ORIGINAL ARTICLE

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Mechanism of size retention on handsheets prepared in rosin soap size–alum systems

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Abstract The mechanism of rosin size retention in rosin soap size–alum systems was studied on the basis of sizing behavior and the rosin size and aluminum contents of handsheets prepared under normal and particular conditions. Rosin size, aluminum, and calcium contents of handsheets prepared with various stirring times of pulp suspensions after pH adjustment suggested that rosin size components adsorbed on pulp fibers predominantly have the structure of free rosin acid rather than rosin aluminum or calcium salt. When a carboxyl group-blocked pulp was used, the rosin size content clearly decreased. This result shows that pulp carboxyl groups play a significant role in rosin size retention. Electrostatic interactions between dissociated carboxyl groups of pulps and anionic rosin size components through cationic aluminum compounds must be present in pulp suspensions. On the other hand, nonionic interactions in pulp suspensions, which occur particularly around pH 6.2–6.5, may also contribute to rosin size retention and appearance of sizing features. When the carboxyl group-blocked pulp was used, some rosin size components were retained in the handsheets in largely coagulated form, resulting in no or quite low sizing levels, when the handsheets were dried at 20°C.

Key words Rosin soap size · Aluminum sulfate · Retention · Carboxyl group · Calcium ion

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Introduction

Rosin soap size–alum systems are still used for producing acidic papers at pH 4–5. Many researchers have studied the mechanism of rosin size retention in papermaking processes, and the following hypothesis seems to be well accepted: Cationic precipitates consisting of aluminum dirosinate and free rosin acid are formed from rosin soap size in pulp suspensions by the alum addition, and these cationic size precipitates are adsorbed on anionic pulp fibers at the wet-end by electrostatic interactions.[1–9] As to the size retention sites on pulp fibers, abundant hydroxyl groups and small amounts of carboxyl groups in pulps were their candidates.[10] Also, nonionic interactions have been proposed to be present between pulp fibers and size precipitates at the wet-end.[11,12] Furthermore, microparticles about 0.1 μm in diameter were observed on handsheet surfaces by scanning electron microscopy (SEM) and are believed to be the size precipitates.[12]

In our previous paper,[13] handsheets were prepared with rosin soap size and alum under various conditions, and the retention behavior of rosin size and aluminum components in the handsheets was studied. When the addition level of the rosin soap size varied from 0% to 4% and that of alum was fixed at 2%, the rosin size content increased with increasing amounts of size addition, whereas aluminum and calcium contents remained roughly constant. This result suggests a new mechanism of rosin size retention, differing from those hypothesized so far. More than half of aluminum compounds originating from aluminum sulfate are adsorbed on pulp fibers immediately after the alum addition, and these adsorbed aluminum compounds form cationic sites on pulp fibers. Free rosin acid components having anionic charges are then adsorbed on the cationic sites of pulp fibers at the wet-end. In addition, because microparticles about 0.1 μm in diameter were observed not only on handsheets prepared with rosin soap size and alum but also those prepared with alum alone, it is uncertain at this point whether the particles comprise rosin size components.[13,14]

In the case of emulsion rosin size–alum systems (i.e., other typical rosin sizing systems under acidic conditions), carboxyl groups of pulp fibers behave as retention sites of the rosin size.[14–16] That is, cationic sites are formed on pulp fibers by electrostatic interactions between the dissociated carboxyl group of pulps and cationic aluminum compounds originating from alum added to pulp suspensions; and anionic rosin emulsion particles are adsorbed on the cationic sites of pulp fibers primarily by electrostatic interactions. This mechanism was confirmed by comparing the rosin size content of rosin-sized handsheets prepared from normal pulp and its carboxyl group-blocked pulp, which was prepared by methylamidation of the carboxyl groups.[14] Similar results in terms of carboxyl groups of pulp for size retention were observed also during alkaline sizing using alkylketene dimers and alkenyl succinic anhydrides.[17,18]

In this study, handsheets were prepared from a beaten pulp, its fines-free pulp, and a carboxyl group-blocked pulp with a rosin soap size and alum under various conditions. The rosin size and aluminum contents in the handsheets were determined by pyrolysis–gas chromatography and X-ray fluorescence analysis, respectively. The mechanism of rosin size retention on handsheets was then studied in terms of the chemical structures of rosin size components and the roles of carboxyl groups in pulp.

