Process Variables and the Performance of Soybean-oil Rosin-based Polyester as an Internal Sizing Agent

Yazhou Xu,[a,b] Yuxiang Chen,[a,b,c,d,]* Zhendong Zhao,[a,b,c] and Shichao Xu [a,b,c]

Soybean-oil rosin-based polyester (SRP) has many uses in papermaking, but its performance as an internal sizing agent differs depending on the circumstances. In this study, a comprehensive laboratory approach was used to investigate the process variables affecting SRP application. Five levels of SRP (0.5%, 1.0%, 1.5%, 2.0%, and 2.5%), five levels of aluminum sulfate (0.5%, 1.0%, 1.5%, 2.0%, and 2.5%), and five levels of cationic polyacrylamide (0.05%, 0.1%, 0.15%, 0.2%, and 0.25%) were considered to determine the best process variables within a pH range of 5.0 to 9.0. Aspects that were considered included the mechanical properties (tensile, burst, and tear indices), water resistance (Cobb test, dynamic contact angle test, and scanning electron microscopy), and chemical usage (economical and environmentally friendly procedures). The optimum conditions based on these factors were 1.0% SRP, 1.0% aluminum sulfate, and 0.15% cationic polyacrylamide levels at a pH of 7.0. The results showed that in the optimal sizing system, 15% calcium carbonate can be tolerated.

Keywords: Internal sizing; Process variables; Soybean oil; Rosin; Polyester

*Contact information: a: Institute of Chemical Industry of Forest Products, CAF, National Engineering Lab for Biomass Chemical Utilization, Key Lab of Chemical Engineering of Forest Products, National Forestry and Grassland Administration, Key Lab of Biomass Energy and Material, Nanjing 210042, Jiangsu, China; b: Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, Nanjing Forestry University, Nanjing 210037, Jiangsu, China; c: Research Institute of Forestry New Technology, CAF, Beijing 100091, China; d: Jiangsu Qianglin Bio-energy and Bio-materials Limited Company, Liyang 213364, Jiangsu, China; *Corresponding author: cyxlhs@126.com*

INTRODUCTION

Paper has a strong tendency to absorb water, especially paper that contains hemicellulose, with poor mechanical properties (Katz *et al*. 2003). To mitigate this limitation and increase the water repellency of paper, hydrophobic sizing is performed for most paper grades, especially for writing and packaging papers.

Soap rosin is a sizing agent with a long history of success in papermaking and is usually suited for a pH less than 6.5 (Rahmaninia *et al.* 2016). When paper is sized under neutral to alkaline conditions, the equipment is not corroded, the paper is not easily hydrolyzed, and calcium carbonate can be used as a filler. Changing the papermaking process to favor neutral-to-alkaline conditions puts pressure on the industry to seek new sizing agents in this respect. Alkylketene dimer (AKD) was the first agent to be used for this process (Varshoei *et al*. 2014). As a reactive sizing agent, AKD is bonded to paper by esterification of a quaternary lactone with a hydroxyl group of cellulose in the paper. It is hydrophobic because of hydrophobic hydrocarbons and has advantages such as operation without alum and sufficient sizing degrees for paper at low addition levels (Lindström and Larsson 2008). However, some problems have been associated with the use of synthetic sizing agents. These include the low friction coefficient of AKD-sized papers, size reversion, deposit formation on the paper machine and press felts, relatively high costs, and insufficient sizing effect in paper when evaluated at the reel of the paper machine (Kitaoka *et al*. 1997; Wu *et al*. 1997).

Because of its nonpolar, tricyclic molecular structure, rosin has excellent water resistance, which is critical for its use in internal sizing (Wang *et al*. 1999). Rosin sizing agents are usually inexpensive, user friendly, and tolerant of other wet-end additives. Also they have a longer shelf life than other sizing agents (*e.g.*, AKD). Because of these advantages, technical teams in many papermaking mills want to switch to neutral-to-alkaline-pH papermaking systems without abandoning rosin-based sizing.

Consequently, modified rosin sizes have attracted interest in the field (Ozaki and Sawatari 1997; Kitaoka *et al*. 2000; Matsushita *et al*. 2004). Alternatively, some researchers have investigated sizing strategies with esterified rosins (Wang *et al*. 2003; Liu *et al*. 2006; Hubbe 2007; Yao *et al*. 2011). Compared with the conventional anionic and dispersed rosin sizing agents, the rosin-ester sizing agent remarkably improves the stability of rosin particles in alkaline pulp suspensions. Therefore, such products can be used as an internal sizing agent for alkaline papermaking (Wang and Tanaka 2000; Wang *et al*. 2000). Although our information about different aspects of rosin application in paper mills (pH adjustment, tolerance assessment, optimum chemical dosages, *etc*.) has considered many issues (Seppänen *et al*. 2000; Kitaoka *et al*. 2001; Mattsson *et al*. 2002; Hamzeh *et al*. 2008), combining rosin-based sizing agents and AKD seems to need more attention, because of lacking research to try to combine the advantages of AKD and rosin. Some of these areas, such as retention aid dosages, pH adjustment, and tolerance assessment, can provide a proper lead for optimizing the process.

Soybean oil has a similar hydrophobic chain structure to AKD. This study attempted to combine the advantages of rosin and AKD and prepared a soybean-oil rosin-based polyester (SRP) sizing agent that can be used for neutral sizing. This study also explored process variables that facilitate the development of an SRP sizing agent in the papermaking field.

