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Mechanism of Retention of Alkenyl Succinic Anhydride (ASA) on Pulp Fibers at Wet-End of Papermaking*

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Abstract: The mechanism of retention of alkenyl succinic anhydride (ASA), which is one of the neutral sizes for papersheet, on pulp fibers at wet-end of papermaking process was studied in terms of roles of carboxyl groups in pulp fibers and those of cationic polymers and aluminum sulfate (alum) added to pulp suspension. ASA content in handsheets were determined using pyrolysis-gas chromatography (PY-GC). The results obtained using carboxyl-group-blocked pulp showed that carboxyl groups present in pulp fibers had a role to form ionic linkages with cationic ASA emulsion particles, and thus the ASA retention was mostly governed by the carboxyl groups of pulp fibers. The additions of cationic polymer and alum to pulp suspension resulted in increases in ASA retention on handsheets, and consequently their sizing features were improved. Some ASA emulsion particles originally having cationic surface charges are turned to those having amphoteric surface charges by alkenyl succinic acid (ASAcid), which are formed from ASA by hydrolysis on the surfaces of the ASA emulsion particles. Therefore, further retention of ASA may have been brought about on papersheet by additional ionic linkages formed between anionic pulp fibers, amphoteric ASA emulsion particles, cationic polymers and cationic aluminum compounds.

1. Introduction

Paper sizing is one of the significant treatments in papermaking process, and water-repellency of papersheet is generally controlled, in the case of internal sizing, by additions of sizing chemicals to pulp suspension. These sizing chemicals have hydrophobic structures in their molecules, and thus hydrophilic pulp fibers can be converted to hydrophobic papersheet by the size components. Alkenyl succinic anhydride (ASA) has been used as one of the neutral sizes for papersheet, and can give water-repellency to papersheet more efficiently than, for example, rosin-based sizes.

Since ASA has the structure of reactive acid anhydride, the formation of ester linkages between ASA and hydroxyl groups of cellulose surfaces in pulp fibers has been proposed for explaining the efficient paper sizing with ASA [1-4]. However, no direct evidences for the ester linkages have been obtained yet. In one of the pre-

vious papers, therefore, the structures of ASA components in ASA-sized handsheets were studied, and the results obtained showed that most of ASA components were present as alkenyl succinic acid (ASAcid), *i.e.* the hydrolyzed product of ASA, in handsheets; consequently, ASAcid molecules in papersheet contribute to the appearance of sizing features [5]. Then, roles of reactive ASA in paper sizing was investigated in terms of coalescent, coagulating and crystallizing behavior of ASA and ASAcid in aqueous media [6]. The results suggest the following mechanism of paper sizing; (A) the reactive structure of ASA is necessary for achieving sufficiently distributed states of hydrophobic size components with smaller coagulating structures on hydrophilic pulp fibers, (B) hydrolysis of ASA to ASAcid proceeds in papermaking process, and (C) ASAcid molecules, thus having sufficiently distributed states, contribute to appearance of sizing features of dried papersheet.

Internal sizing of papersheet with ASA consists of two separate mechanisms; one is, as reported previously [5,6], how reactive ASA molecules retained in papersheet contribute to appearance of sizing features, and

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another is how ASA emulsion added to pulp suspension are retained on pulp fibers at the wet-end of papermaking process. Since the addition levels of ASA emulsion to pulp suspension are generally 0.1-0.2% on dry weight of pulp or lower, efficient retention of ASA on pulp fibers is required for efficient sizing of papersheet. Generally, cationic polymers and aluminum sulfate (alum) are added with cationic ASA emulsion to pulp suspension, and especially the addition of alum gives higher sizing degrees to ASA-sized papersheet [7,8]. However, since suitable methods for determining small amounts of ASA components in papersheet have not been established so far, it has been unknown whether the effects of alum and other wet-end additives on ASA sizing are due to higher retention of ASA in papersheet or are due to some interactions, such as formation of chemical linkages, between ASA and the additives in papersheet. Recently, pyrolysis-gas chromatography (PY-GC) has been applied to determination of small amounts of additives such as sizes and polymers in papersheet [9]. In the case of emulsion rosin size and alum systems, it was found using PY-GC for determining rosin size content of handsheets that carboxyl groups originally present in pulp fibers are the actual interaction sites for the retention of rosin size [10].

In this paper, mechanism of retention of ASA on pulp fibers at wet-end of papermaking process was studied from the following two aspects: (A) roles of carboxyl groups of pulp fibers and (B) roles of alum and cationic polymer added to pulp suspension. PY-GC was used for obtaining relationships between sizing degrees of handsheets prepared under various conditions and their ASA content.

