Roles of Aluminum Sulfate in Rosin Sizing

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Abstract: Roles of aluminum components originating from aluminum sulfate (alum) in rosin sizing were investigated by X-ray photoelectron spectroscopy, X-ray fluorescence analysis and pyrolysis gas chromatography. Handsheets were prepared with 1% alum and 1% anionic rosin emulsion, where the stirring time of pulp suspensions at pH 6.7 or pH 4.5 between the alum and size additions varied from 3 to 3000 min. Sizing effects of the handsheets prepared at pH 6.7 decreased rapidly as the stirring time proceeded, although the sizing appearance of the handsheets prepared at pH 4.5 was observed even at an addition interval of 50 hrs. Under the neutral papermaking conditions, the Al components once adsorbed on pulp fibers were immediately counteracted by OH⁻ ions, followed by the Al desorption and the drop in rosin retention. On the other hand, the acidic circumstances preserved the Al retention and performance, resulting in higher rosin content and better sizing efficiency. The Al components present on pulp surfaces were then aggregated gradually, and the ability as a retention aid eventually became absent, although the Al content remained almost unchanged. However, the Al components that had lost the above function could make a great contribution to sizing appearance by tub-sizing the Al-containing handsheets with the same rosin emulsion. Therefore, alum in rosin sizing must play two individual roles in sizing response: a retention enhancer as which Al cations act at the wet end, and a sizing promoter as which non-ionic Al components perform in the dried paper sheet.

(Received 23 January, 2003; Accepted 28 March, 2003)

1. Introduction

Paper sizing provides controlled water-repellency to porous, hydrophilic paper sheets. Rosin emulsion sizing in combination with aluminum sulfate (alum) as a retention aid at the wet end has long and widely been applied to the practical paper-manufacturing processes because of low cost, easy operation and high efficiency. The sizing technologies have recently attracted much attention from industrial circles for the effective surface modification of biomass-based ecomaterials. Thus, the mechanisms of paper sizing are of very interest, and have been studied in many aspects.

Major interest in rosin-alum sizing is how the alum contributes to sizing, and then whether the salt formation of rosin sizes with aluminum components occurs or not. On the mechanisms proposed at the early stage for rosin-alum sizing systems, the formation of rosin-Al salts was based on the discussion since the rosin sizing without alum stimulated only little sizing effect [1-3]. However, the recent advancement of various analytical techniques has offered new findings: (1) anionic rosin emulsions were retained at dissociated carboxyl groups on pulp

fibers through the Al moieties [4], (2) most of the size components in dried paper sheets with good sizing were present as free acids without forming any aluminum salts after thermal treatment [5-7], (3) even in fatty acid soap size-alum systems, quite few Al salts were confirmed by solid-state ¹³C-nuclear magnetic resonance analysis, being minor components in the size constituents [8], and (4) the alum also played an important role in sizing with rosin-related sizes mainly consisting of ester-type rosin molecules having no chance to form Al salts [9, 10].

Reconsideration for the sizing phenomena reported so far resulted in a notice to confusion for the roles of alum at the wet end and in the dried paper sheets. Al components originating from alum must have a positive charge to retain anionic emulsions onto pulp. Thus, in alkaline papermaking the lapse of time between the alum and size additions was a striking factor for sizing because the Al cations immediately lost their positive charge by OH⁻ attack [9]. On the other hand, in surface sizing with dispersed rosin size the Al components in the dried sheets contributed to sizing enhancement, and the Al content closely reflected the sizing features [7, 11]. Do the Al components recover their ionic charges in aqueous

sizing media and act in a similar manner to that of alum at the wet end?

In this study, the roles of alum added at the wet end in rosin sizing were investigated in detail by drawing a clear distinction between retention and sizing appearance. Surface characterization of sized handsheets was carried out by X-ray photoelectron spectroscopy (XPS) with X-ray fluorescence analysis (XFA) or with pyrolysis gas chromatography (PyGC). The validity of the combined use of XPS and XFA was confirmed in our previous study [12]. The XPS/PyGC comparative analysis also exercised its power for the surface characterization [13]. Factors influencing sizing features were studied when two papermaking parameters, pH of paper stock and time intervals of additives' supply, were varied. Another effect of Al components with function insufficiency as a retention aid on surface sizing was also discussed.