EXPERIMENTAL

Materials

Bleached wood pulp (50% conifer and 50% broadleaf) with a beating degree of 34 °SR was kindly provided by Anhui Baiyi Biological Technology Co., Ltd. (Anhui, China). Wetland rosin was a commercial product from Guangxi, China. Soybean oil (The oleic acid mass fraction is 51.0%, the linoleic acid mass fraction is 28.0%, and the palmitic acid mass fraction is 11.9%, the acid value is 0 mg/g, and the hydroxyl value is 22.4 mg/g) and maleic anhydride (99%) were from Shanghai Lingfeng Chemical Reagent Co., Ltd. (Shanghai, China). Glycerol (99%) and calcium carbonate ($CaCO_3$) were purchased from Aladdin Industrial Corporation (Shanghai, China). Ethoxylated nonylphenol sulfosuccinic acid half ester disodium salt (40%) was supplied by Shanghai Jinjinle Industry Co., Ltd. (Shanghai, China). Cationic polyacrylamide (CPAM) (molecular weight of 6 million g/mol, charge density of 1.95 mmol/g) was from Yixing Bluwat Chemicals Co., Ltd. (Yixing, Jiangsu, China). Aluminum sulfate ($Al_2(SO_4)_3$) and other chemicals were analytically pure reagents. All materials were used without further purification.

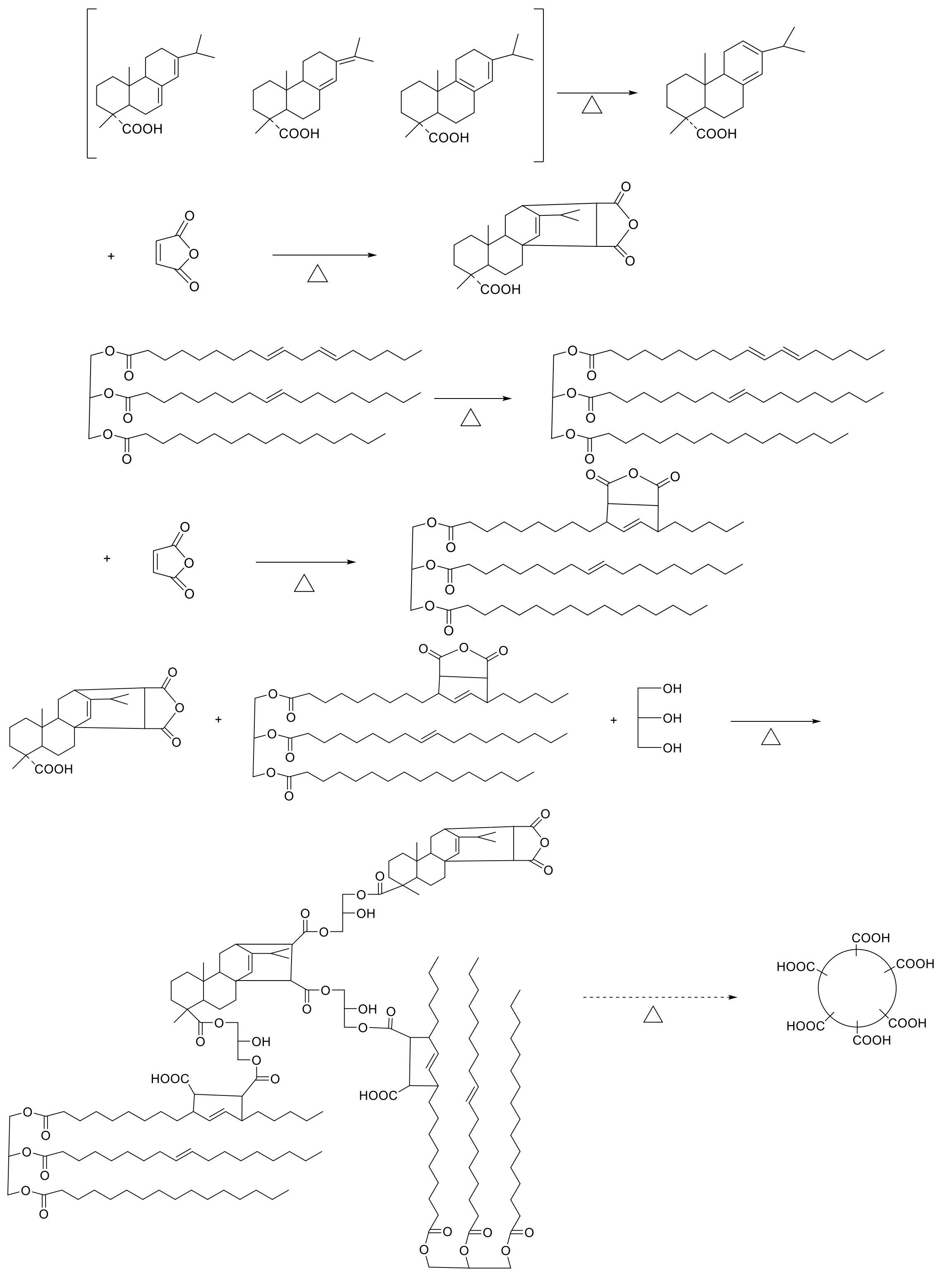

Fig. 1. The synthesis route of SRP

Preparation of the SRP sizing agent

According to Xu *et al*. (2019), into a four-necked flask equipped with a stirring device, 50 g of rosin, 20 g of soybean oil, and 10 g of maleic anhydride were placed and protected with nitrogen. Maleopimaric acid and the anhydride adduct of soybean oil were obtained by reacting at 185 °C for 2 h. Then 2.5g of glycerol was added to make the material carboxy-carboxyl ratio equal to 0.25 (the amount of carboxyl groups in the material can be obtained by measuring the acid value, thereby obtaining the ratio of the amount of the material hydroxyl group to the carboxyl group). After each reaction at 210 °C and 225 °C for 1 h, soybean-oil-rosin-based polyester SRP was prepared by heating to 250 °C for 3 h. Figure 1 shows the synthesis route of SRP.