2. Experimental

2.1 Materials

Commercial hardwood bleached kraft pulp (HBKP) beaten to 450 mL of Canadian Standard Freeness was used as a normal HBKP sample for handsheet-making. Carboxyl groups in the beaten HBKP were converted to methylamide with methylamine HCl salt and water-soluble carbodiimide (WSC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide HCl salt, Wako Co.) according to the reported method [10]. After washing the methylamine-treated HBKP thoroughly with water, the amidation treatment was repeated again to the HBKP. An ASA sam-

ple (containing about 5% PEG), 2-hydroxypropyl-3-trimethylammonoyl starch Cl salt (HPTMA-starch) with degree of substitution (DS) of 0.03, and polyamideamine-epichlorohydrin resin (PAE : WS-570, Japan PMC Co.) were commercial products. Other chemicals and solvents used are of pure grade.

2.2 Preparation of Handsheets

ASA emulsion containing 0.5% ASA and 1% HPTMA-starch was prepared by using a double-cylinder type homogenizer, and were used for handsheet-making generally within 30 min after the emulsion preparation. An ASA emulsion, in which all ASA molecules were hydrolyzed to ASAcid by being left standing for 3 days at room temperature, was used as an "old ASA emulsion" sample. Handsheets with basis weight of 60 g/m² were prepared according to TAPPI Test Method [11]. In general procedure, the ASA emulsion, PAE and alum were added in this order to the 0.15% pulp suspension. Some handsheets were prepared without alum and/or PAE. The pHs of the pulp suspensions were about 6.5 and 6.9 for the systems with and without the 1% alum (on dry weight of pulp) addition, respectively. The pressed wet handsheets were dried at 20 °C and 65% relative humidity (R.H.) for more than one day. A part of the handsheets thus prepared were cured at 105 °C for 30 min, and then they were conditioned at 20 °C and 65% R.H.

2.3 Determination of ASA Content in Handsheets by PY-GC

About 0.5 mg of a handsheet was set in a small platinum pot for pyrolysis. The sample was pyrolyzed at 500 °C under the flow of He gas using a pyrolyzer (GP-1018, YANACO Co.), which was directly attached to a gas chromatograph (GC-9A, Shimadzu Co.) equipped with a capillary column of OV-1 (60 m × 0.25 mm) and an FID-detector. Injection and detector temperatures were set at 250 and 280 °C, respectively. The column temperature was initially set at 150 °C, and then was heated up to 300 °C at 5 °C/min.

2.4 Other Analyses

Sizing degrees of handsheets were measured according to the JIS method, and were expressed as Stöckgt sizing degrees [12]. Carboxyl content of pulps was measured according to TAPPI Test Method [13]. Optical microphotographs of ASA emulsions were obtained using Olympus model PM-10-A.

Fig.1 Gas chromatogram of pyrolyzed products of typical ASA-sized handsheet. Two peaks at allows are due to ASA components in handsheet.

3. Results and Discussion

3.1 Effects of Amidation of Carboxyl Groups in Pulp Fibers on ASA Sizing

Fig. 1 shows a typical gas chromatogram of pyrolyzed products of ASA-sized handsheets. Two peaks with allows in Fig. 1 originate from ASA components in handsheet. Since ASA content was obtained for several handsheet samples by the fibrous-form extraction method under alkaline conditions in the previous paper [5], relationship between ASA content obtained by the fibrous-form extractions and percentages of the two peaks' area due to ASA components in the PY-GC patterns was established for the handsheet samples. ASA content of the handsheets was obtained from PY-GC data by calibration on the basis of the above-obtained relationship. Then all data about ASA content in handsheets prepared in this study were obtained by the PY-GC method, and the deviation of the values were within $\pm 3\%$.

In order to make clear the interaction sites on pulp fibers, which participate in the retention of ASA emulsion particles at wet-end of papermaking process, sizing degrees and ASA content of handsheets prepared from normal HBKP were compared with those prepared from the HBKP, whose carboxyl groups were converted to non-ionic methyl amide groups. Carboxyl content of HBKP decreased from 0.061 to 0.002 mmol/g by the amidation

Fig.2 Sizing degrees (bar graphs) and ASA content (○) of handsheets prepared from normal HBKP and HBKP whose carboxyl groups were converted to non-ionic methylamide. Sizing degrees were measured after curing the handsheets at 100 °C for 30 min.

treatment [10]. Since this selective amidation of carboxyl groups in pulp fibers proceeds in aqueous media of pulp suspension, effects of carboxyl groups in pulp fibers on retention of sizes, retention-aids, strength resins and other wet-end additives can be evaluated without any changes in other pulp properties such as freeness.

