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Solid-state ^{13}C -NMR analysis of size components in handsheets prepared by fatty acid soap size–alum systems

Received: December 1, 2000 / Accepted: May 28, 2001

Abstract The mechanism of paper sizing in fatty acid soap size–alum systems was studied by structural analyses of the size components in handsheets prepared with ^{13}C -labeled fatty acid soap size. Patterns of sizing performance and aluminum content of the handsheets were similar to those for the rosin soap size–alum sizing systems, although the patterns of calcium content were different. Solid-state ^{13}C -nuclear magnetic resonance analysis of the handsheets revealed that fatty acid calcium salt was the predominant size component in the handsheets prepared using tap water. This calcium salt is formed from the fatty acid soap size (fatty acid potassium salt) by ion exchange with calcium ion in pulp suspensions and retained on pulp fibers through aluminum compounds originating from alum added. On the other hand, when deionized water was used, free fatty acid was the major component in the handsheets. Fatty acid aluminum salt was present as a minor component in the handsheets prepared in both tap water and deionized water systems. Therefore, all size components (i.e., fatty acid calcium salt, free fatty acid, fatty acid aluminum salt) seem to contribute to the appearance of sizing features.

Key words Sizing · Paper · Soap size · Alum · Solid-state ^{13}C -NMR · Fatty acid · Calcium ion

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This research was presented in part at the 64th Pulp and Paper Research Conference of Japan TAPPI, Tokyo, June 1997

Introduction

Paper sizing an efficient surface modification method of cellulosic fibers, allowing adequate water repellency or hydrophobic properties to be efficiently added to originally hydrophilic paper sheets for practical papermaking processes. Sizing systems with rosin soap size and alum at pH 4–5 have been used for producing acidic paper for about 200 years. Recently, rosin acid emulsion sizes and rosin-ester emulsion sizes have been developed, and the conventional fortified rosin soap sizes have been replaced to some extent by the new rosin-related sizes. The rosin ester sizes, which are prepared from mixtures of fortified rosin acids, glycerin trirosinate esters, and synthetic emulsion stabilizers, are applicable to alkaline papermaking conditions, where CaCO_3 filler is present.¹ However, rosin soap size–alum systems are still used in part for producing acidic paper.

Retention and sizing mechanisms in the rosin soap size–alum systems have been extensively studied from various aspects. Because aluminum compounds originating from alum added to pulp suspensions must participate in both size retention in the wet-end and sizing development after drying of the paper, researchers have especially focused on the roles of alum and structures of rosin size components in paper. The reported results, including model experiments, indicated that the formation of aluminum rosinate in pulp suspensions and during the drying process of wet web govern both retention of the rosin size and sizing development.^{2–6} When hard water is used for papermaking, a large amount of calcium rosinate is formed; consequently, sizing levels of the papers clearly decrease. Calcium rosinate molecules form largely agglomerated particles in pulp suspensions after alum addition and are retained in paper with uneven distribution, resulting in inefficient sizing performance.^{4,5}

On the other hand, in the case of rosin acid emulsion sizes, free rosin acids are present as predominant size components in handsheets; free rosin acid molecules presumably contribute to the sizing development.⁷ Model experiments using fatty acid emulsion sizes, prepared from

^{13}C -labeled fatty acids and an anionic emulsion stabilizer, and solid-state ^{13}C -nuclear magnetic resonance (NMR) analysis of the handsheets prepared thereof also suggested that most size components were present as free fatty acid structures in handsheets.⁸ Therefore, chemical structures of rosin size components and the role of each size component for paper sizing must be examined to rationalize the overall mechanisms of the rosin-related paper sizing.

In this study, fatty acid soap sizes were prepared and used as models of rosin soap sizes for handsheet-making at pH 4.5. On the basis of the results of the sizing performance, palmitic acid potassium salt, whose carbonyl carbon was labeled with ^{13}C , was used for handsheet-making; then the chemical structures of the size components in handsheets were analyzed by solid-state ^{13}C -NMR.