The SRP was first melted at 120 °C. Ethoxylated nonylphenol sulfosuccinic acid half ester disodium salt, preheated to 90 °C, was introduced within 10 min with gentle stirring to obtain a homogenous water-in-oil emulsion. The emulsion was inverted to an oil-in-water emulsion by quickly adding 90 °C deionized water at a stirring speed of 1000 rpm. The emulsion was then cooled to the ambient temperature in a cold water bath. The SRP latex was obtained, and its physical and chemical properties were measured (Table 1).

Table 1. Physical and Chemical Properties of SRP Latex

Property	Description or Value
Appearance	Milky bluish-white liquid
pH	5 to 6
Viscosity	<100 mPa·s
Particle size	0.2 µm
Solid content	Approximately 25%

Methods

Characterization

Fourier transform infrared (FTIR) spectroscopy (Vertex 70; Bruker Optik GmbH, Ettlingen, Germany) analyses of samples were carried out by using compressed pellets of KBr with SRP. All FTIR spectra were recorded using absorbance mode in the wavenumber range of 500 cm^{-1} to 4000 cm^{-1}. The hydrodynamic diameter and size distribution were measured by dynamic light scattering (Zetasizer 3000; Malvern Instruments, Malvern, UK) three times to yield an average.

The apparent viscosity of the latexes was determined using a rotational viscometer (NDJ-5S; Shanghai Geological Instrument Research Institute, Shanghai, China). Droplets having a volume of 5 µL of deionized water were dropped onto the surface of the paper, and the water contact angle for the sized paper was measured with an optical contact angle apparatus (DSA 100; Kruss Scientific Instruments, Hamburg, Germany) equipped with a video measuring system and high-resolution CCD camera. The surface morphology of the sized paper coated with gold was observed using a scanning electron microscope (S-3400I, Hitachi, Tokyo, Japan).

Internal sizing method

Handsheets with a basis weight of 70 g/m^2 were made using a CHCP-02 round sheet former (Jinan Shengtuo Mechanical and Electrical Equipment Co., Ltd., Jinan, China.). To prepare sized handsheets, 1.0% SRP sizing agent (relative to the absolute dry pulp mass) was added to a 0.5% pulp suspension, followed by 1.0% $Al_2(SO_4)_3$ (relative to the absolute dry pulp mass) and 0.15% CPAM (relative to the absolute dry pulp mass) at pH 7.0 (adjusted with 0.15 mol/L HCl and 0.15 mol/L NaOH). The handsheets were dried in a CHGZ-01 dryer (Jinan Shengtuo Mechanical and Electrical Equipment Co., Ltd., Jinan, China.) at 105 °C. The paper was allowed to dry at 23 °C and 50% relative humidity for over 24 h until further analysis; then, its properties were measured (Table 2).

Table 2. Measured Physical Properties and Measurement Methods of Prepared Sheets

Property	Standard
Basis weight (g/m^2)	ISO 536 (2012)
Cobb-60	ISO 535 (2014)
Tensile index	ISO 1924-2 (2008)
Burst index	ISO 2758 (2014)
Tear index	ISO 1974 (2012)
Contact angle	Instrument manual

RESULTS AND DISCUSSION

FTIR Analysis

The polyester was characterized by FTIR spectroscopy. The specific adsorptions of the main functional groups are shown in Fig. 2. The absorption peak at 1760 cm^{-1} corresponds to –COO–, which suggests that the reaction produced esters. No hydroxyl absorption peak appeared at 3490 cm^{-1}, indicating that the glycerin in the reaction completely reacted. The absorption peak at 1710 cm^{-1} was due to –COOH. These results imply that SRP with a terminal carboxyl group was obtained.

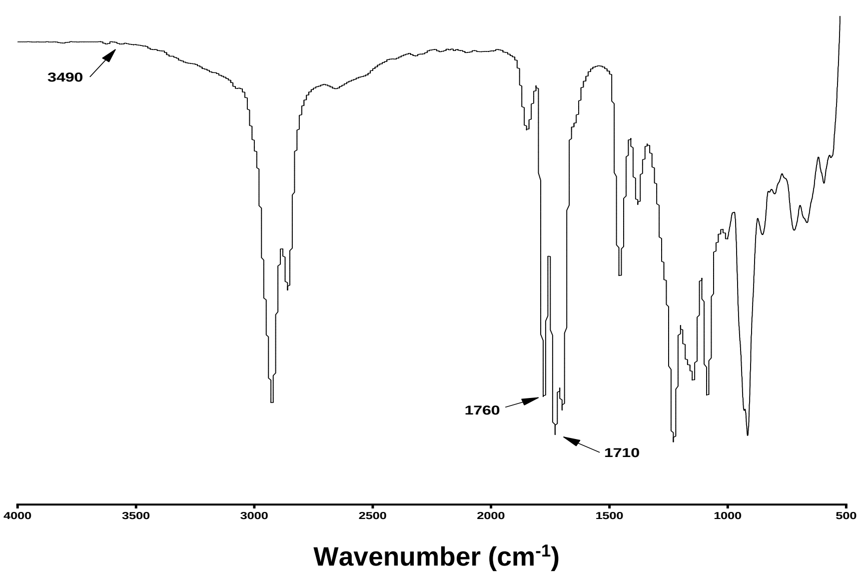

Fig. 2. FTIR spectrum of the SRP

Particle Size Distribution of SRP Latex

As the most important characterization parameter of the SRP latex, the particle size of the emulsion directly affects the emulsion's sizing effect and has an important influence on its stability.