Materials and methods

Materials

A commercial bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. A fines-free pulp was obtained from the above beaten pulp.[19] A carboxyl group-blocked pulp was prepared from the beaten pulp by methylamidation with water-soluble carbodiimide and methylamine.[14,17,18] The carboxyl content decreased from 62 μEq/g to 2 μEq/g by this methylamidation. A fortified rosin soap size and other chemicals were the same as those used in our previous study.[13] Tap water used for handsheet production contains Ca and Mg ions at 0.60 and 0.22 mEq/l, respectively. The general conditions of handsheet-making were the same as those reported in the previous paper.[13] That is, to a 0.15% pulp suspension, certain amounts of rosin soap size, and aluminum sulfate were added in this sequence, and then 0.1 N HCl was added to the pulp suspension to adjust it to pH 4.5.

Analyses

Rosin size contents in the handsheets were determined by pyrolysis–gas chromatography (PY-GC) using the on-line methylation technique with tetramethylammonium hydroxide.[13] A scanning electron microscope (SEM) (S-4000, Hitachi, Japan) was used to observe the surfaces of the handsheet samples after Pt-Pd coating. An X-ray fluorescence analyzer (XFA) (MESA 500, Horiba, Japan) was used to determine aluminum and calcium contents in the handsheets under the conditions reported in the previous paper.[20]

Results and discussion

Effect of stirring time of pulp suspension on sizing degree

Figure 1 shows the sizing degree of handsheets prepared from pulp suspensions that had various stirring times of the pulp suspensions between the addition of a 0.1 N HCl solution and subjecting the pulp suspensions to handsheet-making. Sizing degrees increased with the increasing stirring time of pulp suspensions for both the original pulp and the fines-free one. Especially, the handsheets prepared from the fines-free pulp had a marked increase in sizing degree by extending the stirring time from 2 to 4 min. Thus, the stirring time of pulp suspensions after the pH adjustment has a significant influence on the resultant sizing levels of the papers.

Rosin size content increased with increasing stirring time in a similar manner for the two pulps (Fig. 2). Therefore, the increase in sizing degree in Fig. 1 is essentially ascribed to the increase in rosin size content by extending the stirring time of pulp suspensions. Furthermore, the rosin size components additionally retained in the handsheets by extending the stirring time seem to contribute greatly to sizing features, especially for the handsheets prepared from the fines-free pulp.

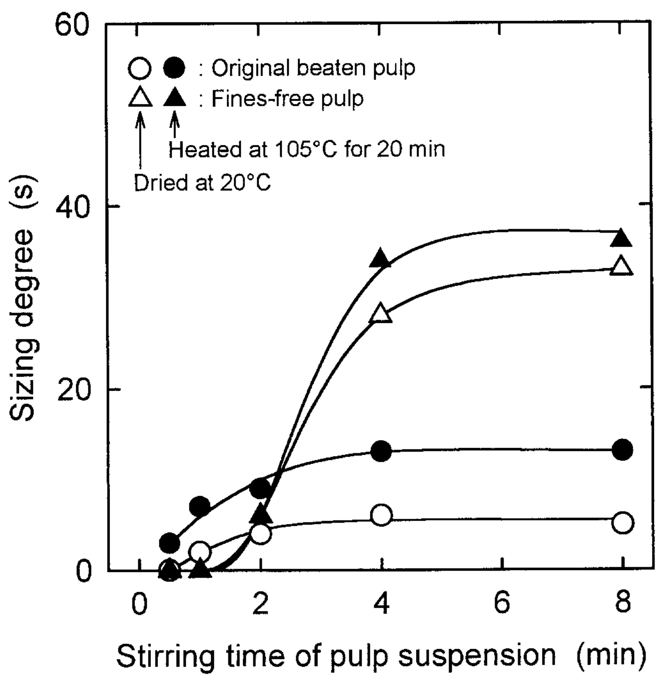

Fig. 1. Sizing degree of handsheets prepared from the original beaten pulp and its fines-free pulp with 0.5% (based on dry weight of pulp) rosin soap size and 2% (based on dry weight of pulp) aluminum sulfate at different stirring times of the pulp suspension after pH adjustment to 4.5