Materials and methods

Materials

A commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. In particular, experiments to prepare handsheets with deionized water, both disintegration and the above beating, were carried out in deionized water. ^{13}C -labeled palmitic acid was a commercial product (Aldrich, USA). Fatty acid soap sizes (aqueous fatty acid potassium salt solutions with 1% fatty acid content) were prepared from fatty acid or a fatty acids mixture with a diluted KOH solution for 100% neutralization by heating at about 70°C. Palmitic acid calcium and aluminum salts were prepared from palmitic acid potassium salt on the basis of the reported method.⁹ An aqueous solution (50 g) of 2% palmitic acid potassium salt (Wako Chemicals, Japan) was added to an approximately 5% aqueous CaCl_2 or AlCl_3 solution (50 g), and the precipitate thus formed was washed thoroughly with water and finally with ethanol; it was then dried at 40°C in a vacuum oven for 1 day. Other chemicals and solvents used were commercial products of laboratory grade (Wako Chemicals).

Preparation of handsheets

The tap water used in this study contained calcium and magnesium ions of 0.60 and 0.22 mmol/l, respectively. To a 0.15% pulp/tap water suspension at about 20°C with continuous stirring, the fatty acid soap size solution of 1 wt%, which was heated at 70°C to avoid solidification of the size solution, was added. The pH of the pulp suspensions were in the range of 6.8–7.3, depending on the addition level of the alkaline fatty acid soap size. After stirring for 1 min, an alum solution was added to the pulp suspension. When 2% (dry weight of pulp) aluminum sulfate was added to the pulp suspension, its pH was about 6.0. After stirring for 1 min, the pH of the pulp suspension was adjusted to 4.5 with a diluted HCl solution. Then handsheets with basis weights of 60 g/m² were prepared from this pulp suspension.¹⁰ In some cases deionized water was used for the whole

process of handsheet-making. Wet-pressed handsheets were dried at 20°C and 65% relative humidity for 1 day. Some of these once-dried handsheets were heated at 105°C for 20 min in an oven. Cellulase treatment was carried out on some of these handsheets according to a previously described method.⁷

Analyses

Stöckigt sizing degree of the handsheets was measured according to the JIS method.¹¹ Aluminum and calcium contents in handsheets were determined using an X-ray fluorescence analyzer (MESA 500; Horiba, Japan).¹² X-ray diffraction patterns of the cellulase-treated residues of the handsheets were collected in reflectance mode by means of a RINT 1000 (Rigaku, Japan).⁷ Handsheet samples (about 0.2 g) were defibrated in air using a domestic coffee mill, and the defibrated fibers were set in a rotor for solid-state ^{13}C -NMR analysis. Solid-state ^{13}C -NMR spectra were collected on a JNM-A400 (Jeol, Japan) under the following conditions: spinning rate 5500 Hz, pulse delay 5 s, contact time 5 ms, data accumulation times 720.

Results and discussion

Sizing behavior of handsheets prepared with fatty acid soap sizes

In this study, three fatty acid soap sizes prepared from palmitic acid, stearic acid, and a mixture of palmitic and stearic acids (1:1 by weight) were used as models of rosin soap size for structural analysis of the size components in handsheets. However, all these fatty acid soap sizes with 1% concentration were a solid mass at room temperature, whereas usual rosin soap sizes are liquid. This phenomenon of solidification of the fatty acid soap sizes is due to the crystallization behavior of the fatty acid salts with long aliphatic chains. In this study, therefore, the fatty acid soap sizes were heated at 70°C for melting and added in solution form at 70°C to pulp suspensions at about 20°C. The fatty acid soap sizes did not form any precipitates in the pulp suspensions but dissolved completely. This complete dissolution of the fatty acid soap sizes was confirmed by measuring light transmittance of the diluted size solutions in tap water and deionized water at concentrations similar to those in the pulp suspensions. However, because of the solidification of the 1 wt% fatty acid soap sizes at about 20°C, there might be some differences in sizing behavior between the fatty acid soap sizing and the practical rosin soap sizing. Then sizing behavior of the handsheets prepared by the fatty acid soap sizes is studied first.