As shown in Fig. 3, the polydispersity index of the SRP latex was 0.251, indicating that the particle size distribution of the latex was uniform, and the average particle size was 0.224 µm. The average diameter of commercially available sizing agent latex is less than 0.4 µm, and SRP latex can meet the requirements for practical use in terms of particle size.

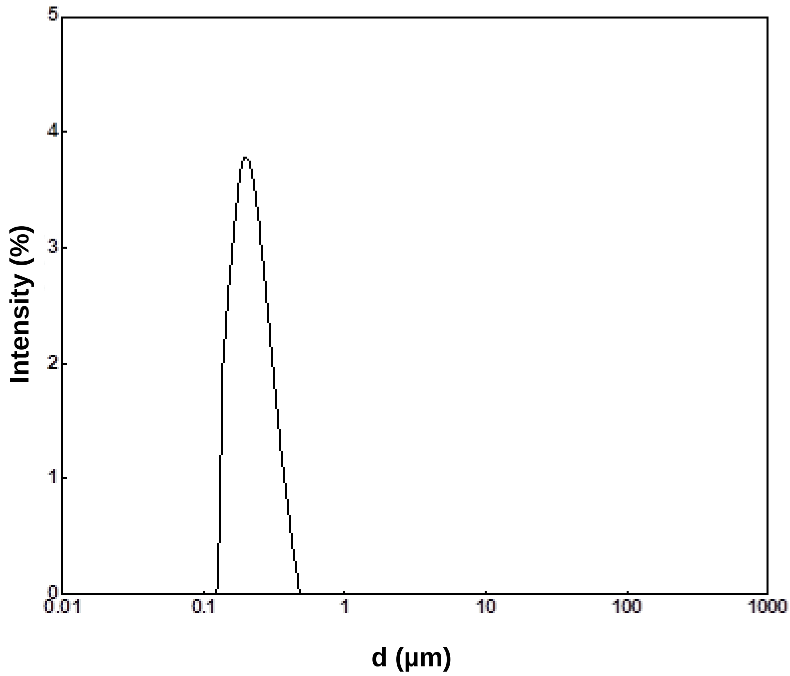

Fig. 3. Particle size distribution of SRP latex

Effect of SRP Dosage on Water Resistance

As shown in Fig. 4, under the conditions of 1.0% $Al_2(SO_4)_3$ and 0.15% CPAM at pH 7.0, the Cobb-60 of the handsheet decreased when increasing the SRP dosage from 0.5% to 2.5%. When the SRP dosage reached 1%, the rate of increase of the sizing degree markedly decreased. This was because the adsorbed amount of the polyester on the surfaces of the paper fibers increased with the increasing SRP sizing agent dosage, and the sizing degree correspondingly increased. However, the adsorption of the polyester particles to the fibers was nearly saturated when the SRP sizing agent dosage was increased to a certain value.

When increasing the amount of glue beyond this point, the fiber adsorption of polyester particles did not increase much, and the sizing degree slowly changed. Based on the conditions of the fiber, precipitant, and retention aid, the sizing degree could be effectively increased without simply increasing the amount of sizing agent. The appropriate sizing agent dosage should be selected based on the sizing cost and the sizing degree.

