Research Article

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Synthesis of highly branched water-soluble polyester and its surface sizing agent strengthening mechanism

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Abstract: Solvent-free and highly branched water-soluble polyester (WPET) is prepared through self-emulsification methodology, using dimethyl terephthalate (DMT), sodium dimethyl isophthalate-5-sulfonate (SIPM), trimethylolpropane (TMP), and ethylene glycol (EG) by the transesterification and polycondensation. The WPET were first utilized as surface-sizing agents for cellulose fiber paper. The structure, average molecular weights, and physical properties of the water-soluble polyester were characterized by FTIR, ^1H NMR, gel permeation chromatography (GPC), dynamic light scattering (DLS), X-ray diffraction (XRD), and dynamic rheometer. The effects of polymer structure and properties, as well as the surface sizing of the paper, were investigated. WPET displayed better surface sizing properties when it was prepared under the following conditions: $-\text{COO}/-\text{OH}$ molar ratio of 1:2, the SIPM content of 17.98%, and TMP content of 11.10%. The relationships between the WPET structure and sized paper were clearly illustrated. The mechanical properties and water resistance of sized paper did not only depend on multi-branched hydroxyl groups of the WPET chains but also relied on the interactions among polymers and fibers, as well as the high toughness of surface sizing agent. The sizing paper possesses excellent mechanical properties as well as water resistance.

Keywords: highly branched, water-soluble polyester, transesterification and polycondensation, surface sizing agent

1 Introduction

Water-soluble polyesters (WPETs) are widely used as fundamental materials for preparing the dye, water-soluble chemical fiber (1–5), and many other materials. As the existence of similar groups to polyester, water-soluble polyesters can bond well with polyester fibers and are capable to improve its adhesion to fibers. Water-soluble polyesters have a better sizing performance than other normal compounds such as starch, polyvinyl alcohol, and polyacrylic acid. Hence, the synthesis of water-soluble polyesters has been the focus of research in relevant fields (6–8). It has good water solubility due to the introduction of hydrophilic groups into the molecular structure, which not only meets the needs of sizing but also is easy to desizing. Water-soluble polyesters can reduce viscosity and improve liquidity, which is quite suitable for the surface sizing agent (9,10). At the same time, solvent-free synthesis can reduce not only costs but also harmful gas emissions. The water-soluble polyesters with multichain hydroxyl groups have more polar groups. Thus, they can react with the hydroxyl groups on the paper fibers to form hydrogen bonds. In summary, the water-soluble polyester is used as a paper surface sizing agent to improve various properties of the paper.

Surface sizing is a cost-effective and efficient roll-to-roll manufacturing technique widely used in the paper industry to improve the physical properties of paper, including surface strength, wet ability, surface morphology, and barrier properties (11,12). The most widely used surface sizing agent in papermaking is polyvinyl alcohol (PVA) (13–15) due to excellent transparency, elasticity, and high strength. However, a single PVA film can be poor in heat resistance, water resistance, paper

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strength, and surface properties (16). Moreover, PVA has poor biodegradability and relatively large environmental pollution (16). Water-soluble polyester has water-soluble, stable colloidal dispersion, solubility, good film-forming, hygroscopic, heat resistance, thermal viscosity (17), and excellent mechanical properties, which can well meet the requirements of paper surface sizing. Water-soluble polyester contains an organic macromolecular structure capable of having high adhesion to the fiber macromolecules. At the same time, polar groups of water-soluble polyester react with the hydroxyl group on the paper fiber. After drying, hydrogen bonds are formed to form a network structure of plant fibers, resulting in the increase of the strength of paper and other physical properties. In conclusion, applying the water-soluble polyester to the surface sizing of paper can not only improve the various properties of paper but also contribute to environmental protection. It is a new type of environmentally friendly surface sizing agent. Currently, the application of water-soluble polyester on paper surface sizing has not been reported.

In this article, solvent-free multibranched water-soluble polyester was prepared by introducing trimethylolpropane and adopting a two-step transesterification-copolymerization method, which increases the activity of water-soluble polyester. Hence, the toughness of the polymer and the ability to form hydrogen bonding with fiber hydroxyl are increased. The prepared water-soluble polyester is first applied to the paper surface sizing, providing a new idea for the research and development of the surface sizing agent. The properties of WPET are investigated based on the average relative molecular weight, dynamic light scattering (DLS), and rheology. Subsequently, the paper features are studied by testing folding endurance, tear resistance, deflection, tensile index, and contact angle. Finally, the surface sizing process is studied through SEM.