Figure 1 shows the sizing degree of the handsheets prepared with the three fatty acid soap sizes. These sizes gave different sizing patterns to the handsheets, and among the three sizes the mixture of palmitic and stearic acids provided the highest sizing degrees to both nonheated and heated handsheets. The sizing degree of handsheets pre-

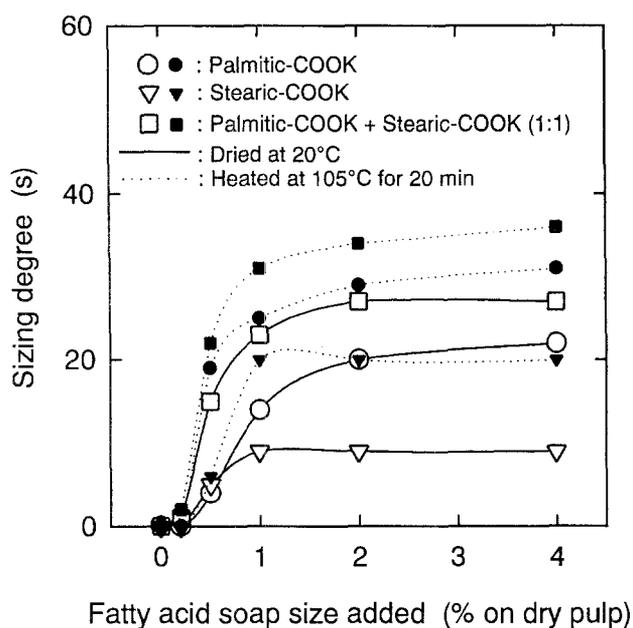


Fig. 1. Sizing degree of handsheets prepared with 0%–4% (on dry weight of pulp) fatty acid soap sizes and 2% (on dry weight of pulp) aluminum sulfate at pH 4.5

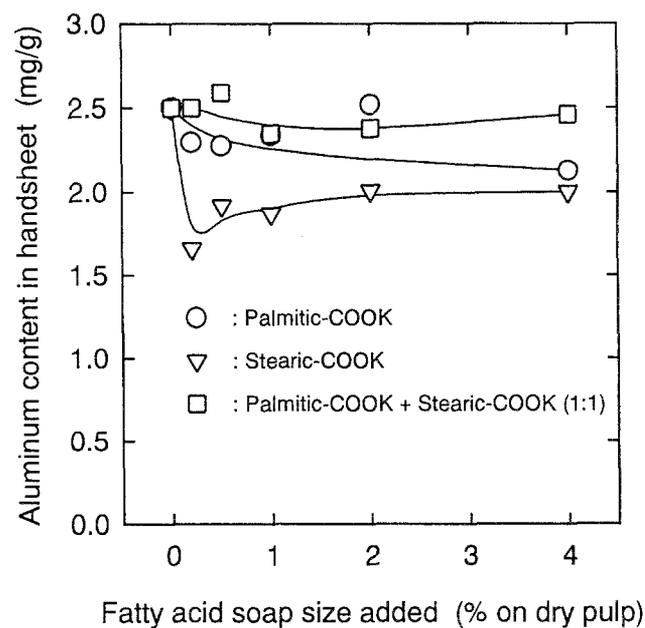


Fig. 2. Aluminum content in handsheets prepared with 0%–4% (on dry weight of pulp) fatty acid soap sizes and 2% (on dry weight of pulp) aluminum sulfate at pH 4.5

pared with 4% stearic acid soap size was still lower than that of handsheets prepared even with the 0.5% palmitic and stearic acids mixture size. Results similar to this different behavior for the three fatty acid soap sizes were also observed for the corresponding three fatty acid emulsion sizes, which were prepared from free fatty acids and an anionic emulsion stabilizer.⁸ Thus, the sizing behavior of fatty acid–alum systems cannot be explained simply in terms of the size addition level. Probably, crystallization or agglomeration behavior of the size components in the handsheets is different for the three fatty acid soap sizes, resulting in the different sizing pattern.⁸