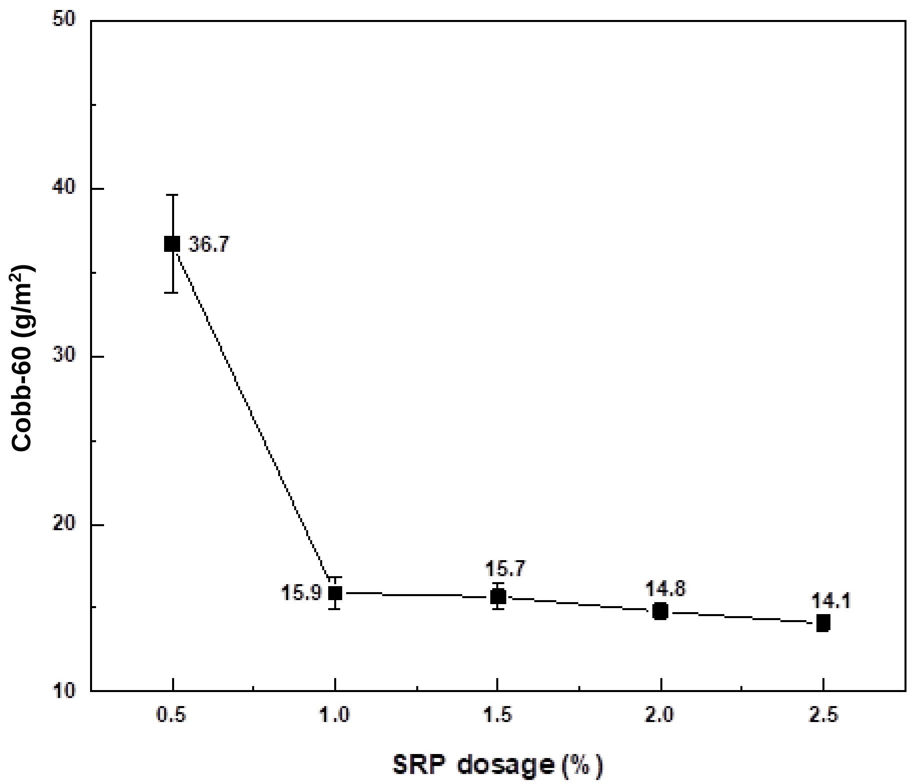

Fig. 4. Effect of SRP dosage on water resistance

Effect of SRP Dosage on the Mechanical Properties

As shown in Table 3, under the conditions of 1.0% $Al_2(SO_4)_3$ and 0.15% CPAM at pH 7.0, when decreasing the SRP dosage from 0.5% to 2.5%, the bursting index decreased 25.6%; the tear index decreased 8.2%; and the tensile index decreased 18.9%. This was probably because the tensile strength and the burst strength are mainly affected by the fiber bonding force and the average fiber length, whereas the main factor influencing the tear strength is the average fiber length. In the sizing process, the polyester granules mainly affected the bonding between the fibers, and they had no effect on the average length of the fibers. Consequently, the tensile strength and the breaking resistance were greatly decreased, while the tearing degree decreased less.

Table 3. Effect of SRP Dosage on the Mechanical Properties

SRP Dosage (%)	Burst Index ($kPa·m^2/g$)	Tear Index ($mN·m^2/g$)	Tensile Index (N·m/g)
0.5	3.01	17.03	45.66
1.0	2.95	16.51	43.06
1.5	2.73	16.33	41.23
2.0	2.52	15.95	38.55
2.5	2.24	15.63	37.02

Considering all aspects, such as avoiding superfluous chemical usage and the mechanical properties, the use of 1.0% SRP sizing agent was selected as the best treatment option.

Effect of Aluminum Sulfate Dosage on Water Resistance

Aluminum sulfate ($Al_2(SO_4)_3$) has important roles in internal sizing, affecting the retention of the sizing agent, the attachment of the sizing agent to the fibers, and the anchoring and orientation of the sizing agent molecules. Figure 5 shows that for 1.0% SRP sizing agent and 0.15% CPAM at pH 7.0, the water resistance effects of $Al_2(SO_4)_3$ dosages ranged from 0.5% to 2.5%. With increasing $Al_2(SO_4)_3$, the Cobb-60 values decreased at first and then increased slightly, and the sizing degree of the paper increased and then decreased slightly. This was because a certain amount of sizing agent only combined with a certain amount of aluminum sulfate; therefore, the optimum amount of aluminum sulfate was 1.0%.

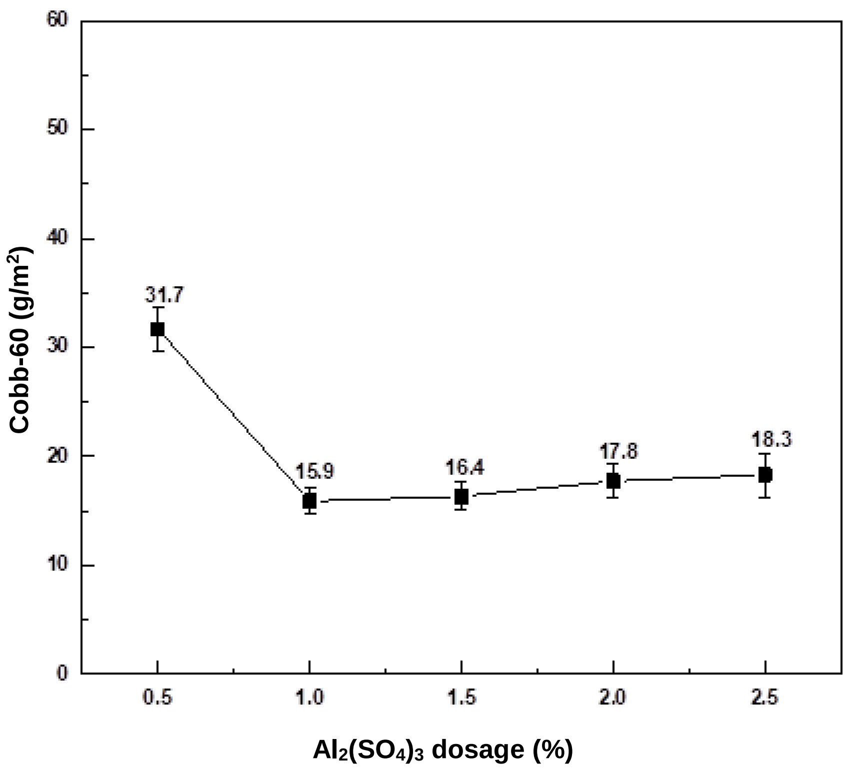

Fig. 5. Effect of $Al_2(SO_4)_3$ dosage on water resistance

Effect of CPAM Dosage on Water Resistance

Cationic polyacrylamide mainly achieves the retention effect by flocculation. It can resist the effects of fluid shearing forces to a certain extent, and it has good effects on sizing. However, if the amount of CPAM is too great, flocculation also occurs, resulting in uneven paper sheets; hence, the amount of CPAM is also an important parameter.

As shown in Fig. 6, with 1.0% $Al_2(SO_4)_3$ and 1.0% SRP sizing agent at pH 7.0, the CPAM dosage was changed from 0.05% to 0.25%. As the amount of CPAM increased, the Cobb-60 values decreased and then increased, and the sizing degree of the paper increased and then decreased. The decrease in sizing at the higher dosage levels might have been due to flocculation. Therefore, the optimum amount of CPAM was judged to be 0.15%.

