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NOTE

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Application of cationic polymer prepared from sulfuric acid lignin as a retention aid for usual rosin sizes to neutral papermaking

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Abstract Cationic polymers that acted as the retention aids for usual rosin sizes in neutral papermaking were prepared from sulfuric acid lignin (SAL), one type of acid lignin. To convert SAL to the cationic polymer (MP-SAL), SAL was phenolated and then treated by the Mannich reaction to introduce the amino groups. In the MP-SAL single system, MP-SAL exhibited high sizing effectiveness in neutral papermaking with the rosin emulsion size. However, MP-SAL showed no sizing effectiveness when soap rosin size was used. MP-SAL showed increased sizing effectiveness as the pK_a of the introduced amino group increased. From this and comparison of the sizing degrees of MP-SAL and polyethylenimine, which possesses a linear structure, it was suggested that the sizing effectiveness was not only affected by the charge density and molecular weight, but also by the basicity of the introduced amino groups and the molecular structure of the retention aid. In the alum–MP-SAL dual system, alum and MP-SAL synergistically enhanced the sizing effectiveness in the rosin emulsion sizing at neutral pH. In turn, this allowed a decrease in the MP-SAL dosage and resulted in a small decrease in brightness.

Key words Lignin · Rosin size · Retention · Mannich reaction · Paper

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Introduction

Much attention has been paid to the utilization of biomass energy as a potential replacement for fossil fuel energy because of its abundance and renewable nature. Among procedures using biomass, the acid saccharification of woody materials is an effective method for the production of monosaccharides and ethanol. However, this method yields a large amount of less reactive acid lignin as a by-product. One of the key considerations in developing this acid saccharification process is to find effective ways to utilize acid lignin.

Acid lignin possesses a highly condensed structure, which is derived from intermolecular dehydrative condensation[1,2] between benzylic carbons and aromatic nuclei. Recently, the condensed aromatic nuclei of sulfuric acid lignin (SAL), a type of acid lignin with a diarylmethane structure, were selectively exchanged with phenol in the presence of a sulfuric acid catalyst.[3] As a result, the reactivity of phenolized sulfuric acid lignin (P-SAL) is enhanced because a reactive *p*-hydroxyphenyl moiety is introduced at the side chain α-position instead of condensed-type aromatic nuclei. Thus, P-SAL could be easily converted to functional materials by chemical reactions.[4–8]

Incidentally, papermaking conditions have shifted from acidic to neutral–alkaline in recent years because of the closed-circuit papermaking system, the use of recycled waste paper, and lower cost. In our previous study, cationic polymers (MP-SAL), which have high surface activity, were prepared from P-SAL by the Mannich reaction[7] (Fig. 1) and it was found that they could serve as a retention aid for the rosin-ester emulsion size in neutral papermaking.[9]

Usual rosin sizes such as rosin emulsion size and soap rosin size function under acidic conditions as size reagents, and as rosin-ester emulsion sizes under neutral or alkali conditions. The rosin-ester emulsion size, however, needs about three times the addition than that of synthesized size reagents such as alkylketen dimers and alkenylsuccinic anhydrides.[10]

Table 1. Mannich reaction conditions of phenolized sulfuric acid lignin and properties of the products

MP-SAL	Reaction conditions[a]				Reaction products		Sizing degree[b] of handsheet (s)
	Amine	Dosage (%)		Time (h)	Yield (%)	N content (%)	
		Amine (mmol)	HCHO (mmol)				
1	$HN(CH_3)_2$	0.16	0.11	4	78	4.2	38
2	$HN(CH_3)_2$	0.16	0.11	6	88	4.3	39
3	$HN(CH_3)_2$	1.6	1.1	24	90	4.4	43
4	$HN(C_2H_5)_2$	2.6	1.1	24	78	3.8	47
5	H_2NCH_3	1.1	1.1	72	78	4.2	54
6	$H_2NC_2H_5$	1.6	1.1	72	89	3.8	58

MP-SAL, cationic polymer prepared from sulfuric acid lignin
[a] Phenolized sulfuric acid lignin (100 mg) was reacted at 60°C in the mixed solution of 80% aqueous dioxane (10 ml) and AcOH (4 ml)
[b] Sizing degree of handsheet prepared with the product (1%) and rosin emulsion size (0.35%) in MP-SAL single system at pH 7.5