Figure 2 demonstrates aluminum contents in the handsheets prepared with the three fatty acid soap sizes. Interestingly, the handsheets had roughly constant aluminum content to the 0.2%–4.0% (based on dry weight of the pulp) size addition levels, and these patterns of aluminum content were quite similar to those observed for rosin soap size.¹³ Thus, fatty acid size components additionally adsorbed on pulp fibers by the increased addition level of the fatty acid soap sizes have some chemical structures other than fatty acid aluminum salts. Although the stearic acid soap size gave slightly lower aluminum contents than the other two, this result could not explain the clearly lower sizing performance of the stearic acid soap size.

Calcium contents in the handsheets are shown in Fig. 3. These values clearly increased with increasing size addition level for the three fatty acid soap sizes. This result indicates that calcium ions were retained in the handsheets as counterions of fatty acids, which were added to pulp suspensions in the form of their potassium salts. Palmitic acid soap size gave relatively high calcium content to the handsheets among the three fatty acid soap sizes. X-ray

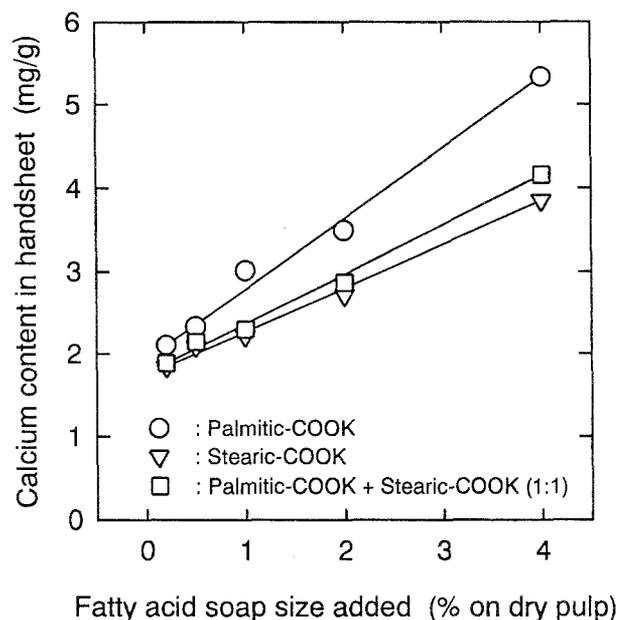


Fig. 3. Calcium content in handsheets prepared with 0%–4% (on dry weight of pulp) fatty acid soap sizes and 2% (on dry weight of pulp) aluminum sulfate at pH 4.5

fluorescence analysis revealed that no potassium ions were present in the handsheets.

The results in Figs. 1 and 2 (i.e. the patterns of sizing degree and aluminum content of handsheets in the fatty acid soap sizing) were similar to those reported for rosin soap sizing.¹³ However, in the case of rosin soap sizing, the calcium content in handsheets was roughly constant for 0%–4% size addition levels,¹³ differing from the patterns in

