Structures of Alkenyl Succinic Anhydride (ASA) Components in ASA-Sized Papersheet*

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Abstract: Alkenyl succinic anhydride (ASA) is one of the reactive sizes used as cationic emulsions at wet-end of papermaking process. In order to make clear the mechanism of ASA sizing, structures of ASA components retained in handsheets were studied using model compounds and analytical techniques. The results of model experiments using low-molecular-weight cellulose and cationic starch showed that ASA was predominantly hydrolyzed to alkenyl succinic acid (ASAcid) in the presence of water without forming ester linkages with hydroxyl groups of carbohydrates. Sheet-form and fibrous-form extractions with organic solvents under various conditions indicated that most of ASA components were present as the structure of ASAcid in ASA-sized handsheets. The results of curing treatments of ASA-sized handsheets and impregnation treatments of ASA-related compounds into filter papers also were negative to the formation of ester linkages between ASA and cellulose-OH. Cellulase-treatments of ASA-sized handsheets followed by IR analysis of the obtained residues showed that ASA components were mostly present as the structure of ASAcid in papersheet. ASAcid aluminum salts may be present to some extent in papersheet prepared by ASA-alum systems. All these results imply that appearance of sizing features for ASA-sized papersheet is brought about by ASAcid molecules in papersheet. However, since non-reactive ASAcid has no sizing effect when added to pulp suspension, the reactive structure of ASA must be necessary for paper sizing because of some mechanisms other than the formation of ester linkages with hydroxyl groups of pulp fibers.

1. Introduction

Alkenyl succinic anhydride (ASA) is one of the typical neutral sizes as well as alkyl ketene dimer (AKD) for paper, giving water-repellency to paper efficiently by being added as cationic emulsions to pulp suspension even at 7-9 of pH due to the presence of calcium carbonate used as a filler. ASA is synthesized from internal olefin hydrocarbons (average carbon numbers = 18), originating from oil, and maleic anhydride by the ene-addition reaction. Commercially available ASA generally contains polyethylene glycol (PEG) to some extent, and is emulsified with aqueous cationic starch solutions in each paper mill just before using as a wet-end additive. Since ASA in the emulsion is easily hydrolyzed to alkenyl succinic acid (ASAcid), which has nearly no sizing effect, the ASA emulsion has to be used within 30 min after the emulsion preparation (1). The amounts of ASA required for sufficient sizing degrees of papersheet in the practical internal sizing process are 0.1-0.2% on dry weight of pulp or lower.

Since ASA has the structure of reactive acid anhydride, the ester formation between ASA and hydroxyl groups of cellulose surfaces of pulp fibers in ASA-sized papersheet has been believed to bring about the highly efficient sizing effects (Fig. 1). Primary reasons for supporting this ester-linkage formation are; 1) reactive structure of ASA is necessary for paper-sizing as in the case of AKD, and 2) even after Soxhlet extractions of ASA-sized papersheets with chloroform, ASA components remained partly in the sheets and they had still sufficient sizing features (2.4). However, since ASA content in papersheet is so low (generally lower than 2 mg/g) that the structure of ASA components retained in papersheet could not be analyzed by the usual methods, and thus the mechanism of paper sizing with ASA has not been established yet.
Fig. 1 Possible reactions of ASA with cellulose, water, PAE and alum in papersheet.

Generally a strong catalyst such as sulfuric acid, methanesulfonic acid or triethylamine is necessary for esterifications of cellulose with acid anhydrides, and sometimes non-aqueous media were used for the esterifications (4-6). However, ASA-sized handsheets have sufficient sizing degrees even after drying the wet paper web at 20°C without curing treatments. Furthermore, since water is always present in the papermaking process, it is not plausible that the ester formation proceeds predominantly in papersheet rather than the reaction between ASA and water (or hydroxyl ion). Especially, under alkaline papermaking conditions, where calcium carbonate is present, the reaction between ASA and OH seems to occur predominantly rather than the solid-phase reactions between ASA and cellulose-OH. Since Soxhlet extractions of papersheet with chloroform, which has nearly no swelling effect on cellulose, can not extract even physically-trapped organic compounds completely from cellulosic fibers, extractions of papersheet must be carried out in swollen fibrous form with aqueous organic solvents (7).