2 Materials and methods

2.1 Materials

Dimethyl terephthalate (DMT, >99%), sodium dimethyl isophthalate-5-sulfonate (SIPM, >99%), trimethylolpropane (TMP, >99%), and ethylene glycol (EG, >99%) were analytically pure and purchased from Shanghai McLean Biochemical Technology Co. Ltd. *N,N*-Dimethyl ethanolamine (DMEA, >99%) were analytically pure and

purchased from Tianjin Fuchen chemical reagent factory. All the solutions were prepared in distilled water.

2.2 Synthesis of water-soluble polyester (WPET)

WPET was synthesized according to the reaction pathway presented in Scheme 1. The synthesis of the water-soluble polyester was performed through two steps of transesterification and polycondensation. In the first step, DMT, SIPM, EG, and TMP as monomers with catalysts of dibutyltin oxide were placed in a 500 mL three-neck flask equipped with a magnetic stirrer and a thermometer. The mixture was heated in an oil bath at 180°C until dissolved. Then, the mixture was reacted for 1 h with methanol flowing out. Finally, the temperature of the mixture was gradually increased to 190°C and was held there for 4 h until no methanol flowed out. The esterification reaction was completed.

In the second step, the mixture was heated to 200°C and stirred for 1 h. Then, the pressure in the reactor was reduced to about 100 Pa. Meanwhile, the mixture was heated to 210°C and reacted for 1 h until no diols flowed out. After determination, the distillate of diol was about 30 mL. The reaction stopped. Finally, the viscous product obtained was decanted into a ceramic bowl and cooled to a hard tough resin.

According to our experiments and the following conditions: $-\text{COO}/-\text{OH}$ molar ratio of 1:2, we synthesized four water-soluble polyesters with different raw material ratios, which are presented in Table 1.

2.3 The dispersing process of water-soluble polyester solution

Twenty milliliters of distilled water and 0.2 g dry WPET were added into a 50 mL three-neck flask and stirred. The mixture was heated to 90°C and maintained at the temperature under stirring to dissolve the sample. Finally, *N,N*-dimethyl ethanolamine was added into the WPET solution to adjust the pH to 7, which was to meet the paper surface sizing requirements.

2.4 Surface sizing of cellulose fiber paper

A sheet of pristine 80 g/cm² cellulose fiber paper was placed on the working plate of an ST-1-260 coater (Shaanxi University of Science and Technology, China).

Step 1. Transesterification

Step 2. Polycondensation of the reaction products generated in transesterification.

Scheme 1: Schematic of the synthesis of WPET.

Before surface sizing, the paper sheet was firmly pressed onto the working plate to prevent any folding or curling and was then fixed. Next, the sizing solution was poured on one side of the paper sheet, and a coating roller was used at a constant rate of 3.0–4.0 mm/s for the purpose of sizing the paper uniformly. The sized paper sheet was dried for 5 min at 100°C. The sizing schematic diagram is shown in Figure 1.

2.5 Characterization of water-soluble polyester (WPET)

Fourier transform infrared (FTIR) spectra were recorded on an FTIR spectrometer (VECTOR-22, Bruker) in the range of 4,000–500 cm⁻¹ using the KBr pellet technique (resolution = 4 cm⁻¹, number of scans = 10).

The ¹H NMR spectra were recorded on a Bruker AVANCE-400 MHz nuclear magnetic resonance (Bruker, Germany) using dimethyl sulfoxide (DMSO) as solvent of the water-solution polyester.

The molecular weight was determined by a waters/1,515 gel permeation chromatography (GPC). Dimethylformamide (DMF) was used as a solvent, and polystyrene standards were used for calibration.

Table 1: Proportion of raw materials

Product number	SIPM (mol)	DMT (mol)	TMP (mol)	EG (mol)
WPET1	3.5	6.5	1	19
WPET2	3	7	2	18
WPET3	2.5	7.5	3	17
WPET4	2	8	4	16

Figure 1: Schematic diagram of water-soluble polyester sizing solution sizing on paper surface.