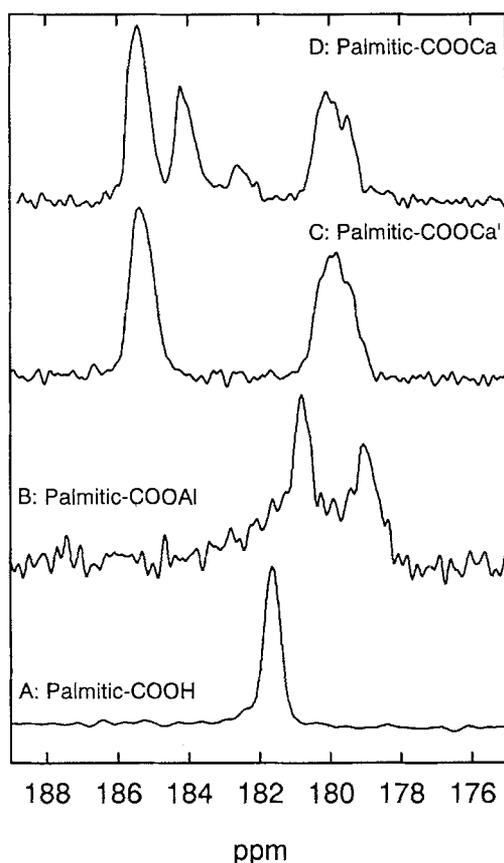


Fig. 4. Solid-state ^{13}C -NMR (nuclear magnetic resonance) spectra of model samples. *A*, palmitic acid; *B*, palmitic acid Al salt; *C*, palmitic acid Ca salt (synthesized); *D*, palmitic acid Ca salt (commercial product)

Fig. 3 for the fatty acid soap sizing. From this aspect, then, fatty acid soap sizes may not be relevant as models of rosin soap sizes. To clarify the role of calcium ions in fatty acid soap sizing and to distinguish between fatty acid soap sizing and rosin soap sizing, the chemical structures of fatty acid components in the handsheets were then studied using a ^{13}C -labeled palmitic acid soap size by solid-state ^{13}C -NMR analysis of the handsheet samples prepared.

Solid-state ^{13}C -NMR analysis of handsheets

Figure 4 shows carbonyl regions in solid-state ^{13}C -NMR spectra of palmitic acid and its calcium and aluminum salts. Palmitic acid has a single peak at 181.6 ppm, and its aluminum salt has two peaks at 179.0 and 180.8 ppm. Stearic acid showed an NMR pattern almost identical to that of palmitic acid in Fig. 4; there is no significant difference in NMR spectra for stearic and palmitic acids. Commercial stearic mono- and dialuminate also had a pattern almost identical to that of palmitic acid aluminum salt (Fig. 4, *B*) prepared in this study from palmitic acid potassium salt with AlCl_3 . On the other hand, as shown in Fig. 4 (*C*, *D*), palmitic acid calcium salt prepared in this study and that of the commercial product had different NMR patterns. In the latter case, the two large and small peaks were additionally present at

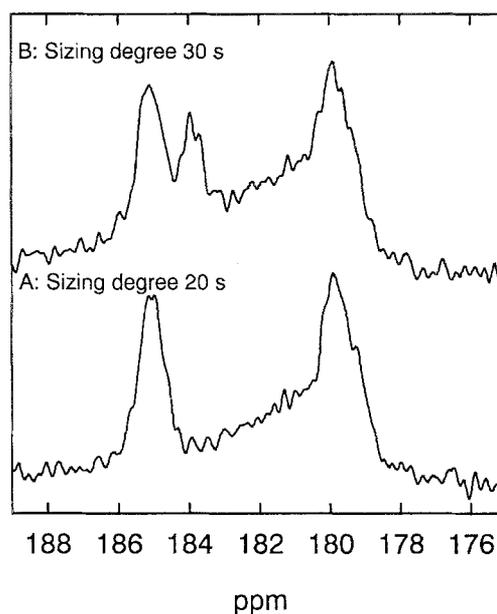


Fig. 5. Solid-state ^{13}C -NMR spectra of handsheets prepared with 2% (on dry weight of pulp) palmitic acid soap size and 2% (on dry weight of pulp) aluminum sulfate. Tap water was used for handsheet preparation. *A*, dried at 20°C (sizing degree 20s); *B*, heated at 105°C for 20 min (sizing degree 30s)

184.2 and 182.6 ppm, respectively. It was found that these two peaks in the commercial product appeared after thermal treatment of palmitic acid calcium salt, which was prepared without thermal drying. Therefore, additional crystal or solid-state structures must be formed by the thermal treatment and are present in the commercial palmitic acid calcium salt.