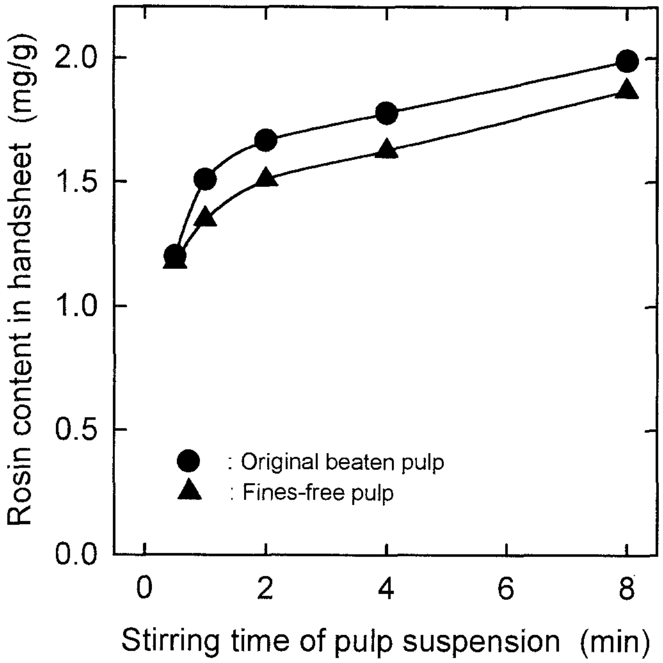

Fig. 2. Rosin size content in handsheets prepared from the original beaten pulp and its fines-free pulp with 0.5% (based on dry weight of pulp) rosin soap size and 2% (based on dry weight of pulp) aluminum sulfate at different stirring times of the pulp suspension after pH adjustment to 4.5

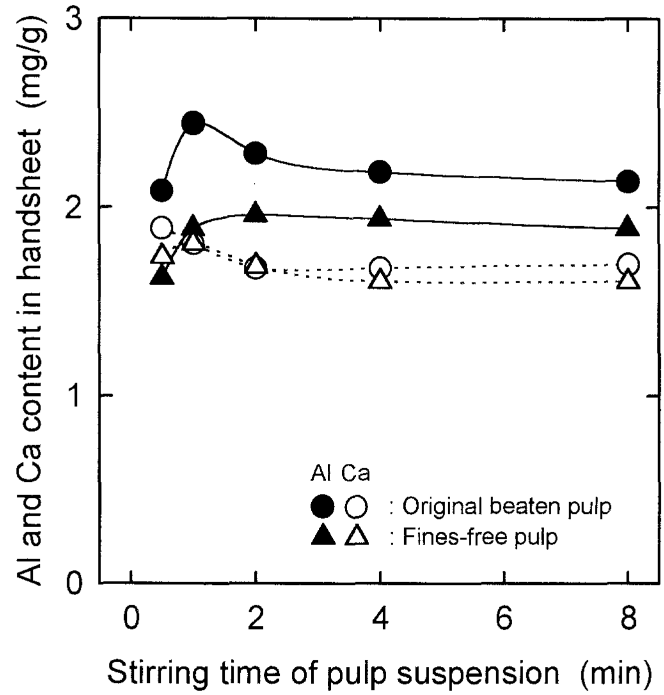

Fig. 3. Aluminum and calcium contents in handsheets prepared from the original beaten pulp and its fines-free pulp with 0.5% (based on dry weight of pulp) rosin soap size and 2% (based on dry weight of pulp) aluminum sulfate at different stirring times of the pulp suspension after pH adjustment to 4.5

Figure 3 illustrates the aluminum and calcium contents in the handsheets. The aluminum content slightly increased when the stirring time of pulp suspensions was extended from 0.5 min to 1 min. However, when the stirring time was longer than 1 min, aluminum contents were roughly constant for the two pulps. The calcium content was almost unchanged by extending the stirring time. These results show that rosin size components additionally retained in the handsheets by extending the stirring time are adsorbed on pulp fibers as rosin acid forms and maybe rosin aluminum salt also in pulp suspensions. Especially, rosin size components having only free acid form seemed to be additionally retained in the handsheets when the pulp suspensions were stirred for longer than 1 min after the pH adjustment. It was suggested in the previous paper that most aluminum components are adsorbed on pulp fibers immediately after the alum addition.[13] As seen from the result in Figs. 2 and 3, rosin size components are likely to be adsorbed on pulp fibers as rosin acid forms for both pulps.

