Study on the application properties of high hydrophobic paper yarn base paper

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Abstract. As a new kind of paper-based textile materials and thanks to its healthiness and environmental protection, the paper yarn and its production will have a good future. This study mainly explores the papermaking process as follows: the beating degree of hemp pulp is 75°SR, the addition amount of PVA fiber, polyamide polyamine epichlorohydin (PAE) and alkenone dimer (AKD) is 2.0%, 2.5% and 0.2%, respectively. In addition, the pressure light pressure is 15 N/mm. The high hydrophobic paper yarn base paper has the wear resistance, water resistance, acid and alkali resistance. The analysis shows that the paper yarn base paper can be used as raw material in textile and weaving industries, thus reducing the use of viscose, polyester, plastic, etc.

1. Introduction
Paper yarn base paper, which is made from natural hemp pulp at specific conditions by papermaking machine, can be tailored into required width for various application(such as Fig.1(a)). And also, yarn base paper can be composited with thin nylon(such as Fig.1(b)), then twisted into string, by which enlarged its application in textiles and packing industrials [1].

Fig.1 Paper yarn base paper follow-up processing. a) The appearance of a yarn base paper after cutting strips. b) Yarn base paper twisted with nylon.
Nowadays, braided twine, bedroom accessories, ornaments, wearable and different types of furniture (armchairs, sofas, beds, air purification filters etc.) can be made from paper yarn, carpets, upholstery fabric, and the blinds [2-4]. Besides, the blinds also can be made of paper or combined with cotton and wool yarn, yarn paper reduces the development of the viscose and the use of leather products, etc. At the same time, yarn base paper can also be used to make straw, paper bags and other to replace plastic products. Although, these products are becoming more and more popular, the disadvantage of the high manufacturing cost, high technical content [5,6]. Therefore, it seems that the above products only seem to be aimed at the elite market. On the contrary, the domestic research is very few, so it is necessary to explore and develop this technology to develop paper yarn base paper products suitable for public use.

The paper yarn not only had low basis weight (around 20 g/m²), but also affected by complex forces such as stretching and torsion in the process of cutting into a narrow series of paper, paper line. So that its paper performance put forward higher requirements. The yarn base paper was required to have higher strength and elongation. In addition, due to the reusable characteristics of paper yarn products, it was also required to have good water resistance, friction resistance and acid and alkali resistance [7].

2. Materials and Methods

2.1. Materials
The manila hemp, with a length of 2.8 mm and a width of 21.3 μm, was provided by Shandong Longde Composites Technology Co., Ltd. PVA fiber was provided by Jinan Chida Technology and Trade Co., Ltd, and its length is 6.0 mm, water solubility temperature is 60 ℃. The experimental regents included PAE was bought from Nantong Huachuan Chemical Industry Co., Ltd. The AKD, sodium hydroxide and hydrogen chloride were bought from Sinopharmaceutical Chemical Reagents Co., Ltd, respectively.

2.2. Methods

2.2.1. Preparation of handsheets
The hemp pulp fibers were beaten by Valley for 20 min and by PFI grinding to 75 °SR. Then, 2.0% PVA fiber was added to disperse together, and 2.5% PAE, 0.05% AMPAM and 0.2% AKD were added successively after stirring for a period of time. Finally, take a certain amount of paste to make a quantitative 20g/m² of handwritten sheet. The handwritten sheet was wet pressed, dried at 85℃, and pressed with a light pressure of 15 N/mm. Handsheets produced under these conditions would be used for further research.

2.2.2. Determination of wear resistance of handsheets
Ground the surface of the handsheets several times until the internal fibers were exposed. The contact Angle of the surface was observed with a contact Angle contact. The wear test schematic diagram is shown in Fig. 2.
2.2.3. Determination of water resistance of handsheets
Several handsheets were cut into strips of 15 mm wide and put into a beaker filled with water. The paper was stirred in a magnetic stirrer (200 r/min) for a period of time to test the wet strength of the paper pattern. Spread out the mixed pattern on the press cloth and re-dry to test its tensile strength.