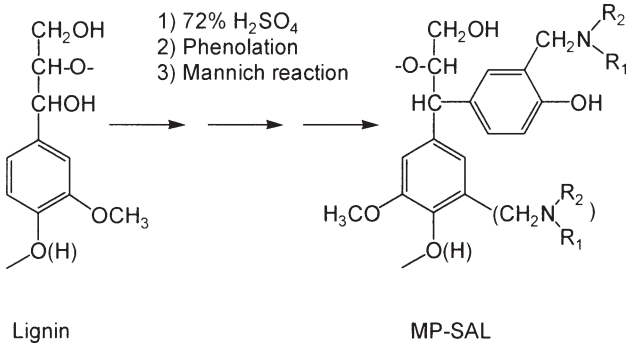

Fig. 1. Preparation of cationic polymer (MP-SAL) from lignin by the Mannich reaction

In this study, the application of MP-SAL prepared from P-SAL as retention aids for the rosin emulsion size and soap rosin size under neutral conditions was investigated.

Materials and methods

Materials

A commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a TAPPI standard Niagara beater. Rosin emulsion size (Harsize NES-500) and soap rosin size (Harsize L-750) were obtained from Harima. Polyethylenimine (PEI), with a molecular weight of 70000, was purchased from Tokyo Kasei Kogyo. Cellulose tube (BioDesignDialysis Tubing #D306-50) for dialysis was obtained from BioDesign.

Preparation of cationic polymer from sulfuric acid lignin

Sulfuric acid lignin (SAL) was prepared from red pine (*Pinus densiflora* Sieb. et Zucc) by the Klason method.[11] Phenolation of it was carried out according to our previous procedure.[3] The cationic polymers were obtained by reaction of P-SAL with amines in the Mannich reaction[7] at 60°C under various conditions as shown in Table 1. After the reaction mixture was dialyzed with a cellulose tube (3500 molecular weight cutoff), the reaction products were lyophilized to yield water-soluble cationic polymers (MP-SAL **1**–**6**).

Measurement of nitrogen content and charge density of cationic polymers

Nitrogen content of MP-SAL was measured by elemental analysis using a Perkin Elmer 2400 II elemental analyzer. The charge densities of cationic polymers were determined by colloid titration with a 0.0025N solution of potassium polyvinyl sulfate.[12]

Preparation of handsheets

To a 1.3% pulp suspension, 0.5% NaOH or 0.5% H_2SO_4 solution was added to adjust to the desired pH. Then, the rosin emulsion size or the soap rosin size and MP-SAL were added and stirred for 3 min. In the alum–MP-SAL dual system, alum was added before the rosin emulsion size, while the soap rosin size was added before the addition of alum. The pH of the pulp suspension was measured just before making the handsheet. The pulp suspension was subjected to handsheet making with a basis weight of 60 g/m^2. Wet-pressed handsheets were dried at room temperature for 1 day and then cured at 110°C for 30 min in an oven.

Measurement of Stöckight sizing degree of handsheets

The Stöckight sizing degree of handsheets was measured according to the JIS method.[13]

Measurement of brightness of handsheets

The brightness of handsheets was measured by a Nippon Denshoku ND-300A color difference meter.

Results and discussion

Sizing behavior in the MP-SAL single system

Recently, it was reported that some polyamines could serve as retention aids in the rosin size system in neutral or alkaline conditions.[14–19] In our previous study,[9] cationic polymers (MP-SAL in Fig. 1) prepared from P-SAL by the Mannich reaction with various amines and formaldehyde exhibited good performance in the rosin-ester emulsion system at neutral pH.

The Mannich reaction mechanism of P-SAL has been confirmed in a separate experiment[7] with lignin model compounds. The yield of the product ranged from 78% to 90%. The reaction conditions and the properties of the products are summarized in Table 1. All prepared cationic polymers were soluble in water.

To determine the suitability of MP-SAL as a retention aid, sizing behavior with MP-SAL only (MP-SAL single system) was investigated first. Figure 2 shows the relationship between MP-SAL **1** dosage and the sizing degree of handsheets prepared with MP-SAL **1** and 0.35% of the rosin emulsion size at pH 7.5. Addition of 0.2% MP-SAL **1** did not exhibit sizing effectiveness; however, the sizing degree was raised with the increase of MP-SAL **1** dosage and about 40 s of Stöckight sizing degree was obtained by adding 1% MP-SAL **1**.

To investigate the influence of pH, we prepared handsheets at different pH levels. The results are shown in Fig. 3. The sizing degrees of the handsheets prepared with rosin emulsion size and MP-SAL **1** were not influenced by pH and they maintained high effectiveness, whereas the performance of alum was dependent on pH. The handsheets prepared with the soap rosin size and MP-SAL **1** did not show any sizing effectiveness at every pH. Wu et al.[16] also reported that some polyamines were not suitable for soap rosin size under neutral papermaking conditions. This implies that the retention mechanisms of each rosin sizes were different. It was difficult to determine the difference in sizing development mechanism of the rosin emulsion size and soap rosin size in this experiment.