ASA components may form other structures than the esters and/or ASAcid in papersheet. Generally, polyamideamine-epichlorohydrin resin (PAE) or other cationic polymers as well as aluminum sulfate (alum) are added as wet-end additives to pulp suspension in ASA-sizing, and therefore ester linkages between ASA and PAE, and/or ASAcid aluminum salt may be present in the ASA-sized papersheet as shown in Fig. 1. Hence, the efficient sizing of papersheet with reactive ASA may not be explained by the simple mechanism of the ester formations between ASA and cellulose-OH.

In this paper, therefore, structures of ASA components in ASA-sized papersheet are studied, using analytical techniques similar to the AKD studies reported previously (7). Especially, the possibility for ASA to form ester linkages with cellulose-OH in ASA-sized papersheet was examined.

2. Experimental

2.1 Materials

Commercial hardwood bleached kraft pulp (HBKP) beaten to 450 mL of Canadian Standard Freeness was used for handsheet-making. An ASA sample (containing about 5% PEG), 2-hydroxypropyl-3-trimethylammonium starch Cl salt (HPTMA-starch) with degree of substitution (DS) of 0.03, and PAE (WS-570, Japan PMC Co.) were commercial products. Low-molecular-weight cellulose with degree of polymerization (DP) of 7, which is soluble in DMSO, was prepared from Whatman CF1 according to the reported method (8). Other chemicals and solvents used were of pure grade.

ASA emulsion containing 0.5% ASA and 1% HPTMA-starch was prepared by using a double-cylinder type homogenizer, and was used within 30 min after the emulsion preparation for usual handsheet-making. 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. Complete hydrolysis from ASA to ASAcid in the "old ASA emulsion" was confirmed from the IR spectrum of its freeze-dried material.

Handsheets with basis weight of 60 g/m² were prepared according to TAPPI Test Method (9). 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 humid-
ity (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.

ASAcid was prepared from ASA by refluxing with aqueous acetone (water : acetone = 1 : 1) for 3 h, and ASAcid monomethyl ester was prepared from ASA by refluxing with dry methanol for 3 h. The structures of these ASA-related compounds containing a small amount of PEG were confirmed by 1H- and 13C-NMR, and IR spectroscopy.

2.2 Model Experiments
The low-DP-cellulose, ASA and water (1 : 1 : 1, by weight) were sufficiently mixed on a metal plate, and the mixture was dried at 20-105 °C for 30-120 min. Then, the mixture was extracted with acetone at 80 °C for 4 h. The acetone-soluble fraction and the acetone-insoluble residue were dissolved in chloroform-d$_1$ and DMSO-d$_6$, respectively, for their NMR analysis. The low-DP-cellulose (0.1 g) was suspended in dioxane (50 mL) containing ASA (0.1 g), and this suspension was heated at 80 °C for 4 h. The residue was collected by filtration and washing thoroughly with acetone. The ASA emulsion containing 0.5% ASA, 1% HPTMA-starch and 98.5% water was spread on a metal plate, and was dried at 105 °C for 30 min. The dried film-like material was collected, and was extracted with acetone at 80 °C for 12 h.

2.3 Sheet-Form Extractions
Extractions of ASA-sized handsheets with chloroform were carried out using a Soxhlet extractor in sheet form for 12 h. In the case of water-acetone extraction, a handsheet samples were soaked in water at room temperature for 1 day for swelling, and then were heated in acetone at 80 °C for 4 h. For DMSO extraction, sheet samples were heated in DMSO at 90 °C for 4 h, followed by the Soxhlet extraction with chloroform for 12 h. These extracted samples were conditioned at 20 °C and 65% R.H. for more than one day before being subjected to sizing tests.

