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Intrafiber distribution of aluminum components in alum-treated handsheets

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Abstract The distribution of aluminum components in cross sections of pulp fibers for alum-treated handsheets was successfully measured by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis. In this case, gas-phase osmium coating of paper samples is necessary for the samples to have improved stability to long-term irradiation by electron beams at high magnification during the SEM-EDX measurements. The EDX line-analysis method was superior to the elemental mapping image method in the quantification of aluminum components. According to the SEM-EDX measurement for handsheets prepared from a pulp suspension by adding 2% (on dry weight of pulp) aluminum sulfate, the aluminum components were distributed almost homogeneously in the cross sections of pulp fibers. Aluminum species with smaller sizes than those of $Al(OH)_3$ flocs could probably penetrate the pulp fibers. Thus, aluminum components present only at the pulp fiber surfaces may contribute to retention of colloidal substances in pulp suspensions. From this aspect, a large amount of aluminum components present in the inside pulp fibers may be wasted.

Key words Aluminum sulfate · Intrafiber · Distribution · SEM-EDX · Osmium coating

Introduction

Aluminum compounds, especially aluminum sulfate (alum), have been used as retention aids in papermaking for about 200 years. Many studies have been reported to clarify structures and roles of aluminum components in aqueous solutions and in solid paper samples.[1–5] Because aluminum compounds added to pulp suspensions behave as retention aids of anionic substances such as sizes, polymers, dyes, fines, and colloidal pitches on the surfaces of pulp fibers, it is significant to elucidate intrafiber distribution of aluminum components in papers prepared under various conditions. Conventional electron probe X-ray microanalyzers (EPMA) have been used for mapping elements of inorganic fillers and pigments in cross sections of base and coated papers. However, intrafiber distribution of aluminum components in alum-treated paper using scanning election microscopy (SEM)-EPMA has not yet been reported. This is because general paper samples coated with platinum, gold, or carbon by means of an ion-spattering apparatus are unstable to long-term irradiation by electron beams at high magnification during the SEM-EPMA measurements.

This paper describes that distributions of aluminum in cross sections of pulp fibers for alum-treated handsheets were successfully measured using an SEM equipped with an energy dispersive X-ray (EDX) analyzer.

Materials and methods

Handsheet production

A commercially available bleached hardwood kraft pulp was beaten to 450 ml Canadian Standard Freeness with a PFI mill. Aluminum sulfate (Wako Chemicals, Tokyo, Japan) was added as a 1% aqueous solution to a 0.15% pulp suspension. For adjusting pulp suspensions to about pH 7, a 0.1 N NaOH solution was added to the pulp suspension after the aluminum sulfate addition. After the suspension was stirred for 30 s, handsheets were prepared using tap water according to the TAPPI test method.[6] The wet-pressed handsheets were dried at 20°C and 65% relative humidity (RH) for more than 1 day.

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Analyses

Cross sections of the handsheet samples were set on SEM mounts and were coated with osmium by a plasma coater (APC-120, Meiwa Shoji, Tokyo, Japan) set with anhydrous osmium tetraoxide (Wako Chemicals). Elemental mapping images in cross sections of pulp fibers of handsheet samples were obtained using an FE-SEM (S-4000; Hitachi, Tokyo, Japan) equipped with an EDX analyzer (EMAX-5770; Horiba, Kyoto, Japan). Conditions for this mapping image method were: 20 kV accelerating voltage, 15 μA emission current, 15 mm working distance, ×7000 magnification, 30 s for one scanning time, 120 accumulation scans with the highest quantitative mode for EDX, and 512 × 512 pixels for both SEM and mapping image resolutions. For elemental mapping analysis along lines (line-analysis method), the following conditions were adopted: 15 kV accelerating voltage, 15 μA emission current, 15 mm working distance, ×25000 magnification, 30 s for one scanning time, 50 accumulation scans with the highest quantitative mode for EDX, and 256 × 256 and 5 × 256 pixels for SEM image and the line-mapping resolutions, respectively. It took about 100 and 40 min to measure one sample by the mapping image and line-analysis methods, respectively.

Results and discussion

For the SEM-EDX measurement at magnifications of ×5000 or more to analyze the distribution of aluminum in a cross section of pulp fiber, at least 20 min of irradiation by electron beam is needed. However, when handsheet samples coated with platinum by means of an ion-spattering apparatus were subjected to SEM observation at ×5000 magnification and 10 kV, the surfaces were ruptured within a few minutes owing to charging up during the electron irradiation. In contrast, the stability of handsheet samples to electron beam irradiation was clearly improved by gas-phase osmium coating using the plasma coater. The pulp fiber surfaces observed in an SEM monitor often maintained their shapes even for several hours at ×25000 magnification and 15 kV accelerating voltage. Thus, mapping aluminum components in the cross sections of pulp fibers in alum-treated handsheets can be measured only using the gas-phase osmium coating technique by the SEM-EDX method.