The Zetasizer nano-ZS90 laser light scatterer was used to measure the particle size and particle size distribution of the emulsion (Malvern, UK). The test temperature was 25°C. The laser angle was 90°, and the laser wavelength was 633 nm.

The Ultima IV X-ray powder diffractometer (Nippon Science Co, Ltd) was used to measure the diffraction peak of water-soluble polyester with a step length of 0.02° with the range from 5° to 50°.

The AR2000ex dynamic rheometer was used to measure the viscosity curve and flow curve of 20% water-soluble polyester emulsion at 30°C, 60°C, and 90°C. The shear rate range was 10–200 s⁻¹.

2.6 Characterization of the sized cellulose fiber paper

The sized cellulose fiber paper characteristics are as follows:

- For each folding endurance test, seven specimens (15 × 100 mm²) were prepared, and all tests were performed on an YQ-Z-31 vertical folding tester (Sichuan Changjiang Paper Instrument, China).
- For each tear resistance test, seven specimens (63 × 75 mm²) were prepared, and all tests were performed on an SLD-J paper tear degree tester (Sichuan Changjiang Paper Instrument, China).
- For each deflection test, seven specimens (70 × 38 mm²) were prepared, and all tests were performed on a Derrick DRK106 paper board stiffness tester (Sichuan Changjiang Paper Instrument, China).
- For each tensile index test, seven specimens (250 × 15 mm²) were prepared, and all tests were

performed on a ZL-100A/300A paper and cardboard tensile testing machine (Sichuan Changjiang Paper Instrument, China).

- For each contact angle test, seven specimens (10 × 15 mm²) were prepared, and all tests were performed on a Static drop contact angle tester.
- The papers without sizing and after sizing were cut into 100 × 100 mm². The weight of the paper without sizing was determined as w_0 , and the weight of the paper after sizing was determined as w . Then, the paper dried to the constant weight in an oven at 105°C. The glue-hanging quantity in the paper was calculated according to Eq. 1:

$$\text{The glue-hanging quantity} = (w - w_0)/w \times 100\% \quad (1)$$

- The surface and cross-sectional morphology of the paper sheets were observed on an environmental scanning electron microscope (SEM; s-4800 Hitachi, Tokyo, Japan). All of the samples were coated with gold under a vacuum before SEM observation.

3 Results and discussion

3.1 Water-soluble polyester properties

3.1.1 FTIR and ¹H NMR analysis

WPET3 sample was used for testing the IR and ¹H NMR spectrum of WPET. The IR spectrum of WPET and SIPM is shown in Figure 2. The infrared spectrum of SIPM is

shown in Figure 2a. The stretching vibration peak of the ester group ($\text{C}=\text{O}$) is at $1,735\text{ cm}^{-1}$. The peak of out-of-plane bending absorption of ($\text{C}-\text{H}$) on the aromatic ring is at 752 cm^{-1} . The peaks at $1,228$, $1,138$, and $1,049\text{ cm}^{-1}$ are the characteristic absorption peaks of $\text{S}=\text{O}$ of sulfonic acid groups. The infrared spectrum of WPET is shown in Figure 2b. The absorption peaks with a broad distribution at $3,608$ and $3,278\text{ cm}^{-1}$ are the alcoholic hydroxyl groups. The peaks at $2,954$ and $2,887\text{ cm}^{-1}$ are attributed to the $-\text{CH}_3$, $-\text{CH}_2-$, and tertiary alkyl groups, indicating that trimethylolpropane is polymerized to the molecular chain. The absorption peaks of carboxylic acid ester ($\text{C}=\text{O}$) on the aromatic ring are at $1,720$, $1,460\text{ cm}^{-1}$. The peak of out-of-plane bending absorption of ($\text{C}-\text{H}$) on the aromatic ring is at 752 cm^{-1} . The absorption peaks with strong bands are at $1,271$, $1,121$, and $1,028\text{ cm}^{-1}$, which showed the absorption peak of $\text{S}=\text{O}$ in WPET (26), which could be regarded as the presence of $-\text{SO}_3\text{Na}$ that could improve the water solubility of WPET and contribute to its better performance in sizing.