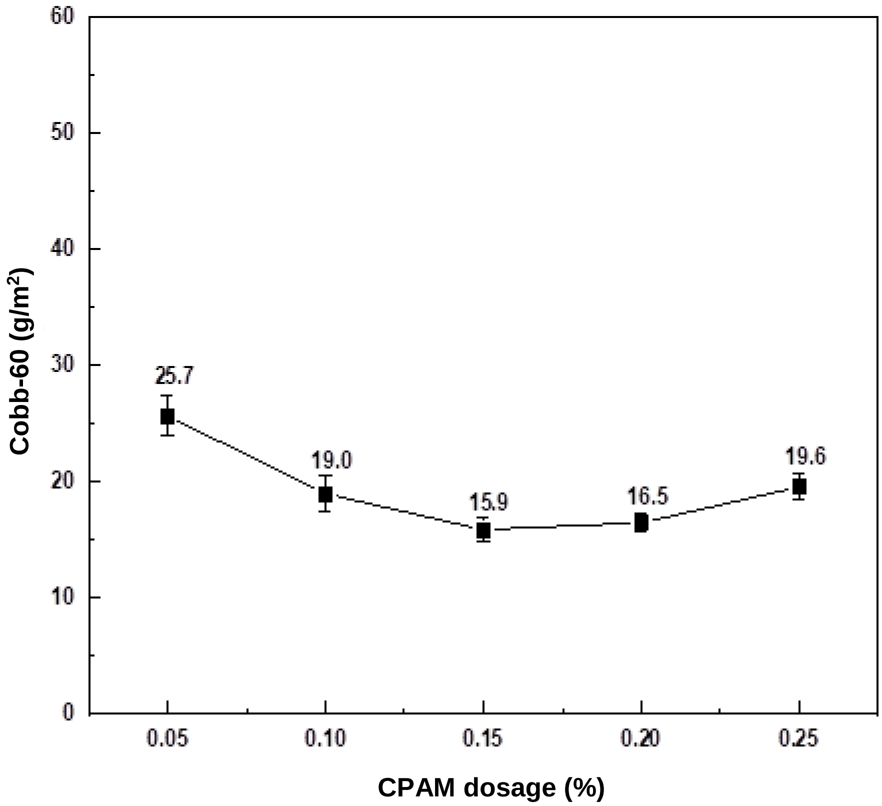

Fig. 6. Effect of CPAM dosage on water resistance

Effect of pH on Water Resistance

As shown in Fig. 7, with 1.0% SRP sizing agent, 1.0% $Al_2(SO_4)_3$, and 0.15% CPAM, the pH adjusted with 0.15mol/L HCl and 0.15mol/L NaOH was changed from 5.0 to 9.0. Cobb-60 remained mostly unchanged for pH $\leq$ 7.0, and the polyester sizing agent Cobb-60 value was 15.9 g/m^2 at a pH of 7.0. This result indicates that the SRP sizing agent can fully meet the requirements of neutral sizing. As the pH exceeded 7.0, Cobb-60 began to increase, and the sizing degree began to decrease. The first possible reason for this result is that aluminum sulfate began to exist as precipitated aluminum hydroxide, gradually reducing the effect of eliminating anionic impurities and joining the fibers to the polyester particles. Secondly, the pH affected the degree of ionization of the rosin acid carboxyl group in the polyester. As the pH increased, the degree of ionization of the carboxyl group also increased, along with the hydrophilicity. Therefore, the sizing degree began to decrease with pH > 7.0.

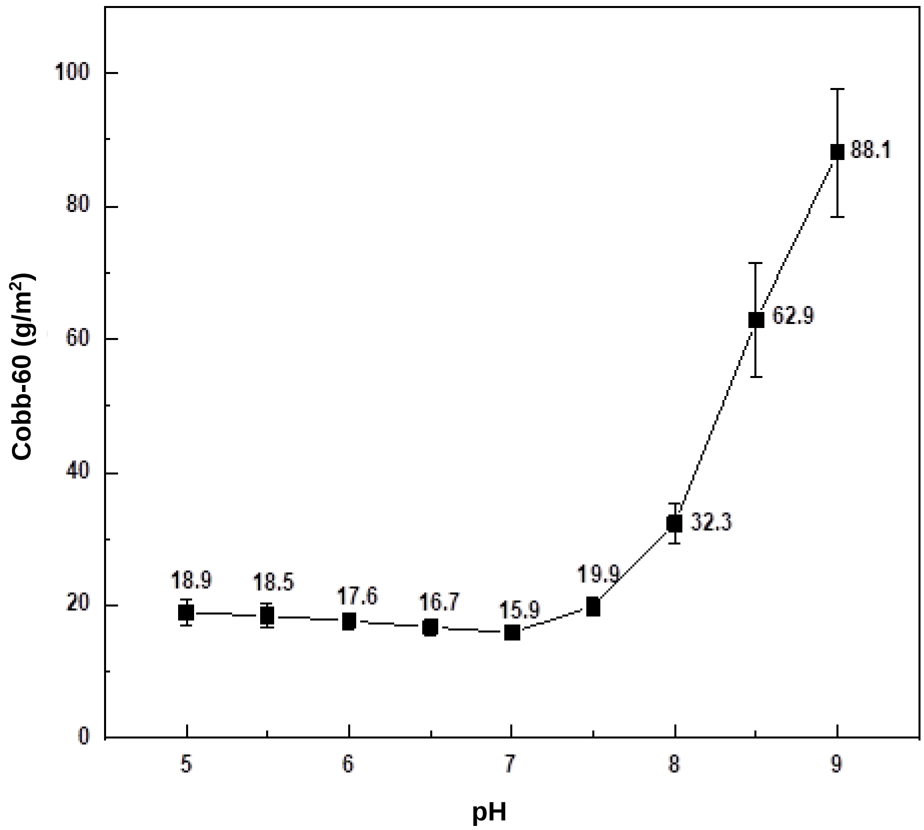

Fig. 7. Effect of pH on water resistance

In summary, the optimum sizing conditions were as follows: The SRP sizing agent dosage was 1.0% of the absolute dry pulp mass, the $Al_2(SO_4)_3$ dosage was 1.0% of the absolute dry pulp mass, and the CPAM dosage was 0.15% of the dry pulp mass at a pH of 7.0. For the paper obtained under these conditions, Cobb-60 was 15.9 g/m^2, the burst index was 2.95 kPa·m^2/g, the tear index was 16.51 mN·m^2/g, and the tensile index was 43.06 N·m/g.