Figure 1 shows SEM and aluminum mapping images of cross sections of pulp fibers in the handsheets. When the handsheet was prepared with 2% (dry weight of pulp)

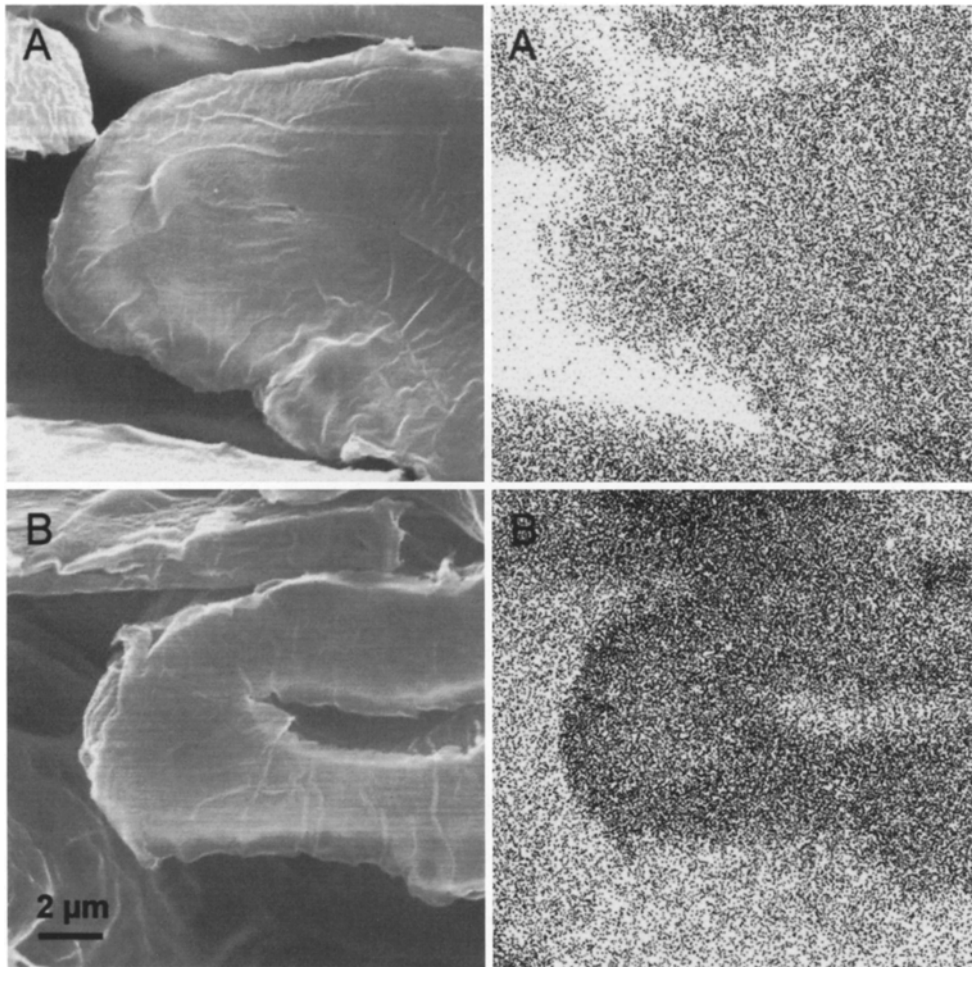

Fig. 1. Scanning electron micrographs and the corresponding energy dispersive X-ray analysis (EDX) elemental mapping images due to aluminum components of cross sections of pulp fibers in handsheets. **A** Handsheet was prepared with 2% (on dry weight of pulp) aluminum sulfate. **B** Handsheet was prepared with 8% aluminum sulfate followed by adjustment to about pH 7 with 0.1 N NaOH

aluminum sulfate (handsheet A), the dots due to aluminum were distributed almost evenly in the cross section of the pulp fibers. Thus, aluminum components originating from aluminum sulfate added to pulp suspensions seemed able to penetrate pulp fibers. In our previous paper, large amounts of $Al(OH)_3$ flocs were present on pulp fiber surfaces when the handsheet was prepared with 8% aluminum sulfate followed by adjustment to about pH 7 (handsheet B).[7,8] Those $Al(OH)_3$ flocs were formed from aluminum compounds in the pulp suspension during the pH adjustment with 0.1 N NaOH. As shown in Fig. 1B, aluminum dots in handsheet B seemed to be relatively rich at the surfaces of the pulp fibers, although a difference in aluminum distribution between handsheets A and B was not clear in these aluminum-mapping images.