2.2.4. Determination of acid and alkali resistance of handsheets
Hydrochloric acid and sodium hydroxide were prepared into solutions with different pH values. A number of handsheets were cut into strips of 15 mm wide and immersed in the solution for 30 min. The changes before and after treatment of morphology of fibers were observed under a scanning electron microscope (SEM). The tensile strength and elongation were measured and the rate of decrease in tensile strength and elongation was calculated. The calculation formula is as follows:

\[
\text{Decreasing rate} = \frac{X_0 - X}{X_0} \times 100\%
\]

\(X_0\): targeted value before treatment
\(X\): targeted value after treatment

3. Results & Discussion

3.1. Hydrophobic properties of handsheets
Due to the low quantity and thickness of the yarn base paper, AKD was added into the pulp to make the paper have hydrophobic property [8]. The addition of AKD would affect the wear-resistant and washer-resistant properties of the paper. Meanwhile, the change of contact Angle was one of the methods to characterize the wear-resistant and washer-resistant degree of the paper.

As can be seen from Fig. 4 (a) and Fig. 4 (b), the contact Angle of the handwritten sheet was larger and the hydrophobic performance was greatly improved. As can be seen from the comparison between Fig. 4(c) and Fig. 4(d), with the addition of AKD, AKD molecules were spread on the surface of fibers. AKD had hydrophobicity due to its aliphatic hydrocarbon long chain functional groups. After adding AKD to the dredged slurry, during the drying process, hydrophobic groups were oriented outward, and AKD was oriented toward the hydroxyl group and active functional group of the fibers to react and form β-ketone ester bond, which was fixed on the fibers. The alkyl group with hydrophobicity was outward, resulting in the hydrophobicity of the paper. At the same time, AKD also reacted with water molecules to produce unstable β-ketoic acid, which was decarboxylated to form ketones [9-14], as shown in Fig. 3.
Fig. 3 Mechanism of action of AKD with cellulose and water

Fig. 4 The wettability of handshheets changed before and after adding AKD. a) SEM image of handshheets surface before adding AKD. b) Contact Angle diagram of handshheets surface before adding AKD. c) SEM image of handshheets with AKD content of 0.2%. d) Surface contact Angle of handshheets with 0.2% AKD added.
3.2. The wear resistance of handsheets

Due to the subsequent processing process of paper yarn base paper needed to suffer twisting, weaving and other processes, and paper yarn products were often rubbed, so it needed good wear resistance.

![Fig. 5 Surface wettability of worn handsheets. a) Influence of friction times on wettability of handsheets. b) Contact Angle diagram of handsheets after 2 times of friction.](image)

As can be seen from Fig. 5 (a), with the increase of the number of friction, the static contact Angle between the handsheets and water increased first and then decreased. When the water drops on the surface of the handsheets were not friction, the static contact Angle of the water drops on the handsheet was 102.0°, and when the paper handsheets was friction for 2 times, the static contact Angle of the handsheets reached the maximum value of 103.1° in Fig. 5 (b). As the friction continues, the static contact Angle began to decrease. This was because the paper surface was slight friction handsheets, fibers slightly damaged, form a tiny nap, in the density of handsheets surface fibers cluster, made the water droplets and formed a layer of air layer on the surface of handsheets, had the effect to hold up water. Water and paper yarn on the surface of the handsheets contact area was reduced, eventually the contact Angle was increased performance for yarn handsheets. As the friction continues, the fibers surface were seriously damaged. The air layer formed by the fibers clusters disappears, and the contact area between the fibers surface and the water drops gradually increased, making the contact Angle of the handsheets decreased \([15,17]\). After 10 times of friction, handsheets still had strong hydrophobic property, and the contact Angle was 98.0°, which indicated that handsheets had good wear resistance.