Figure 3 shows the ^1H NMR spectra of water-soluble polyesters. The resonance overlapping peaks of para-disubstituted and meta-substituted hydrogen on the benzene ring appear at 8.09 and 8.41 ppm , respectively. The absorption peak of active hydrogen hydroxyl hydrogen appears at 4.97 ppm . The proton peaks of the near carbonyl group of trimethylolpropane and ethylene glycol appear at 4.66 and 4.32 ppm , respectively. The absorption peaks of hydrogen on a methylene carbon bonded to the hydroxyl group appear at 4.51 and 3.72 ppm , respectively. The hydrogen on the methylene carbon and hydrogen on the terminal methyl group of trimethylolpropane appear at 1.36 and 0.91 ppm , respectively.

Figure 2: FTIR spectra of WPET.

Figure 3: ^1H NMR spectra of WPET.

Based on the spectra, it can be concluded that the target product (WPET) is successfully prepared (28,29).

3.1.2 Average molecular weight and particle size of WPET

The molecular characteristics of water-soluble polyesters are presented in Figure 4. For polymer solutions, weight-average molecular weight (M_w) represents the average molecular weight per unit weight. The values of M_w are shown in Figure 4. It can be revealed that the M_w decreased from $19,143$ to $8,731\text{ g/mol}$ when the SIPM content increased from 16.43% to 23.95% , as expected for the synthesis method used. This is due to the increase of steric resistance caused by the mesosulfonic acid group of SIPM, resulting in drop of the polymerization degree. Meanwhile, the smaller molecular weight is beneficial to permeate the paper fiber (18) and to make the physical crosslinking effect of surface sizing solution on paper fiber more obvious.

In this study, sodium sulfonate ($-\text{SO}_3\text{Na}$) in the SIPM unit is a strong ionic group that exhibits high polarity. The amount of $-\text{SO}_3\text{Na}$ ionic groups changes therewith. This directly leads to the variation of WPET polarity and the interaction of WPET molecules and water, which allow the homogeneous dispersion in water. Favorable water solubility of a sizing agent is good for uniform dispersion of WPET molecules in water and is conducive to the surface sizing. The better the dispersibility in water, the smaller the particle size of the solution. Figure 5 shows the effects of the SIPM content on the particle

Figure 4: Average molecular weight at different mass concentrations of SIPM.

size. It is clear that the particle size of the WPET solution decreases from 220.2 to 126.2 nm and decreases first and then increases with the increasing SIPM content. However, the particle size of the WPET solution reaches a minimum of 126.2 nm when the SIPM content is 17.98%. It can be ascribed that the sodium sulfonate ($-\text{SO}_3\text{Na}$) in SIPM is present in small quantity, and SIPM will have difficulty dissolving. Nevertheless, when the amount of is more than 17.98%, the particle size increases. It may be due to the larger steric hindrance of the sulfonate group, which reduces the solubility. Meanwhile the much sulfonic acid groups will add more hydrophilic chain segments, resulting in poor water-resistance after surface sizing.

To sum up, SIPM mole is 2.5 mol (SIPM mass concentration is 17.98%) and DMT mole is 7.5 mol.

Figure 5: Particle size of emulsion at different mass concentrations of SIPM.

3.1.3 Crystallization properties

The XRD patterns of different content of TMP are shown in Figure 6. In agreement with the literature, WPET shows main diffraction peaks at 21.03, assignable to (021) reflection planes of the a-form crystal (19,20) when the molar number of TMP is 1 and 2. Conversely, as the TMP content increases, the diffraction peak intensity of WPET decreases, showing patterns typical of an amorphous polymer. In conclusion, the decreasing crystallinity is due to the destruction of the original linear molecular chain structure and the formation of the branched structure. The branching structure destroys the regularity of the molecular chain and weakens the movement ability of the chain segment, resulting in a decreased crystallization rate. According to the previous studies (24,25), increasing the flexibility of polymer segments and reducing the crystallinity of polymers are effective methods to improve polymer toughness, resulting in an enhancement of the strength of the paper. Therefore, TMP mole is 3 mol (TMP mass concentration is 11.10%) and EG mole is 17 mol.

3.1.4 Rheological behavior

At a certain shear rate, the flow of water-soluble polyester solution conforms to the power law (Ostwald–de Waele) model, namely,

$$\tau = K\gamma^n, \quad (2)$$

where τ is shear stress (Pa). γ is the shear rate (s^{-1}), K is the viscosity coefficient, and n is the flow exponent. Taking the logarithm of both sides of Eq. 2 can yield the following equation:

$$\lg \tau = \lg K + n \lg \gamma. \quad (3)$$

Figure 6: XRD patterns of different contents of TMP.