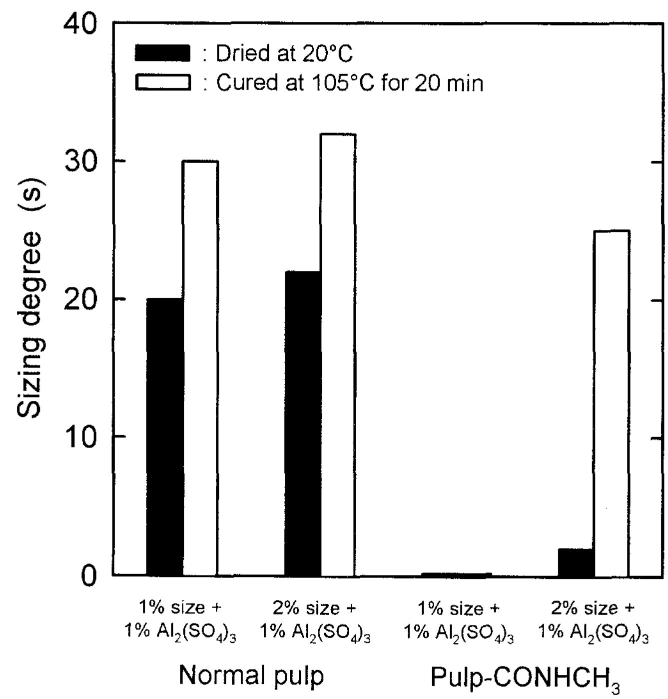

Fig. 4. Sizing degree of handsheets prepared from the original beaten pulp and its carboxyl group-blocked pulp with 1% or 2% (based on dry weight of pulp) rosin soap size and 1% (based on dry weight of pulp) aluminum sulfate using tap water at pH 4.5

Role of carboxyl group of pulp in rosin size retention

To study the role of carboxyl groups of pulp in rosin size retention, the sizing behavior and rosin size and aluminum contents were compared for handsheets prepared from the normal beaten pulp and those prepared with its carboxyl group-blocked pulp. Figure 4 shows the sizing behavior of

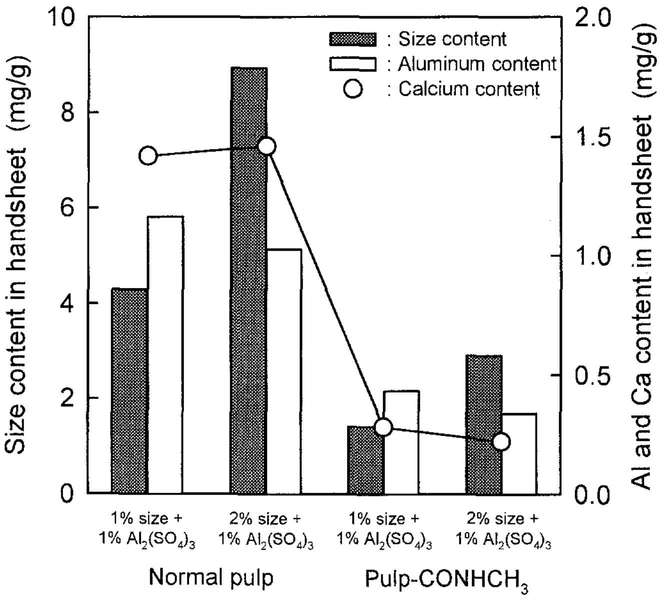

Fig. 5. Rosin size and aluminum and calcium contents in handsheets prepared from the original beaten pulp and its carboxyl group-blocked pulp with 1% or 2% (based on dry weight of pulp) rosin soap size and 1% (based on dry weight of pulp) aluminum sulfate using tap water at pH 4.5