3.3. Washable property of handsheets

In order to ensure that the paper yarn base paper products could still be reused after washing, it was required to have good washable performance.

As can be seen from Fig. 6 (a), the wet strength of handsheets decreased gradually with the increase of mixing time, while the redrying tensile index changed little with the increase of mixing time. This was because with the increase of washing time, water slowly permeates into the fibers of handsheets, and finally completely permeates, resulting in the decrease of wet strength \([18,19]\). After washing for 30 min, the tensile index of handsheets decreased from 81.1 N·m/g to 79.6 N·m/g, which was only 1.85% lower than that of handsheets without washing, and the contact Angle between handsheets and water decreased from 102.0° to 97.2° after washing for 30 min. The contact Angle of handsheets are 4.71% lower than that of handsheets without washing. The contact Angle is shown in Fig. 6 (b), indicating that handsheets of paper yarn had strong washable performance.
Fig. 6 The mechanical properties of handsheets after washing and the surface wettability of handsheets after drying again. a) Effect of stirring time in water on strength of handsheets. b) Contact Angle of handsheets after 30 min washing.

3.4. Acid and alkali resistance of handsheets

In order to store paper yarn base paper for a longer time and increase the service life of paper yarn products, it is necessary to explore the acid and alkaline resistance of paper yarn base paper and minimize the damage caused by the external environment to the fibers.

Fig. 7 SEM image of fibers surface morphology after solution treatment with different pH values. a) SEM image of fibers surface without acid-base treatment. b) SEM image of fibers surface treated with solution of pH 1. c) SEM image of fibers surface treated with solution of pH 5. d) SEM image of fibers surface treated with solution of pH 9. e) SEM image of fibers surface treated with solution of pH 13.

As can be seen from Fig. 7 (a), without acid-base treatment of the fibers surface of handsheets was smooth, with almost no gullies. Fig. 7 (c) and Fig. 7 (d) show that after handsheets were treated with a lower concentration of acid-base solution, the fibers surface became rough and there were fewer ravines. As can be seen from Fig. 7 (b) and Fig. 7 (e), when the acid-base concentration was high, the surface of the fibers had more gullies, and the depth and width of the gullies became larger. However,
by comparing the fibers on the surface of handsheets treated with the same concentration of acid and alkali solution, it could be seen that the surface of fibers treated with acid was more and the depth of the gullies was larger than that treated with alkali \[20\].

As can be seen from Fig. 8 (a), as the concentration of acid solution decreases, the decrease rates of tensile strength and elongation of handsheets decrease as the concentration of acid solution decreases. As can be seen from Fig. 8 (b), the decrease rate of tensile strength and elongation of handsheets increase with the increase of alkali solution concentration. This is because with the increase of the concentration of acid and base solution, the more severe the damage to the fibers structure, the strength of the fibers itself decreases, resulting in the reduction of the strength of the handsheets \[21\]. However, the decrease rate of tensile strength and elongation of handsheets treated with the same concentration of alkali solution was lower than that treated with acid solution. This is because the alkali resistance of hemp pulp fibers are better than that of acid solution and the damage degree of the fibers treated with alkali are lower than that treated with acid \[22, 23\]. In the actual production and use, attention should be paid to the control of the concentration of acid and alkali solution, as far as possible to avoid contact with the acid and alkali concentration of the liquid.

4. Conclusions
The handsheet prepared in this study has good hydrophobic property. After 10 times of wear, the contact Angle of the handsheet is 98°, which only decreases by 5.77%, indicating that the handsheet has good wear resistance. After the handsheet is stirred in water for 30 min, the tensile index of the handsheet is 79.6 N·m/g after drying, which only decreases by 1.85%, which proves that the handsheet has excellent washable property. After the handsheet is treated with different concentration of acid and alkali, the fibers are damaged, and its strength and elongation are decreased. Therefore, the handsheet and other paper yarn products should be avoided from being placed in the environment with high concentration of acid and alkali for a long time.

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