Confirming the SRP Treatment Effects on Water Resistance Using Dynamic Contact Angle Measurement

After application of the SRP sizing agent, the dynamic contact angle (DCA) of a water droplet with the paper surface was tested (Fig. 8). The DCA of the treated papers (approximately 125°) was much greater than the DCA of the control samples (less than 90°), indicating that the applied sizing system successfully decreased the surface free energy of the fibers. The results showed that the paper treated under the optimal conditions required more time for the water droplet to absorb than did the control paper. In the control paper, the contact angle drastically decreased in only 5 s.

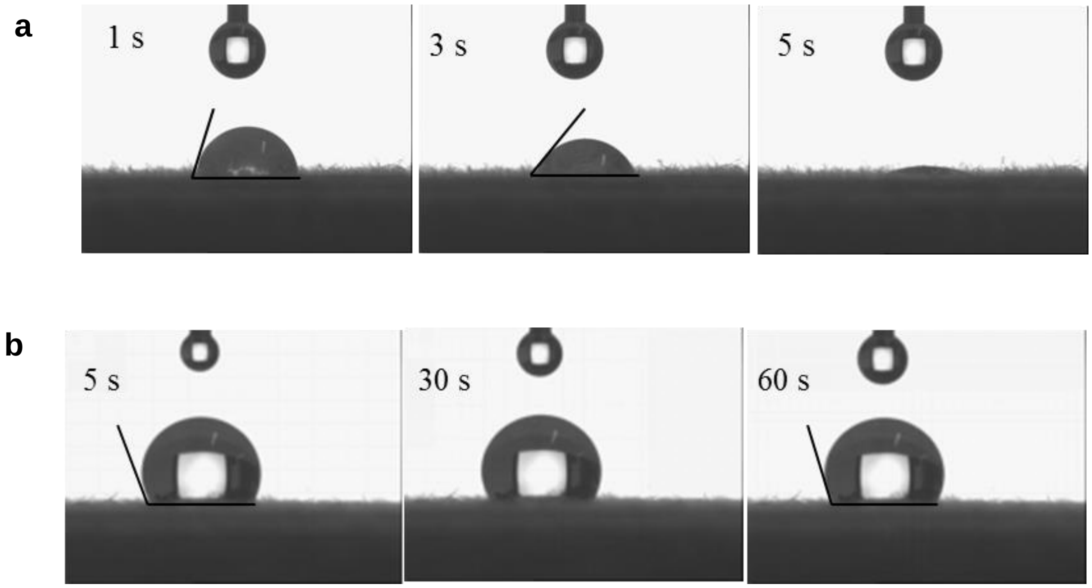

Fig. 8. The differences in the contact angles of the water droplets with the surfaces between (a) the control paper and (b) the treated paper (under the optimal conditions)

Confirming the SRP Treatment Effects on Water Resistance Using Scanning Electron Microscopy

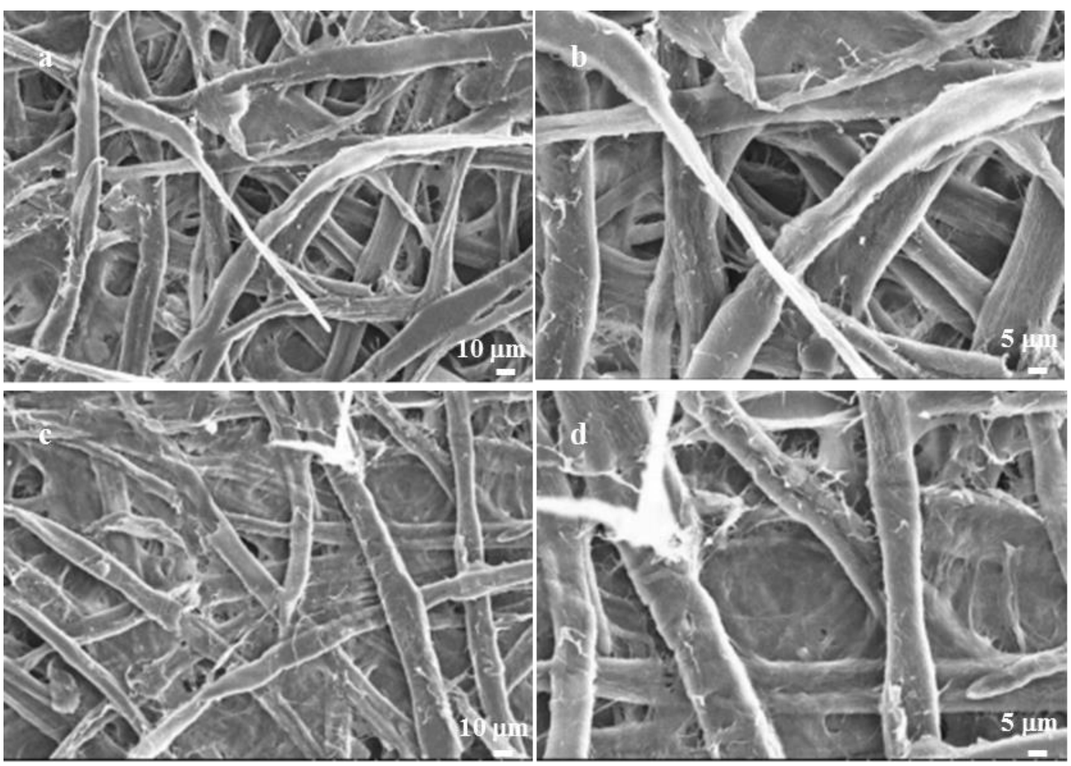

Fig. 9. Scanning electron micrographs of the surfaces of the control paper (a and b) and the SRP sizing agent-treated paper (c and d)