Subsequently, the line-analysis method was applied to the cross sections of pulp fibers in handsheets A and B (Figs. 2A and 2B, respectively) for obtaining aluminum distribution. Expectedly, aluminum components were distributed almost homogeneously from the pulp fiber surface to the inside for handsheet A, whereas the aluminum content in handsheet B was clearly higher at the pulp fiber surface than inside the pulp fiber. Judging from the peak intensity due to aluminum in Fig. 2B, aluminum content at the pulp fiber surface was about 1.3 times as much as that of the inside pulp fiber. Probably the $Al(OH)_3$ flocs formed in pulp suspensions are adsorbed on the pulp fiber surfaces without penetrating the inside pulp fibers.[7] On the other hand, aluminum components smaller than the $Al(OH)_3$ flocs, such as Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^{+}$, and polyaluminum cations, which originate from the added aluminum sulfate, can penetrate pulp fibers in pulp suspensions and become fixed there by ionic or nonionic interactions.[7,8] Thus, the EDX line-analysis method gives important information about the distribution of aluminum components in cross sections of pulp fibers of alum-treated paper.

Because anionic colloidal substances such as size emulsion particles, fillers, fines, and colloidal pitches are too large to penetrate the inside pulp fibers, aluminum components present only at the pulp fiber surfaces can contribute to retention of these anionic substances in pulp suspensions. From this aspect, the large amount of aluminum components present in the inside pulp fibers may be wasted, whereas anionic polymer additives and anionic trashes dissolved in pulp suspensions may be fixed even in the inside pulp fibers where aluminum components are present. Furthermore, such large amounts of aluminum components present in the inside pulp fibers may bring about some changes in paper properties, such as reswelling capability in aqueous solutions.[9]

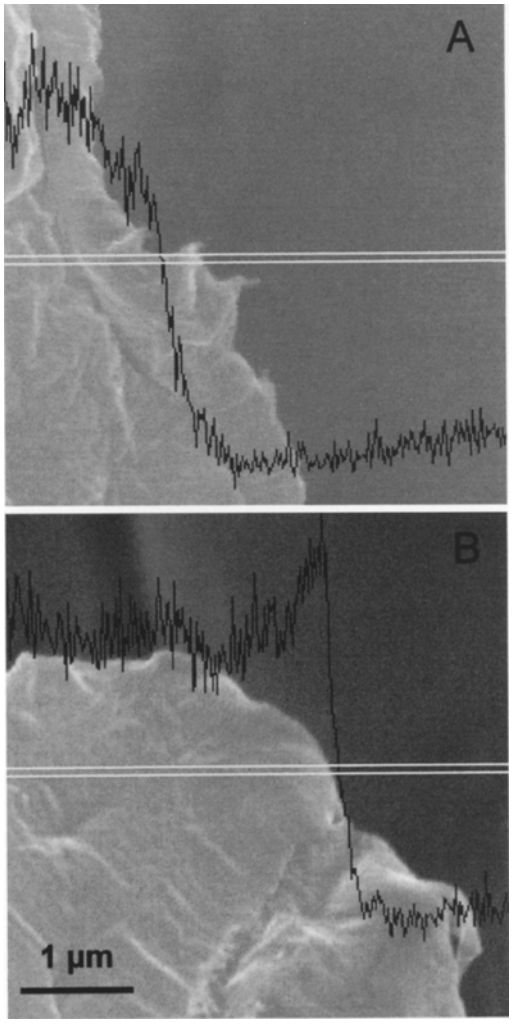

Fig. 2. Distribution of aluminum components determined by the EDX line-analysis method of cross sections of pulp fibers in handsheets **A** and **B** of Fig. 1. Areas between the two lines were analyzed

Conclusions

The gas-phase osmium coating of paper samples made it possible to measure distributions of aluminum components in cross sections of pulp fibers in alum-treated papers by the EDX line-analysis method. When 2% aluminum sulfate was added to pulp suspension, aluminum components in the prepared handsheets were distributed almost evenly in the cross sections of pulp fibers. Probably aluminum species smaller than $Al(OH)_3$ flocs can easily penetrate the inside pulp fibers in pulp suspensions. Therefore, only limited amounts of aluminum components present on pulp fiber surfaces must behave as retention aids of anionic colloidal substances in pulp suspensions.

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