As shown in Fig. 2, when the normal HBKP was used for the handsheet-making with ASA and PAE, ASA content increased with increasing addition levels of ASA to pulp suspension. Sizing degrees also increased with the addition of ASA, and were leveled off at the 0.2-0.5 % addition levels. Percentages of ASA retention, i.e. $100 \times (\text{ASA content retained in handsheet}) / (\text{amount of ASA added to pulp suspension})$, were about 65, 58 and 46 % at the addition levels of 0.1, 0.2 and 0.5% of ASA, respectively. On the other hand, when the COOH-blocked HBKP was used, the handsheets had clearly lower ASA content as well as lower sizing degrees. Especially, nearly no sizing degrees appeared on the handsheets for the 0.1 and 0.2% addition levels of ASA, and percentages of ASA retention were only about 5%. These results show that the anionic carboxyl groups present in pulp fibers are the interaction sites with cationic ASA emulsion particles in the ASA retention at wet-end of papermaking process; formation of ionic linkages between Pulp-COO⁻ and cationic groups of HPTMA-starch present at the sur-

Fig. 3 Sizing degrees (bar graphs) and ASA content (○) of ASA-sized handsheets prepared with PAE and/or alum.

faces of ASA emulsion particles must be the driving force of the ASA retention. Thus, nearly no interactions occur between abundant hydroxyl groups of pulp fibers and cationic ASA emulsion particles at wet-end.

When 0.5% ASA was added to the COOH-blocked HBKP suspension, the handsheet contained about 0.65 mg/g ASA (about 13% ASA retention). This ASA content was almost equal to that in the handsheet prepared from the normal HBKP with 0.1% ASA. However, sizing degree of the handsheet prepared from the COOH-blocked HBKP was lower than that prepared from the normal HBKP. Since nearly no ionic interactions occur between the COOH-blocked pulp fibers and ASA emulsion particles, flocculated ASA emulsion particles, in this case, must have been retained in the handsheet by simple filtration effect, as described later. Thus, the distributed states of ASA emulsion particles must be different between handsheets prepared from the normal HBKP and the COOH-blocked HBKP even at the same ASA content.

3.2 Effects of PAE and Alum Additions on ASA Sizing and Retention

Fig. 3 shows sizing degrees and ASA content of handsheets prepared from the normal HBKP with ASA emulsion, and PAE and/or alum. Sizing degrees of the handsheets were in the following order for the systems of additives: ASA-PAE-alum > ASA-alum > ASA-PAE > ASA. ASA content in the handsheets corresponded well with their sizing degrees; as long as the results obtained in

Fig. 4 ASAcid content (△) in handsheets prepared with "old ASA emulsion".

Fig. 3, handsheets having higher ASA content had higher sizing degrees. Thus, the additions of cationic polymers such as PAE and alum to pulp suspension lead to increases in ASA retention in papersheet. If ASA emulsion particles prepared with cationic starch maintain their cationic surface charges always in pulp suspension, only the following one mechanism is explainable for the results in Fig. 3. Namely, the cationic ASA emulsion particles are predominantly adsorbed on fine fractions of HBKP by ionic interactions between HPTMA-starch on the ASA emulsion particles and Fine-COO⁻ [14]. Then, carboxyl groups of longer pulp fibers and those of fine fractions, on which ASA emulsion particles are adsorbed predominantly, are linked by cationic polymers and cationic aluminum compounds, thus resulting in higher ASA retention. However, similar effects of the additions of PAE and alum to pulp suspension on sizing degrees were observed also for handsheets prepared from fine-free pulp. Thus, the results in Fig. 3 can not be explained only in terms of the higher retention of fine fractions by PAE and alum. The curing treatment of the handsheets resulted in increases in sizing degrees of about 10 s.

Fig. 4 shows ASAcid content of handsheets prepared with the old ASA emulsion, and PAE and/or alum. Especially ASAcid content was higher for handsheets prepared with alum. Since it is known that ASA molecules

Fig.5 Optical microphotographs of ASA emulsions under various conditions: (a) pH = 7 (original state); (b) after addition of alum to ASA emulsion of pH = 7; (c) pH = 10; (d) after addition of alum to ASA emulsion of pH = 10.

are partly hydrolyzed to ASAcid during papermaking process [1], hydrolyzed ASA or ASAcid formed on the surfaces of the emulsion particles may contribute to the formation of anionic sites on the emulsion surfaces even at wet-end. The formation of anionic sites on the emulsion surfaces can explain the higher retention of ASAcid in handsheets in terms of ionic interactions between anionic pulp fibers, anionic emulsion particles and cationic aluminum ions, as reported for the anionic emulsion rosin size-alum systems [10].