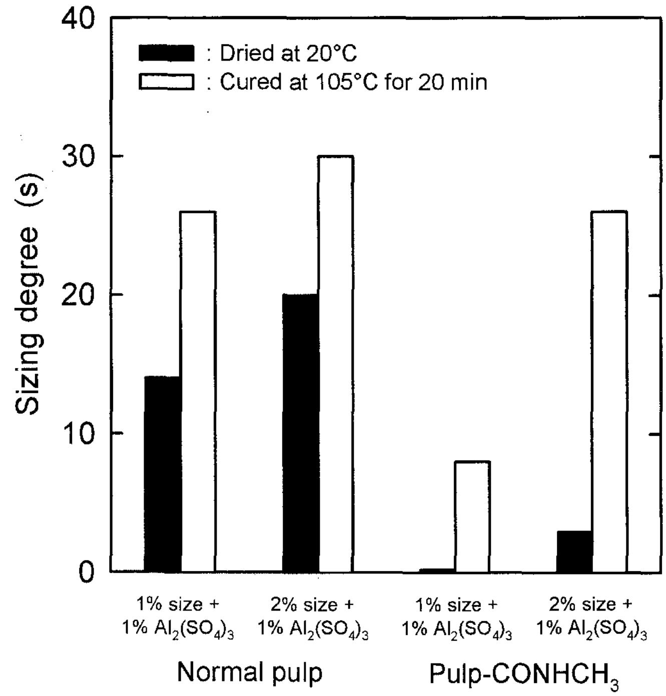

Fig. 6. Sizing degree of handsheets prepared from the original beaten pulp and its carboxyl group-blocked pulp with 1% or 2% (based on dry weight of pulp) rosin soap size and 1% (based on dry weight of pulp) aluminum sulfate using tap water at pH 6.2–6.5

handsheets prepared from pulp suspensions at pH 4.5. When handsheets were prepared from the carboxyl group-blocked pulp and dried at 20°C, they had no or poor sizing features, indicating that carboxyl groups in pulp have a significant role in this rosin soap size–alum system. On the other hand, when 2% (based on the dry weight of pulp) rosin soap size was added to the carboxyl group-blocked pulp suspension, the handsheets had a high sizing degree (25 s) after the curing treatment.

Figure 5 illustrates rosin size, aluminum, and calcium contents in the handsheets shown in Fig. 4. When the normal pulp was used, retention values for the rosin size were about 43% and 45% for the 1% and 2% levels of rosin soap size, respectively. Here, retention values of rosin size are calculated by the following formula:

$$\text{Retention value of rosin size} = \frac{\text{rosin size retained in handsheet}}{\text{rosin size added to pulp suspension}} \times 100\ (\%)$$

On the other hand, rosin size content in the handsheets prepared from the carboxyl group-blocked pulp clearly decreased. Retention values of rosin size were about 14% and 15% for the 1% and 2% levels of rosin soap size, respectively. Thus, retention values of rosin size decreased to about one-third when the carboxyl group-blocked pulp was used in place of the normal pulp. This result shows that carboxyl groups in pulps play a significant role in rosin size retention not only in emulsion rosin size–alum systems but also in rosin soap size–alum systems under acidic conditions.[14–16]

Figure 6 shows sizing behavior of handsheets prepared from the normal pulp and its carboxyl group-blocked pulp without adjusting the pH of pulp suspensions, where pH values naturally became 6.2–6.5 after the alum addition. When the normal pulp was used, sizing levels were a little lower than those of handsheets prepared from the normal pulp at pH 4.5 (Fig. 4). On the other hand, the cured handsheets prepared from the carboxyl group-blocked pulp had higher sizing degrees than those of the handsheets prepared from the carboxyl group-blocked pulp at pH 4.5 (Fig. 4). Rosin size, aluminum, and calcium contents in the handsheets in Fig. 6 are illustrated in Fig. 7. When the normal pulp was used, retention values of rosin size were about 34% and 39% for the 1% and 2% levels of rosin soap size, respectively. On the other hand, retention values of rosin size were about 17% and 18%, respectively, for the carboxyl group-blocked pulp; the retention values decreased to about one-half when the carboxyl group-blocked pulp was used in place of the normal pulp at pH 6.2–6.5. Thus, carboxyl groups in pulps play a important role in rosin size retention also under the conditions of pH 6.2–6.5. However, when the pH was not adjusted to 4.5 after the size and alum additions, rosin size retention values decreased a little for the normal pulp, whereas they slightly increased for the carboxyl group-blocked pulp.

The pattern of calcium content in the handsheets in Fig. 7 was similar to that in Fig. 5; pH values of pulp suspensions have little influence on calcium content. On the other hand, the pattern of aluminum content seen in Fig. 7 was clearly different from that seen in Fig. 5. The handsheets prepared from the carboxyl group-blocked pulp had higher alumi-