Comparison of Fig. 9a and 9b with Fig. 9c and 9d shows that although the SRP sizing agent was used in the internal sizing, there were some layers on the surface of the sized paper. These film layers were formed by the SRP particles adsorbed on the surfaces of the paper fibers being melted during the heating and drying processes. The melted SRP then uniformly flowed on the paper and conferred good hydrophobicity to the paper.

Effect of Calcium Carbonate Dosage on Water Resistance

Because of the good whiteness of precipitated calcium carbonate ($CaCO_3$), it can be used to make high-grade paper varieties. However, its chemical stability is poor, and CO_2 is released under acidic conditions. Because the sizing system prepared in this study is in a neutral (alkaline) environment, it can completely tolerate the addition of $CaCO_3$.

As shown in Fig. 10, under the optimal conditions, the $CaCO_3$ dosage was changed from 0% to 25%. The Cobb-60 level gradually increased with increasing calcium carbonate, but a good sizing degree remained at 15% calcium carbonate, where the Cobb-60 level was 26.0 g/m^2. This result showed that the SRP sizing agent could tolerate the addition of a certain amount of calcium carbonate.

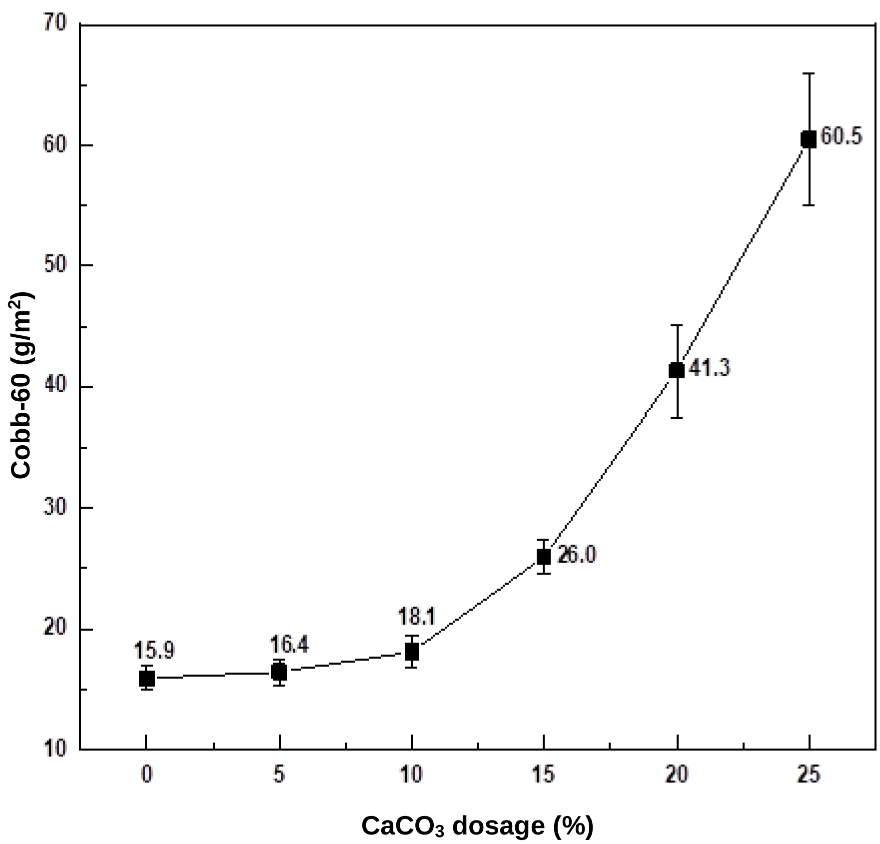

Fig. 10. Effect of $CaCO_3$ dosage on water resistance

CONCLUSIONS

1. Emulsification of soybean oil rosin-based polyester (SRP) with 8% ethoxylated nonylphenol sulfosuccinic acid half ester disodium salt yielded a bluish-white emulsion with an average particle size of 0.224 μm.
2. The SRP sizing agent was found to be favorable for neutral sizing: The SRP sizing agent dosage was 1.0% of the absolute dry pulp mass, the $Al_2(SO_4)_3$ dosage was 1.0% of the absolute dry pulp mass, and the CPAM dosage was 0.15% of the dry pulp mass, preferably at a pH of 7.0. For the paper obtained under these conditions, Cobb-60 was 15.9 g/m^2, the burst index was 2.95 kPa·m^2/g, the tear index was 16.51 mN·m^2/g, and the tensile index was 43.06 N·m/g.
3. Under the optimal conditions, the contact angle of the paper was approximately 125°. Scanning electron microscopy showed that some compact film layers had formed on the surface of the paper, indicating that the SRP had good sizing performance.
4. The SRP sizing agent allowed the addition of $CaCO_3$. When the $CaCO_3$ dosage was 15%, the Cobb-60 of the paper was 26.0 g/m^2.

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