Fig. 5 shows optical microphotographs of ASA emulsion at pH = about 7 and 10 with and without alum. When alum was added to the ASA emulsion of pH = 7, the ASA emulsion particles maintained their well-dispersed states. However, when alum was added to the ASA emulsion of pH = 10, clear flocculation of ASA emulsion particles was observed. Since hydrolysis of ASA to ASAcid proceeds in emulsion particles more at pH = 10, the flocculation of the ASA emulsion particles with alum in Fig. 5c must have been brought about by the formation of anionic sites on the emulsion surfaces. These observations indicate that some ASA emulsion particles behave as amphoteric ones also at the practical wet-end; cationic sites are due to cationic starch used as the emulsion stabilizer of ASA and anionic sites are due

Fig.6 Sizing degrees (bar graphs) and ASA content (○) of handsheets prepared from the COOH-blocked HBKP. Percentages of ASA, PAE and alum are their addition levels on dry weight of pulp to pulp suspension.

to the ASAcid molecules formed at the surfaces of emulsion particles by hydrolysis.

Fig. 6 shows sizing degrees and ASA content of handsheets prepared from the COOH-blocked HBKP with ASA, and PAE and/or alum. At the 0.2% addition level of ASA, the handsheets had nearly no sizing degrees and very low ASA content, irrespective of the additions of PAE and/or alum. In contrast, at the 0.7% ASA addition, the handsheets had clear sizing features and 1-2 mg/g ASA content. Especially when the ASA addition was combined with 4% alum addition (on dry weight of pulp), the handsheets had higher ASA content (about 28% ASA retention) as well as higher sizing degrees after the curing treatment. These results of ASA retention in the COOH-blocked handsheets can be explained in terms of the formation of amphoteric surface charges on the ASA emulsion particles. If the ASA emulsion particles have amphoteric surface charges and they have chances to meet with one another in pulp suspension, flocculation must occur between the ASA emulsion particles without any additives. The additions of PAE and alum may enhance the flocculation of the amphoteric ASA emulsion particles in pulp suspension. Thus, in the case of the 0.7% ASA addition, ASA components were probably retained in the COOH-blocked handsheets by filtration effect of flocs of ASA emulsion particles formed in the pulp suspension.

Fig.7 Schematic representation of amphoteric behavior of ASA emulsion particles in aqueous media, and mechanisms of retention of these amphoteric ASA emulsion particles on papersheet.

The difference in sizing degrees between handsheets dried at 20 °C and those cured at 105 °C in Fig. 6 was quite larger than those observed for handsheets prepared from the normal HBKP in Fig. 4. Since ASA components must be retained in handsheets as flocs in the case of the results in Fig. 6, curing treatments may change the distributed states of ASA components on pulp fibers to some extent and bring about more favorable states for appearance of higher sizing features on papersheet.

3.3 Summary of ASA Retention at Wet-End

On the basis of the results obtained in this study, the mechanisms of ASA retention on pulp fibers at wet-end of papermaking process are summarized in Fig. 7. Carboxyl groups present in pulp fibers are the predominant retention sites of cationic ASA emulsions by the formation of ionic linkages. Since the carboxyl groups must be present homogeneously or as molecular-level on pulp fibers, the retention of cationic ASA emulsion particles at the carboxyl groups of pulp fibers may contribute to more homogeneous distributions of ASA emulsion parti-

cles on pulp fibers. The additions of cationic polymers and alum to pulp suspension may contribute to higher ASA retention through higher retention of fine fractions, on which ASA emulsion particles are adsorbed predominantly. On the other hand, ASAcid components partly formed at the surfaces of emulsion particles by hydrolysis of ASA at wet-end bring about the formation of amphoteric surface charges on the ASA emulsion particles. Thus, it was possible that ASA emulsion particles are further retained in papersheet by the additional ionic interactions formed between pulp fibers, amphoteric ASA emulsion particles, cationic polymers and cationic aluminum compounds. The effects of the addition of PAE and alum to pulp suspension on ASA retention in Fig. 3 may be, therefore, explained partly by this mechanism of the formation of amphoteric ASA emulsion particles. As described in the previous paper [5], the cellulase-treated residue of handsheets prepared with ASA and alum had an absorption due to carboxyl groups of aluminum salt (COOAl) in the IR spectrum. A part of the absorption

must have been due to aluminum salt of ASAcid formed on the surfaces of emulsion particles.

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