2. Materials and methods

2.1 Materials

A commercial hardwood kraft pulp was beaten to 450 ml of Canadian Standard Freeness [14] with a PFI mill [15]. Anionic emulsion rosin size (AL-120, 50% solid content) was kindly provided by Japan PMC Co., Japan. Alum signifying $\text{Al}_2(\text{SO}_4)_3$ and other chemicals were reagent grade (Wako Pure Chemical Industries Co., Japan), and used without further purification.

2.2 Preparation of handsheets

A flowchart of handsheet-making and analyses is illustrated in Fig. 1. Alum (1% on dry weight of pulp) was added to pulp suspension with a 0.15% (wt/vol) consistency using tap water, followed by pH of the paper stock being adjusted to 6.7 or 4.5. An anionic emulsion rosin size (1% on dry pulp) was then added to the stock aliquot after stirring at room temperature for a designated time: 3, 5, 10, 30, 100, 300, 1000 or 3000 min. The handsheets with a basis weight of 60 g/m^2 were prepared by the standard method [16]. The handsheets obtained were air-dried with restraint at 20°C and 65% of relative humidity for more than 24 h. A part of the alum-treated handsheets without internal rosin sizing were tub-sized with the same anionic rosin emulsion of 0.5% (wt/wt), and then conditioned without any thermal treatment.

2.3 Analyses

Sizing level of rosin-sized handsheets was expressed as Stöckigt sizing degree [17]. Total rosin content was determined by PyGC analysis with an online methylation using a 25% tetramethylammonium hydroxide/methanol solution [4, 18]. Total Al content was quantified using

an XFA apparatus (MESA-500, Horiba Co., Japan) [4]. Surface characterization of rosin and Al components on the sized handsheets was performed using an AXIS-HSi spectrometer (Shimadzu/Kratos Co., Japan). The XPS analysis was carried out using a monochromatic $\text{AlK}\alpha$ X-ray source (1486.6 eV) under the X-ray generation conditions at a voltage of 15 kV and a current of 10 mA below $5 \times 10^{-7} \text{ Pa}$ [11-13]. Binding energies of spectra were related to a conspicuous $\text{C}_{1\text{S}}$ signal (unoxidized C-C) at 285 eV. Chemical abundances of rosin size and Al components obtained through the XPS analysis were defined by atomic ratios of $\text{C}_{1\text{S}}[\text{rosin}]/\text{C}_{1\text{S}}[\text{cellulose}]$ [13] and $\text{Al}_{2\text{P}}[\text{alum}]/\text{C}_{1\text{S}}[\text{background carbon}]$ [12], respectively.

Fig. 1 Preparation of handsheets with alum and anionic rosin emulsion size, and their analytical sequence.

3. Results and discussion

3.1 Influences of stock pH and addition intervals on sizing features

Fig. 2 shows the sizing characteristics of handsheets prepared at pH 6.7 or 4.5 by varying the stirring time between the alum and rosin additions. Sequential addition at a 3-min interval resulted in the similar sizing effect over 25 s, although the stock pH gave a great impact on the sizing appearance. At pH 6.7 the 30-min addition interval brought about a drastic sizing disappearance, although at pH 4.5 the sizing effect remained unchanged to some extent. Then, the sizing degrees decreased gradually with the time, while a slight sizing appearance was observed even at a 50-hrs interval. Therefore, the paper sizing in rosin-alum systems is quite sensitive to stock pH and addition intervals. In practical process, it often occurs that the paper furnish is left in the stock inlet for a few hours after the alum

Fig. 2 Sizing degree of handsheets prepared by internal rosin sizing at various intervals between 1% alum addition and 1% rosin addition at pH 6.7 (circles) or at pH 4.5 (squares).

addition, where the pH control is carried out with sulfuric acid according to demand. In recent, the papermaking systems have rapidly shifted from acidic to neutral conditions. Hence, that sizing diminishment may become a fatal disadvantage in the practical cases. In the following section, the factors influencing the sizing behavior are investigated by quantitative and surface analyses.