Compared to PEI, a general cationic polymer which possesses a linearly structure, the sizing effectiveness of MP-SAL **1**, which is considered to be a highly branched polymer because of lignin derivatives, was higher than that of PEI. The cationic charge density of MP-SAL **1** (1.3–2 mEq/g) was lower than that of PEI (over 5 mEq/g) (Fig. 4). Indeed,

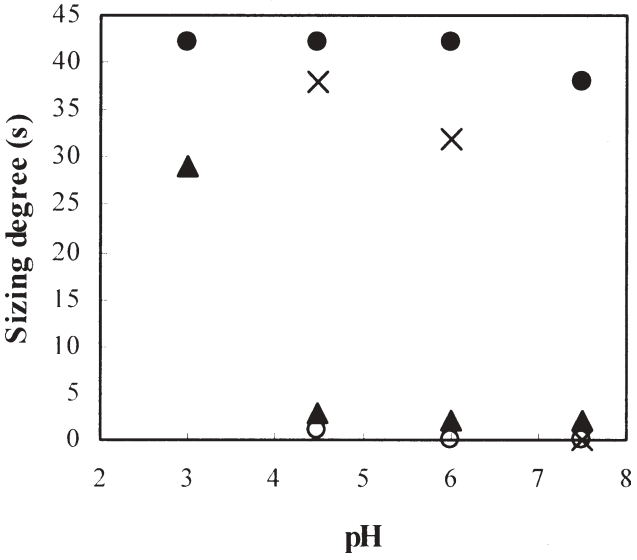

Fig. 3. Effects of sheet-forming pH on sizing degree of acid rosin sizes (0.35%) with cationic polymers (1%) or alum (3%). *Filled circles*, rosin emulsion size with MP-SAL **1**; *filled triangles*, rosin emulsion size with polyethylenimine (PEI); *crosses*, rosin emulsion size with alum; *open circles*, soap rosin size with MP-SAL **1**

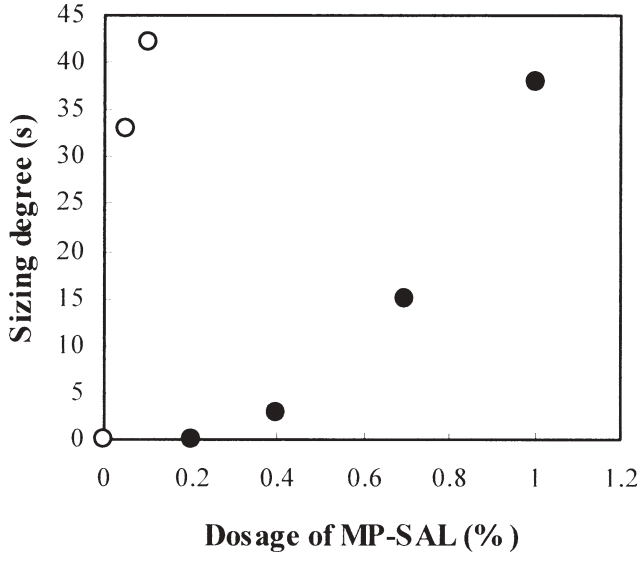

Fig. 2. Sizing degrees of handsheets prepared with rosin emulsion size (0.35%) and MP-SAL **1** (0%–1%) at pH 7.5. *Filled circles*, MP-SAL single system; *open circles*, alum–MP-SAL dual system with 1% alum

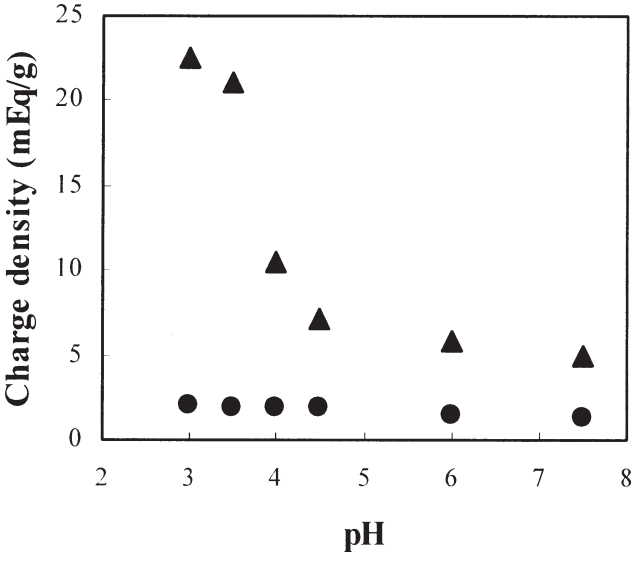

Fig. 4. Effects of pH on cationic charge density of MP-SAL and PEI. *Filled circles*, MP-SAL **1**; *filled triangles*, PEI