Figure 5 shows solid-state ^{13}C -NMR spectra of the nonheated and heated handsheets prepared with the 2% (based on dry weight of the pulp) ^{13}C -labeled palmitic acid soap size and 2% (based on dry weight of the pulp) aluminum sulfate using tap water at pH 4.5. Both had clear sizing degrees: 20s and 30s before and after the heating treatment, respectively. The nonheated handsheets had two clear peaks primarily due to palmitic acid calcium salt prepared at room temperature and had a broad tailing resonance in the range of 180–181 ppm. On the other hand, an additional peak appeared at about 184 ppm in the NMR spectrum of the heated handsheets, and the intensities of the two peaks due to the palmitic acid calcium salts originally present in the nonheated handsheets relatively decreased. This additional peak at about 184 ppm in Fig. 5B must be due to the palmitic acid calcium salt with a history of thermal treatment. Thus, the result in Fig. 5 shows that the major size component in the handsheets for both nonheated and heated handsheets is palmitic acid calcium salt, which is formed between palmitic acid potassium salt and calcium ion by ion exchange in pulp suspensions.

Although clear resonance peaks due to palmitic acid aluminum salt could not be observed in Fig. 5 (neither *A* nor *B*), this salt might be present in the handsheets as a minor component, probably partially overlapping one of

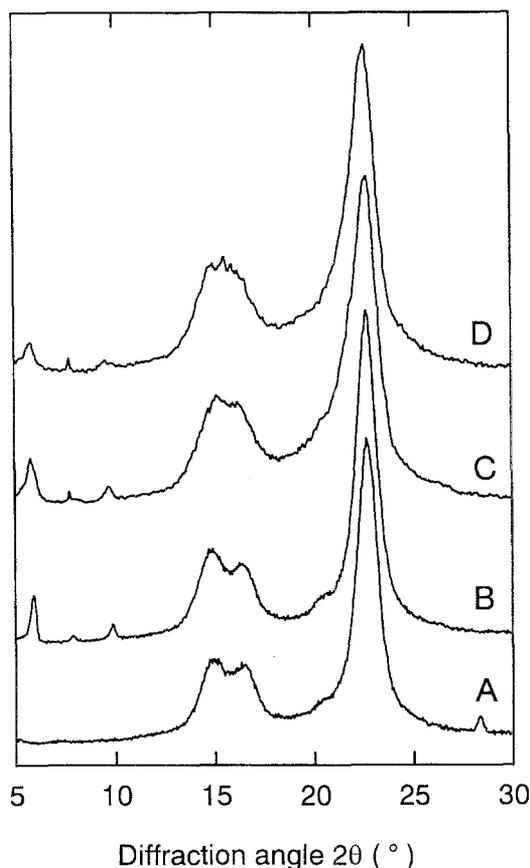


Fig. 6. X-ray diffraction patterns of cellulase-treated residues of handsheets prepared with 2% (on dry weight of pulp) palmitic acid soap size and 2% (on dry weight of pulp) aluminum sulfate. *A*, mixture of microcrystalline cellulose powder (MCP) and palmitic acid Al salt; *B*, mixture of MCP and palmitic acid Ca salt; *C*, cellulase-treated residue of handsheets dried at 20°C; *D*, cellulase-treated residue of handsheets heated at 105°C for 20 min

the peaks of palmitic acid calcium salts in the range of 179–181 ppm. Furthermore, on the basis of the peak shape in 179–181 ppm, the quantity of palmitic acid aluminum salt did not increase by heating the handsheets. This result indicates that the conversion from fatty acid calcium salt to aluminum salt is unlikely to occur in the handsheets by heating. Nevertheless, the sizing degree increased from 20s to 30s by the heating treatment. Thus, some mechanisms other than changes in chemical structures of the palmitic acid components in the handsheets may have resulted in the higher sizing degree by the heating. Partial spreading of the free fatty acid components by melting on pulp fiber surfaces and some changes in distribution of the size components may be candidate explanation for the effect of the heating treatment.