3.2 PyGC, XFA and XPS analyses of handsheets prepared by rosin-alum sizing

Fig. 3 displays the rosin content determined by PyGC and the atomic ratio of carbon that means a relative value of size/cellulose obtained through the XPS analysis. At pH 6.7 both the total and surface rosin contents rapidly

Fig. 3 Rosin content (open) and atomic ratio of carbon, size/cellulose (closed), of handsheets prepared by internal rosin sizing at pH 6.7 (circles) or at pH 4.5 (squares).

declined as the time from the alum addition to rosin addition proceeded, and resulted in a sharp decrease in the sizing degrees, as shown in Fig. 2. On the other hand, at pH 4.5 the rosin-related quantities of the sized handsheets decreased gradually with the time, and corresponded to the sizing features in Fig. 2. In a delicate phase, e.g. at pH 6.7 and a 3-min interval as compared with pH 4.5 and a 30-min interval, the sizing effect was well accounted for by the atomic ratios indicating surface rosin abundance rather than the conventional rosin content. The sizing parametric values of rosin content: 1 mg/g of pulp and atomic ratio of carbon: 0.6 gave tentative criteria for sizing appearance. In any cases, lowering sizing effect was caused by the interference with the rosin retention as expected. In the internal sizing with emulsion-type sizes, the size emulsions must be retained on the surfaces of pulp fibers at the wet end, and therefore the decrease in the attractive force acting between the rosin emulsions and the fiber surfaces was presumed from these results.

Fig. 4 compares the total Al content quantified by XFA and the surface Al abundance determined by XPS. The Al content of the handsheets prepared at pH 6.7 was inclined to decrease, however at the addition intervals until 10 min, a slight decrease in the Al content induced a drastic drop in the rosin content as in Fig. 3, whereas the surface Al abundance increased by the heterogeneous Al distribution [12]. Hence, a plenty of the Al components present on the pulp surfaces must lose the ability as a retention aid, resulting in the Al desorption. In contrast, at pH 4.5 the Al content in the handsheets increased continuously with the time, while the surface Al

Fig. 4 Al content (open) and atomic ratio of Al/C (closed) of handsheets prepared by internal rosin sizing at pH 6.7 (circles) or at pH 4.5 (squares). Symbols A-D in this fig. are marked for Table 1.

abundance showed a tendency to be constant and then to decrease gradually at the intervals over 30 min. Rosin content closely related to the electrostatic attraction of Al components declined all through, and thus it appeared unlikely to be the major cause that other substances such as anionic trash were additionally adsorbed onto the Al cores on pulp fibers. These interesting phenomena suggested two characteristic behavior of Al species on pulp surfaces: (1) a slow step that the positive charge of Al moieties faded on the pulp fiber surfaces, and (2) the sequential flocculation of the Al components on the surfaces. It was reported in our previous study that the charges of the fiber surfaces in pulp suspension containing alum could be controlled up or down by varying the pH of paper stock, and the Al components on the pulp surfaces were localized by the Al-O aggregation before the Al desorption [12]. Under the acidic paper-making conditions, the OH⁻ attack to consume the Al charges is expected not to occur dominantly. However, most Al-O components formed on pulp are insoluble in aqueous media at pH 4.5 [19, 20]. Thus, an irreversible reaction of Al ions with OH⁻ ions must promote the Al retention but reduce the fixing ability of Al components.

3.3 Two roles of Al components in rosin sizing

On the basis of the results obtained, it was supported that the ability of Al components as a retention aid was sensitive to the stock pH and irreversibly became lost. However, in the surface sizing with rosin emulsion size, internal alum addition remarkably enhanced the sizing performance, and the rosin content was related to the Al content [7, 11]. Once the alum-treated base paper was dried, the Al components in the dried sheet should be electrically neutral, and it is difficult to consider that the Al components recover their ionic charges in aqueous size solutions. Therefore, another function of non-ionic Al components on rosin sizing was presumed regardless of a retention enhancer at the wet end.