WPET3 sample was used for testing the rheological behavior of WPET. Figures 7 and 8 show, respectively, viscosity curves and rheological curves of water-soluble polyester solutions. Combined with Table 2 and Figure 7, it can be seen that the regression coefficient (R^2) of water-soluble polyester solutions at different temperatures is close to 1. It is indicated that the Ostwald-de Waele model can be used to describe the rheological behavior of water-soluble polyester solutions. Figure 8 shows that the viscosity of water-soluble polyester solution decreases with the increase of the shear rate. Furthermore, it indicates that water-soluble polyester solution presents shear thinning behavior and is a typical pseudoplastic fluid, which is conducive to the sizing process of the paper surface (21,22).

Figure 8 shows that the relationship between $\lg \tau$ and $\lg \dot{\gamma}$ is linear, which is in line with the characteristics of pseudo-plastic fluids. At the same time, as the flow index n increases with the increase of temperature, the flow performance will increase. It can be ascribed to the molecular chain section containing hydrophobic chain of dimethyl terephthalate. The hydrophobic chain joints are arranged in a curly conformation in water and will aggregate with each other due to the hydrophobic action, which indicates certain microscopic heterogeneity. As the temperature increases, the thermal movement of hydrophobic segments increases and the hydrophobic effects are weakened. Meanwhile, the hydrophobic microzone is vulnerable to shear failure and the crimp conformation is easy to stretch in the shear flow field (27). Therefore, the flow degree and flow index n increase. In Table 2, it is clear that the consistency coefficient (k) decreases with the temperature increases, which indicates the decrease of the fluid viscosity. Therefore, the retention of the water-soluble polyester fluid on the paper can be

Figure 7: Viscosity of WPET at different temperatures.

Figure 8: Rheological of WPET at different temperatures.

increased, which affects the strength of the paper and other physical indicators.

3.2 Surface sizing agent strengthening mechanism

Water-soluble polyester contains the organic macromolecular structure and the existence of highly branched hydroxyl. Simultaneously, the paper fiber has more hydroxyl groups. Hydroxyl groups on water-soluble polyester combine with hydroxyl groups on paper fiber to form hydrogen bonding force, which can improve the adhesion strength of the fiber and shorten the distance between the fibers to form a dense mesh structure. The strength of the paper and waterproof performance and other properties of paper are improved. Subsequently, WPET3 sample was used for testing the paper performance.

3.2.1 Effects on paper performance

Figure 9a and b show the effects of different WPET mass concentrations on the properties of sized paper. The water-resistance and mechanical properties of sized paper are improved with the appropriate mass concentration of

Table 2: Rheological parameters of WPET at different temperature

Temperature (°C)	n	k	R^2
30	0.42	5.36	0.99517
60	0.47	3.98	0.99976
90	0.59	2.21	0.99836

WPET. It is clear that the mechanical properties (folding endurance, tear resistance, deflection, and tensile index) of sized paper increase first and then slightly decrease with the increasing WPET mass concentration. It can be observed that hydroxyl groups on water-soluble polyester increase with the increasing WPET mass concentration. Hydrogen bonding force combining with hydroxyl groups is increased. Thus, it can improve the adhesion strength of the fiber and decrease the distance between the fibers to form a more dense mesh structure. In addition, more dense mesh structure has better resistance to an external extension force, and the strength of the joint between the fibers can be improved, resulting in the improved tensile strength, tear resistance, and other surface strengths.

However, the mechanical properties of sized paper slightly decrease when WPET mass concentration is larger than 4% (relatively to dry pulp) since it may react with the hydroxyl group on PVA to produce a self-cross-linking phenomenon, resulting in difficulties to penetrate into the paper. The folding strength decreases slightly from 115 to 105 times when WPET mass concentration is

more than 4% (relatively to dry pulp), owing to the increased self-crosslinking and rigidity.

