that the pH value became acidic, which indicated that the acidification of the paper could only be alleviated, but could not be fully avoided even with the addition of Wikstroemia bark pulp.

![Fig. 4. Surface pH of the paper with different Wikstroemia bark pulp ratios and the changes with aging time (Note: proportions of Wikstroemia bark pulp: (1) 0%; (2) 25%; (3) 50%; (4) 75%; and (5) 100%)](image)

Mechanical strength property

There are many mechanical strength property indexes for paper, among which the tensile properties and folding endurance can better reflect the mechanical strength properties of paper. Hence, this study only measured these two indexes (Zhang et al. 2017). Although the mechanical properties of paper can be improved by beating pulp or using a dry strength agent, the mechanical properties of paper are primarily produced by the hydrogen bonding force between the fibers and the interweaving between fibers. The properties of the fiber itself and the contact between the fibers affect the upper limit of the mechanical properties of paper (Li et al. 2020). Some studies have shown that the influence
of the fiber on the mechanical properties of paper primarily include the strength of the fiber itself, the bond strength between the fibers, and the arrangement and distribution of the fibers (Li et al. 2014).

As can be seen in Fig. 5A, the paper prepared using only bagasse pulp had poor tensile performance; the initial tensile index was low, and the retention rate was only 33.7% after 12 d of aging. The paper prepared with pure *Wikstroemia* bark pulp had a higher initial tensile resistance index and a strength retention of 93.3% after 12 d of aging.

![Graph A](image)

![Graph B](image)

**Fig. 5.** (A) Tensile index of the paper with different proportions of *Wikstroemia* bark pulp and the changes with aging time (Note: proportions of *Wikstroemia* bark pulp: (1) 0%; (2) 25%; (3) 50%; (4) 75%; (5) 100%); and (B) Relationship between the tensile index and the paper samples with different proportions of *Wikstroemia* bark pulp (Note: the dotted line is the trend line of exponential function)
The strength index of the paper prepared with the mixture of two kinds of pulp increased as the proportion of *Wikstroemia* bark pulp increased, and the strength retention after aging for 12 d also followed this trend. The unaged paper and the paper aged for 12 d were selected for drawing, as shown in Fig. 5B. The results showed that the tensile resistance index had an exponential relationship with the proportion of *Wikstroemia* bark pulp.

It can be concluded that the mechanical properties of *Wikstroemia* bark pulp paper were excellent and adding *Wikstroemia* bark pulp into bagasse pulp can improve the mechanical properties of the paper. In addition, there was an exponential relationship between the amount of *Wikstroemia* bark pulp and mechanical properties; the greater the content of *Wikstroemia* bark pulp, the better the improvement effect.

**Molecular weight and lifetime**

During the wet-heat aging process of paper, the primary change is the loss of cellulose through hydrolysis, which leads to the gradual decrease in polymerization degree. The degree of polymerization is often used to study the aging degradation characteristics of paper, since it is an easy-to-measure indicator of the number of repeating units in the molecular chain of the reactive cellulose, which can further reflect the aging degree of paper. Some studies have shown that the first order kinetic equation of cellulose degradation can better describe the paper degradation process (Wei 2019). The first-order kinetic equation of cellulose degradation is shown in Eq. 4,

$$\ln \left(1 - \frac{1}{DP_t}\right) - \ln \left(1 - \frac{1}{DP_0}\right) = -kt$$

where $DP_t$ is the degree of polymerization of paper at time (t); $DP_0$ is the degree of initial polymerization; and $k$ represents the degradation rate, which is a constant to be determined.

As can be seen from Fig. 6A, the degree of initial polymerization of the paper with only bagasse pulp was low, while that of paper using pure *Wikstroemia* bark pulp was high. The initial degree of polymerization of the paper with the mixture of two kinds of pulp was linearly positively correlated with the content of *Wikstroemia* bark pulp. Figure 6B shows the results of the first-order kinetics equation of cellulose degradation and days of accelerated aging; it was found that the fitting curve had a good linear relationship. It can be seen that the presence or absence of *Wikstroemia* bark had a great influence on the molecular chain breaking speed. The slope of the fitting curve for the paper containing *Wikstroemia* bark pulp was considerably lower than that for the paper with bagasse pulp. The difference in the fitting curve slope among the four groups of paper containing *Wikstroemia* bark pulp was small.

Table 2 lists the equations of the fitted curve (Fig. 6B) and the corresponding coefficients of determination. When the degree of polymerization is 200 to 250, cellulose has reached its critical level of polymerization, *i.e.*, the paper basically has no performance and experiences failure (Liao *et al.* 2009; Jeong *et al.* 2014). Therefore, the degradation time (TDP = 200) needed for the polymerization degree of the paper to drop to 200 under the conditions of wet-heat aging was calculated, as shown in Table 2. Under the combined influence of low initial polymerization degree and high degradation rate, the paper prepared using only bagasse pulp lost its performance after just 8 d of accelerated aging.

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The durability of pure *Wikstroemia* bark pulp paper was excellent. According to the fitting equation, the paper lost its durability after aging for 210 d. Compared to the paper with bagasse pulp, the paper with a mixture of two kinds of pulp takes much longer time to lose its serviceability, which is primarily due to the lower degradation rate. This shows that when a raw material with a fast degradation rate is mixed with a durable raw material, the degradation rate of the paper obviously slows down, and the durability of the paper is significantly improved. When the mixing ratio of bagasse pulp and *Wikstroemia* bark pulp was 1 to 3, the time required for the paper to lose its serviceability was close to that of pure *Wikstroemia* bark pulp paper.

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Table 2. Kinetic Equations of the Paper Degradation and Paper Degradation Time

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fitting Equation</th>
<th>R^2</th>
<th>TDP = 200</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>y = 2.16E-4x</td>
<td>0.9919</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>y = 6.55E-5x</td>
<td>0.9835</td>
<td>48</td>
</tr>
<tr>
<td>3</td>
<td>y = 3.16E-5x</td>
<td>0.9936</td>
<td>140</td>
</tr>
<tr>
<td>4</td>
<td>y = 2.29E-5x</td>
<td>0.9922</td>
<td>193</td>
</tr>
<tr>
<td>5</td>
<td>y = 1.96E-5x</td>
<td>0.9973</td>
<td>210</td>
</tr>
</tbody>
</table>

CONCLUSIONS

1. In this experiment, *Wikstroemia* bark pulp was mixed with bagasse pulp to make paper using Kaihua paper manufacturing technology. Five groups of paper were obtained, according to the different mixing proportions of *Wikstroemia* bark pulp.

2. Kaihua paper manufacturing technology can considerably improve the durability and mechanical properties of bagasse pulp paper with the addition of *Wikstroemia* bark pulp. This is because the fiber content of *Wikstroemia* bark is high, and the *Wikstroemia* bark fiber is slender and not easily damaged. In addition, paper with *Wikstroemia* bark pulp has a high surface pH and a high degree of polymerization.

3. In the aging process, the decrease in polymerization degree of *Wikstroemia* bark follows the first-order kinetic equation. The paper with pure *Wikstroemia* bark pulp has a high molecular weight and low molecular chain fracture rate. According to the calculation of the polymerization degree, the paper needs to be aged for 210 d to reach the critical state of failure. Furthermore, low content of *Wikstroemia* bark pulp can considerably reduce the molecular chain fracture rate of bagasse pulp paper, thus prolonging the life of the paper.

4. This study provides a basis for the restoration of Kaihua paper manufacturing technology.

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