Table 1 represents the sizing degrees of Al-containing handsheets sized by internal or surface sizing with rosin emulsion size. The base handsheets for surface sizing were prepared from the aliquots of pulp suspension containing alum before the internal rosin addition. Clear sizing response by surface sizing was observed at all paper sheets, although only weak or slight sizing effects appeared by internal sizing. Furthermore the sizing degrees obtained by tub-sizing the handsheets that had been prepared at pH 6.7 were a little higher than those at pH 4.5, and the atomic ratios of Al/C appeared to reflect the sizing phenomena. The Al/C values against the Al content imply the states of the Al-O

Table 1 Sizing degree of handsheets prepared by internal sizing or by tub-sizing with rosin emulsion size.

Sample	Al parameter		Sizing degree, s	
	mg/g	Al/C × 10 ³	Internal	Surface
A	1.1	7.5	1.5	19
B	0.95	6.1	+ 0	15
C	1.2	3.5	3.3	13
D	1.3	3.2	0.8	12

Sheet samples A-D are marked in Fig. 4.

aggregation on the pulp fiber surfaces [12]. Therefore, the differences in the sizing effects may be caused by the rosin size distribution possibly linking to the Al localization/scattering behavior on the surfaces. It was confirmed that the Al components without having any ability to retain the rosin sizes on pulp fibers at the wet end would have a striking significance for a function as a sizing promoter in the dried paper sheets.

4. Conclusion

Alum as a typical retention aid in rosin sizing must play two roles in sizing appearance: a retention enhancer at the wet end and a sizing promoter in the dried paper sheet. The important ability as the retention enhancer was sensitive to the stock pH, and decreased with the time under the acidic to neutral papermaking conditions. However, a decisive function as the sizing promoter was maintained sufficiently, and made a great contribution to sizing appearance in tub-sizing systems. These two functions that the alum is involved are closely related each other, however they should be dealt with as being independent to elucidate the sizing mechanisms in rosin-alum systems.

Acknowledgements

This research was financially supported by the Society of Fiber Science and Technology, Japan and a Grant-in-Aid for Young Scientists (No. 14703030) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. The authors wish to thank Ms. A. Fujii for her assistance with sample preparation and XPS analysis.

References

1. E. Strazdins, *Tappi J.*, **60**, 102 (1977).

2. R. W. Davison, *J. Pulp Pap. Sci.*, **14**, J151 (1988).
3. J. Marton, *Nord. Pulp Pap. Res. J.*, **4**, 77 (1989).
4. T. Kitaoka, A. Isogai, and F. Onabe, *Nord. Pulp Pap. Res. J.*, **10**, 253 (1995).
5. T. Kitaoka, A. Isogai, and F. Onabe, *Nord. Pulp Pap. Res. J.*, **12**, 26 (1997).
6. T. Kitaoka, A. Isogai, F. Onabe, and N. Suguri, *Nord. Pulp Pap. Res. J.*, **12**, 182 (1997).
7. T. Kitaoka, A. Isogai, F. Onabe, and T. Endo, *Nord. Pulp Pap. Res. J.*, **16**, 96 (2001).
8. K. Ohno, A. Isogai, and F. Onabe, *J. Wood Sci.*, **48**, 197 (2002).
9. K. Ito, A. Isogai, and F. Onabe, *J. Wood Sci.*, **45**, 46 (1999).
10. F. Wang, Z. H. Wu, and H. Tanaka, *J. Wood Sci.*, **45**, 475 (1999).
11. T. Kitaoka, H. Yamamoto, R. Nishino, and H. Tanaka, *Sen'i Gakkaishi*, **57**, 212 (2001).
12. T. Kitaoka and H. Tanaka, *J. Wood Sci.*, **48**, 38 (2002).
13. H. Yamamoto, T. Kitaoka, and H. Tanaka, *Sen'i Gakkaishi*, in press.
14. TAPPI Test Methods, T 227 om-94 (1995).
15. TAPPI Test Methods, T 248 cm-85 (1995).
16. TAPPI Test Methods, T 205 om-88 (1995).
17. JIS Methods, P 8122 (1979).
18. Y. Ishida, H. Ohtani, T. Kano, S. Tsuge, and T. Yano, *Tappi J.*, **77**, 177 (1994).
19. W. F. Reynolds and W. F. Linke, *Tappi J.*, **46**, 410 (1963).
20. M. Kato, A. Isogai, and F. Onabe, *J. Wood Sci.*, **44**, 361 (1998).