The graph of the paper contact angle with different WPET mass concentrations is shown in Figure 10. As WPET mass concentration increases, the paper contact angle continues to increase first and then slightly decreases (range from 60.96° to 85.95°). The sizing paper displays the optimum water resistance when WPET mass concentration is 4% (relatively to dry pulp). The phenomena prove that the paper water resistance enhances with the appropriate WPET mass concentration, which can be ascribed to the increase of the ester group content and the hydrophobic groups, resulting in their tight alignment outward and formation of a low energy surface on the surface of the paper. In addition, the water-soluble polyesters have a macromolecular structure similar to fibers, which can increase the adhesion to fibers (23) and decrease the fiber-to-fiber distance to form a firm and tight mesh structure, resulting in an improved water resistance.

3.2.2 Effects of temperature

The glue-hanging quantity in the paper of WPET and PVA sizing fluid with different temperatures are shown in Figure 11. It can be seen that the glue-hanging quantity in the paper of WPET and PVA gradually increases and then slightly decreases when there is an increase in the temperature. Meanwhile, glue-hanging quantity in the paper of WPET is better than PVA. The viscosity of PVA or WPET sizing solution decreases with the increase of the temperature. A lower viscosity is conducive to a better sizing. It is also observed that the hydrogen bonding between PVA and water molecules weakens at the sizing

Figure 9: Mechanical properties of paper at different WPET mass concentrations: (a) folding endurance and deflection and (b) tear resistance and tensile index.

Figure 10: Contact angle of paper at different WPET mass concentrations.

temperature of 80°C, which makes the water solubility become worse. At the same time, some PVA molecules will collect on the surface of the aqueous solution to form a small amount of skinning, which can reduce the glue-hanging quantity in the paper. However, the water-soluble polyesters sizing solution presents a light blue, nonflocculating fluid at 80°C and has a low viscosity, which can increase the glue-hanging quantity in the paper. But the viscosity is too low when the water-soluble polyesters sizing solution is higher than 80°C, which will affect the sizing percentage.

Figure 11: Glue-hanging quantity in the paper of WPET and PVA sizing fluid at different temperatures.

3.2.3 Morphology analysis

Figure 12 shows surface SEM morphology of original paper and sized paper. It can be observed that the space between the fibers is large on the original paper. The distance of fibers in paper sized with WPET dispersion becomes tight, suggesting that a dense mesh structure is able to form on the surface of the paper. In addition, a homogeneous film of WPET can be formed on the surface of the paper, and the gap between fibers is filled with WPET. These phenomena indicate that WPET is able to penetrate into the paper, improve the adhesion strength of the fiber, and enhance the bond strength between fibers.

4 Conclusions

By introducing trimethylolpropane and adopting a two-step transesterification-co-condensation polymerization method, solvent-free multi-branched water-soluble polyester was prepared at high temperature. The properties of WPET and its surface strengthening mechanisms are studied. The average relative molecular weight of the obtained polymer is 9,632, the particle size of the water-soluble polyester microemulsion is 126.2 nm, and the dispersion coefficient is 0.010 when the mass concentration

Figure 12: SEM surface morphology of unsized paper (a) and sized paper (b) at different magnification.

of sodium dimethyl isophthalate-5-sulfonate (SIPM) is equal to 17.98%. WPET solution exhibits good dispersion and stability. With the increase of the TMP content, the crystallization rate of polyester decreases, showing patterns typical of an amorphous polymer. The viscosity of water-soluble polyester solution decreases with the increase of shear rate and the temperature. The flow performance increases and the consistency coefficient decreases with the increase of temperature, suggesting that WPET solution is a pseudoplastic fluid and conducive to the sizing process of the paper surface. The glue-hanging quantity in the paper of WPET and PVA gradually increases and then slightly decreases with the increase in temperature. At the temperature of 80°C, the water-soluble polyesters sizing solution exhibits good stability and the glue-hanging quantity in paper attains 5.95%.

In this study, trimethylolpropane is introduced in the synthesis of polyester, which can improve the activity of polymer and enhance the ability of forming hydrogen bonding with fiber hydroxyl. The prepared water-soluble polyester is used for paper surface sizing for the first time. The mechanical property of paper is studied under the different mass concentrations of WPET. When the ratio of the mass concentration of WPET (relatively to dry pulp) is 4%, the sizing paper mechanical properties reach the optimum. Compared with pure PVA, the sizing paper mechanical properties clearly enhanced. Finally, the surface sizing process is studied through SEM. Compared with the original paper, the sizing paper forms a homogeneous film and a dense mesh structure on the surface of the paper, resulting in enhancing the bond strength between fibers.

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