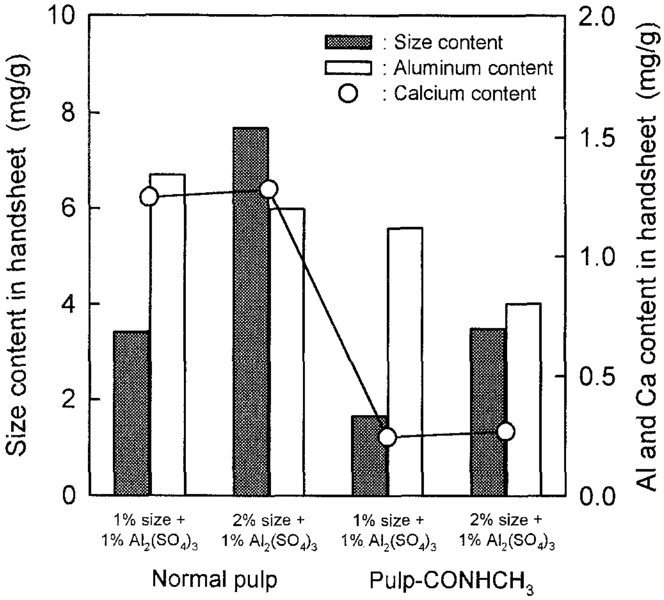

Fig. 7. Rosin size and aluminum and calcium contents in handsheets prepared from the original beaten pulp and its carboxyl group-blocked pulp with 1% or 2% (based on dry weight of pulp) rosin soap size and 1% (based on dry weight of pulp) aluminum sulfate using tap water at pH 6.2–6.5

num content when the pH was not adjusted. As reported in the previous paper,[20] relatively large amounts of aluminum compounds originating from alum are retained in handsheets when the pH of pulp suspensions is controlled at around 7. Under those conditions, nonionic aluminum flocs are preferentially formed in pulp suspensions and are retained in handsheets primarily by filtration effects without any electrostatic interactions. Also in the case of Fig. 7, most aluminum components may be retained in the handsheets without electrostatic interactions.

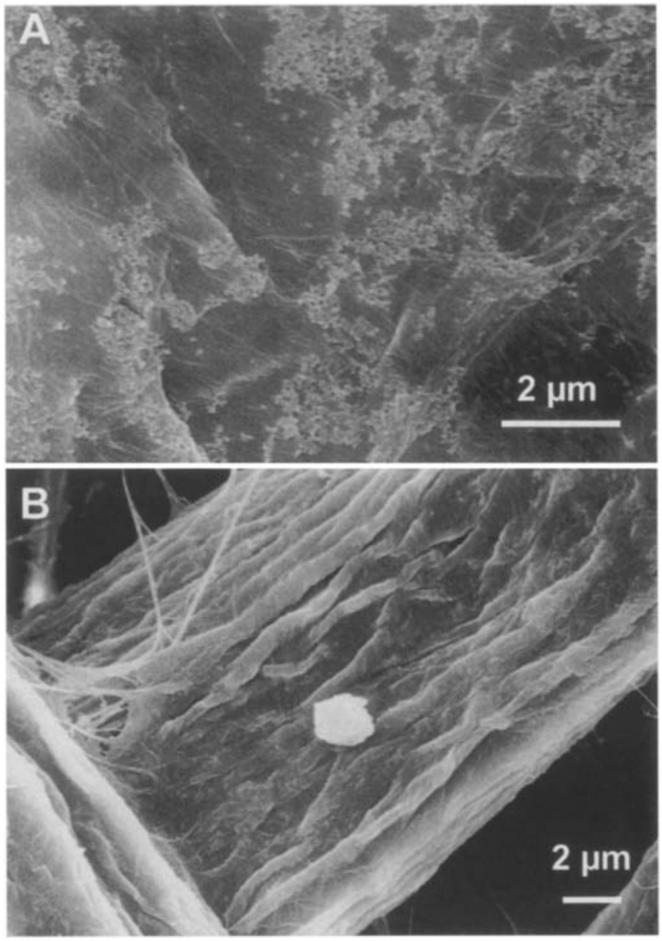

Fig. 8. Scanning electron microphotographs of handsheet surfaces prepared from carboxyl group-blocked pulp with 2% (based on dry weight of pulp) rosin soap size and 1% (based on dry weight of pulp) aluminum sulfate at pH 4.5

Mechanism of rosin size retention in rosin soap size–alum system

The retention behavior of rosin size and aluminum in handsheets prepared in the rosin soap size–alum systems shows that the mechanism of rosin size retention is similar to that in the emulsion rosin size–alum systems, although the addition sequence of rosin size and alum is in reverse for the two systems. That is, aluminum components originating from alum, which is added to pulp suspensions containing rosin soap size, are immediately adsorbed on pulp fibers by electrostatic interactions between carboxyl groups in pulps and the cationic aluminum compounds, and they form cationic sites on pulp fibers. Then, anionic rosin size molecules or emulsion particles (or both), which are formed in situ from rosin potassium salt in pulp suspensions by the addition of alum and the pH adjustment at 4.5, are adsorbed on the cationic sites of pulp fibers by electrostatic interactions.