Table 2. pK_a of amines

	p*K*a
Trimethylamine	9.80
Triethylamine	10.72
Dimethylamine	10.77
Diethylamine	10.98

Data reported by Ootaki[20]

PEI exhibits a cationic charge density of 22.5 mEq/g at pH 3.0. The molecular weights of MP-SAL **1** and PEI were about 10000[5] and 70000, respectively. These results are in accord with reports[14–17,19] that the sizing effectiveness was not only affected by charge density and molecular weight to a great extent, but also by the molecular structure of the retention aid.

Table 1 shows the sizing degrees of handsheets prepared with the rosin emulsion size and MP-SALs. Primary and secondary amines as reaction reagents in the Mannich reaction become secondary and tertiary amino groups, respectively, in the MP-SAL. Biermann[14] concluded that the presence of protonated amines in the polymer chain is important and that the pK_a value of amines affects the capability of a retention aid. In our previous study,[9] it was found that MP-SAL with a higher pK_a value shows higher absorptivity on pulp and exhibits great performance on sizing effectiveness in the rosin-ester emulsion size system. This trend was also observed (Tables 1 and 2) in this study. As expected, the higher amine content of MP-SAL with the same amino group brought an increase in sizing effectiveness (MP-SAL **1**–**3** in Table 1).

It was found from our results that MP-SAL is effective as a retention aid in neutral papermaking conditions with adequate selection of the rosin.

Sizing behavior in the alum–MP-SAL dual system

Wang and Tanaka[19] reported that some cationic polymers and alum synergistically enhance the sizing effectiveness in neutral–alkaline papermaking. In this study, MP-SAL was used together with alum (alum–MP-SAL dual system) to investigate the sizing behavior. Figure 2 depicts the sizing degree as a function of MP-SAL dosage with 1% alum at pH 7.5. It shows that MP-SAL has a synergistic effect with alum, and more than a 0.05% dosage of MP-SAL produces high sizing (over 33 s of Stöckight sizing degree) using the rosin emulsion size. When the soap rosin size was used, sizing effectiveness was not observed. Wang and Tanaka[19] reported that the polymers with lower charge density were not effective for rosin emulsion size, while the polymers with higher charge density were effective for soap rosin size. No efficiency of MP-SAL in the soap rosin sizing may be attributable to low charge density.

Brightness of handsheets prepared with MP-SAL

The brightness of the handsheets prepared with 1% MP-SAL **1** decreased from 83.8% to 59.7%. To obtain more information regarding the brightness drop, simulation was carried out using the Kubelka–Munk theory[9] using the MP-SAL single system data. These results are shown in Table 3. When the original pulp had 85% brightness, the brightness decreased to 60.0% by adding 1% MP-SAL **1** in the MP-SAL single system. In the alum–MP-SAL dual system, however, the dosage of MP-SAL **1** could decrease to 0.05% to obtain a high sizing degree (Fig. 2) and the brightness decreased only 0.4% when the original pulp brightness was 50%. Thus, MP-SAL is expected to be usable as a retention aid in newsprinting paper and mechanical papers that do not require a high level of brightness.

Table 3. Calculation of handsheet brightness by the Kubelka–Munk theory

Original pulp	Handsheet	
Brightness (%)	MP-SAL **1** dosage (%)	Brightness (%)
85	1.0	60.0
	0.1	79.9
	0.05	82.2
50	1.0	43.4
	0.1	49.2
	0.05	49.6

Conclusion

In this study, it was found that the cationic polymers (MP-SAL) prepared from sulfuric acid lignin (SAL) by the Mannich reaction possess high potential as retention aids for the rosin emulsion size under neutral papermaking conditions. In the MP-SAL single system, MP-SAL exhibited high sizing effectiveness in neutral papermaking with the rosin emulsion size. In the alum–MP-SAL dual system, alum and MP-SAL synergistically enhanced the sizing effectiveness in the rosin emulsion sizing at neutral pH. To elucidate the sizing development mechanism, further research will be needed.

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