Because size contents in the handsheets were less than 2%, any diffraction peaks due to the size components could not be detected in the X-ray diffraction patterns of the handsheet samples. The handsheets were then treated with cellulase to concentrate the size components by removing cellulose and hemicellulose in the handsheets under mild conditions; and the cellulase-treated residues were subjected to X-ray diffraction analysis (Fig. 6). Diffraction

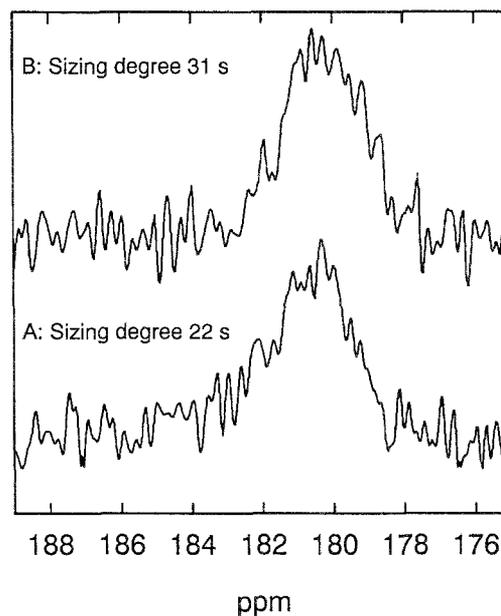


Fig. 7. Solid-state ^{13}C -NMR spectra of handsheets prepared with 2% (on dry weight of pulp) palmitic acid soap size and 2% (on dry weight of pulp) aluminum sulfate. Deionized water was used for preparing the handsheet. *A*, dried at 20°C (sizing degree 22 s); *B*, heated at 105°C for 20 min (sizing degree 31 s)

peaks due to palmitic acid calcium salt were detected in the cellulase-treated residues for both nonheated and heated handsheets. On the other hand, the cellulase-treated residues of neither nonheated nor heated handsheets had diffraction peaks due to palmitic acid aluminum salt. This result also suggests that palmitic acid calcium salt is the predominant structure of the size components in the handsheets.

Figure 7 shows solid-state ^{13}C -NMR spectra of the nonheated and heated handsheets, respectively, prepared with 2% (based on the dry weight of the pulp) ^{13}C -labeled palmitic acid soap size and 2% (based on the dry weight of the pulp) aluminum sulfate using deionized water at pH 4.5. Also in this case the handsheets had good sizing degrees: 22s and 31s before and after the heating treatment, respectively. Neither curve in Fig. 7 (*A* or *B*) had resonance peaks due to palmitic acid calcium salt, and a broad resonance peak was present in the range of 179–182 ppm in each spectrum. Although bulk and crystalline palmitic acid has a sharp resonance peak at 181.6 ppm in the solid-state ^{13}C -NMR spectrum (Fig. 4A), palmitic acid components in handsheets has a broader peak at about 181 ppm.⁸ Thus, the broad resonance peak in Fig. 7 probably consists of a mixture of free palmitic acid and palmitic acid aluminum salt. Because the shoulder part of the broad resonance around 179 ppm slightly increased by the heating treatment, additional palmitic acid aluminum salt might have formed to some extent from free palmitic acid in the handsheets during the heating treatment. Also in the case of these handsheets prepared using deionized water, the sizing degree increased from 22s to 31s by the heating treatment, and these sizing degrees and the increasing ratio by heating

were quite similar to those for the handsheets prepared using tap water (Fig. 5).