However, because some of the rosin size was retained on the handsheets prepared even from the carboxyl group-blocked pulp, rosin size components are retained in handsheets by some mechanism other than the above-noted electrostatic interactions. As shown in Figs. 4 and 6, a high sizing degree appeared on the handsheets prepared from the carboxyl group-blocked pulp after curing treatment at 105°C for 20 min; in contrast, the handsheets dried at 20°C had no or low sizing. These results suggest that rosin size components are retained in the handsheets as large flocs, and the curing treatment may have resulted in higher sizing by partial melting and spreading of the rosin size components (melting point of rosin acid is about 80°C) on pulp fiber surfaces.

Figure 8 shows SEM images of surfaces of the handsheets, prepared from the carboxyl group-blocked pulp with 2% rosin soap size and 1% aluminum sulfate at pH 4.5 and dried at 20°C. Particles about 0.1 μm in diameter formed flocs on the surface (Fig. 8A) in a manner similar to that observed for the handsheets prepared from normal pulps.[13] Because these particles were observed also in handsheets prepared with alum only (without any sizes)[20] they might consist of aluminum compounds, which were formed in pulp suspensions and adsorbed on pulp fiber surfaces by nonionic interactions. In the same handsheets, on the other hand, large coagulants 2–4 μm in diameter were often observed on pulp fiber surfaces (Fig. 8B). No such coagulants have been observed in handsheets prepared from the normal pulp. Probably these coagulants consist of rosin size and aluminum compounds, which are formed from anionic rosin size components and cationic aluminum compounds in pulp suspensions. These coagulants must have been trapped in the pulp fiber mat by simple filtration effects during the drainage stage of the handsheet-making process. Furthermore, because some or most rosin size components are retained in the handsheets in such a manner as unevenly distributed states for the carboxyl group-blocked pulp, the handsheets had no or low sizing levels when the handsheets were dried at 20°C. The curing treatments must have brought about partial melting and spreading of the rosin size components on pulp fiber surfaces, resulting in a higher degree of sizing.

Therefore, when carboxyl groups in pulps are blocked, some rosin size components are unevenly present on pulp fiber surfaces. Consequently, the handsheets have poor sizing levels at the usual level of rosin soap size. In other words, carboxyl groups in pulps contribute to the achievement of more evenly distributed states of rosin size components on pulp fiber surfaces by the ionic retention mechanism between anionic pulp fiber surfaces and anionic rosin size components through cationic aluminum compounds in pulp suspensions. Achieving evenly distributed rosin size components on pulp fiber surfaces must lead to efficient sizing behavior of papers in the rosin soap size–alum systems.

Conclusions

The mechanism of rosin size retention in rosin soap size–alum systems was studied for handsheets prepared under various conditions and using carboxyl group-blocked pulp. Rosin size, aluminum, and calcium contents were evaluated for the handsheets, and the following conclusions were obtained.

1. Sizing level and rosin size content increased with increasing stirring time of pulp suspensions after adjusting the pH. Aluminum and calcium contents in the handsheets suggest that rosin size components are retained in the handsheets primarily in free acid form rather than as rosin aluminum or calcium salt.

2. When the carboxyl group-blocked pulp was used, rosin size, aluminum, and calcium contents decreased. Moreover, the handsheets dried at 20°C had no or low sizing levels, indicating that pulp carboxyl groups play a significant role in rosin size retention. Electrostatic interactions between anionic pulp carboxyl groups and anionic rosin size components through cationic aluminum compounds must be present in pulp suspensions, and these interactions may be the predominant mechanism of rosin size retention.

3. On the other hand, some nonionic interactions may be present among pulp fibers, rosin size components, and aluminum compounds in pulp suspensions, particularly at pH 6.2–6.5. These interactions also contribute to rosin size retention and the appearance of sizing features.

4. Because large coagulants, probably consisting of rosin size components, were often present on the surfaces of handsheets prepared from carboxyl group-blocked pulps, some rosin size components may be coagulated in pulp suspensions and retained on pulp fiber mats as large coagulants by simple filtration effects during the handsheet-making process.

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