With fatty acid soap sizing, both fatty acid calcium salts and free fatty acids seem to contribute to the sizing performance as hydrophobic compounds in paper in similar manners. It is not plausible that only fatty acid aluminum salts formed in quite small quantities in the handsheets govern the overall sizing performance.⁵

Difference between fatty acid soap sizing and rosin soap sizing

Both commercial rosin soap sizes and fatty acid soap sizes used in this study have the structures of carboxylic acid potassium salts, and both had similar relations between size addition level and either sizing degree or aluminum content of the handsheets prepared thereof.¹³ However, the predominant size components in the handsheets prepared using tap water are different. With rosin soap sizing, free rosin acid molecules are the predominant size components in handsheets prepared with alum and tap water at pH 4.5.¹⁴ On the other hand, large amounts of fatty acid calcium salts were present in the handsheets prepared by fatty acid soap size–alum systems under similar conditions.

The difference in chemical structures of the predominant size components in the handsheets for rosin soap sizing and fatty acid soap sizing is due to the difference in stability to acidic conditions of the two carboxylic acid calcium salts. When these two soap sizes (carboxylic acid potassium salts) are added to pulp suspensions in tap water containing calcium ions, carboxylic acid calcium salts are first formed by ion exchange. Although once-dried rosin acid calcium salts [i.e., (Rosin-COO)₂Ca] is insoluble in water, rosin acid calcium salts formed in situ from rosin soap sizes under neutral to alkaline conditions are soluble in water at pH >5.⁴ Also in the case of fatty acid soap sizes, because no precipitates were formed when the melted fatty acid soap size solutions were added to tap water (see above in Results and discussion), fatty acid-COOCa⁺ must be formed and dissolve in pulp suspensions when the pH is at least >7. When alum is added to pulp suspensions and their pH is adjusted to 4.5, rosin-COOCa⁺ molecules become insoluble in water owing to the formation of free rosin acids and rosin acid aluminum salts by ion exchange.⁴

On the other hand, in the case of fatty acid soap size–alum systems, water-soluble fatty acid-COOCa⁺ molecules, which are first formed in pulp suspensions, may partly turn into water-insoluble fatty acid calcium salts [i.e., (fatty acid-COO)₂Ca] together with free fatty acids and fatty acid aluminum salts owing to the alum addition and the pH adjustment at 4.5. That is, fatty acid calcium salts may be more stable in acidic conditions than rosin acid calcium salts. Coagulation or crystalline behavior of fatty acid molecules with long aliphatic chains, differing from rosin molecules, may have resulted in such higher stability.

However, when deionized water was used in all handsheet-making processes for the fatty acid soap size–alum systems, free fatty acids became the predominant size

components in the handsheets, similar to the case of rosin soap size–alum sizing systems using tap water. Because sizing degrees were nearly equal for the handsheets prepared using tap and deionized water (Figs. 5, 7), whether the predominant size components in the handsheets are free fatty acids or fatty acid calcium salts is not the key factor for sizing performance. As described in the previous section, all size components, irrespective of their chemical structures, may contribute to sizing performance in fatty acid soap size–alum systems. Thus, factors such as the distribution of size components in sheets must be more significant for sizing than their chemical structures per se.

Conclusions

Three fatty acid soap sizes prepared from palmitic acid, stearic acid, and a mixture of palmitic and stearic acids gave similar sizing patterns in terms of the size addition level. However, the plateau levels of sizing degree at 1%–4% size addition levels were different among the three sizes.

When tap water was used, calcium contents in the handsheets increased with the size addition level, whereas aluminum contents were roughly constant.

Solid-state ¹³C-NMR spectra of handsheets prepared with ¹³C-labeled palmitic acid soap size using tap water revealed that palmitic acid calcium salt was the predominant size component present in both noncured and cured handsheets. When deionized water was used, free palmitic acid was the major size component in the handsheets.

The obtained results indicate that any particular chemical structures in the size components (i.e., free fatty acids, fatty acid calcium salts, fatty acid aluminum salts) do not simply govern the sizing performance of handsheets during fatty acid soap sizing.

Fatty acid soap sizing is similar to conventional rosin soap sizing in terms of the relations between size addition level and either sizing degree or aluminum content in handsheets. However, the predominant size components in handsheets prepared using tap water were different for the two sizing systems: free rosin acids for rosin soap sizing and fatty acid calcium salts for fatty acid soap sizing.

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