2.4 Fibrous-Form Extractions
A handsheet sample (about 2.4 g) was shredded into small pieces. Eighty mL of water for neutral extraction or 1 N NaOH for alkaline extraction was added to the shredded sample and the suspension was heated at 60 °C for 1 h. After cooling, pH of the suspension was adjusted to 6-7 by adding a dilute HCl solution. Then 80 mL of acetone was added to the suspension, and it was disintegrated with a double-cylinder type homogenizer for 10 min. Fresh 240 mL acetone was added to the suspension, and it was stirred at 70 °C for 12 h. An acetone solution containing 1 mg of tetrdecanolic acid used as an internal standard for gas-chromatography was added to the suspension, and its pH was adjusted to 1-2. The suspension was filtered and the residual fibers were washed thoroughly with fresh acetone. The filtrate and washings were combined, and the mixture was concentrated to about 30 mL by evaporation. Then the oily aqueous solution was extracted three times with chloroform. The chloroform-soluble fractions were combined, and the extracted material was dried by evaporation followed by drying in vacuo. A fresh diazomethane-diethyl ether solution was added to the sample, and then the mixture was stored at room temperature for one day for complete methylation of carboxyl groups of ASA components and the internal standard. The methylated sample was subjected to gas-chromatography for determining ASA components extracted under neutral and alkaline conditions.

2.5 Impregnation of ASA and its Related Compounds into Filter Paper
One % acetone solutions (wt./vol.) of ASA and its related compounds shown in Table 3 were prepared, and a filter paper (5B, basis weight = 108 g/m$^2$, Advantec Toyo Co.) was soaked in the solution for two second. One % chloroform solution (wt./vol.) was used for hydrolyzed AKD (ketone mixture). The solvent was removed by natural evaporation, and sizing degrees of the filter papers were measured before and after curing treatments.

2.6 Cellulase-Treatment
Ten handsheets (9.6 g) were cut into small pieces, and 500 mL of an acetate buffer at and 0.5 g cellulase (Meiserase, Meiji Seika Co.) were added to the sample (7). The mixture was stirred at room temperature for 40 days. After the clear supernatant was removed by decantation, the hydrolyzed residue was washed with fresh water several times by centrifugation. The cellulase-treated residue of ASA-sized handsheets were then obtained by freeze-drying.

2.7 Measurements
IR spectra were recorded on Shimadzu FTIR 8100M using the KBr disk technique or the film method on a thallium salt plate. Gas chromatograms of methylated ASA compounds extracted from handsheets were obtained using a capillary column of silicone OV-101.
3. Results and Discussion

3.1 Model Experiments

In order to elucidate the possibility for ASA to form ester linkages with cellulose-OH in ASA-sized paper sheet, the following three model experiments were carried out: (A) low-DP-cellulose and ASA were sufficiently mixed with water, and the paste-like mixture was dried at 20-105 °C for 30-120 min, and those of ASA (c) and ASAcid (d). DMSO-d$_6$ was used for (a), and chloroform-d$_6$ was used for (b-d).

Fig. 2 $^1$H-NMR spectra of acetone-insoluble (a) and acetone-soluble (b) fractions of mixture of cellulose oligomer (DP = 7), ASA and water dried at 105 °C for 30 min, and those of ASA (c) and ASAcid (d). DMSO-d$_6$ was used for (a), and chloroform-d$_6$ was used for (b-d).

with 0.25 mm X 50 m. Injection temperature was 240 °C, and column temperature was held at 240 °C for 5 min and then heated up to 280 °C at 2 °C/min. $^1$H- and $^13$C-NMR spectra were recorded on Bruker AC-300 spectrometer. Stockigt sizing degrees of handsheets were measured according to the JIS method [10].

Containing cationic starch and water was dried at 105 °C for 30 min.

Fig. 2a and 2b show $^1$H-NMR spectra of acetone-insoluble and acetone-soluble fractions, respectively, of dried material of the ASA/low-DP-cellulose mixture, prepared at 105 °C for 30 min by the above model experiment (A). For convenience, all hydroxyl protons of the low-DP-cellulose were converted to OD groups by the addition of a small amount of DCI into the sample solution (Fig. 2a). The resonance at about 3.6 ppm in Fig. 2b-2d was due to methylene protons of PEG present in the ASA sample. Although the pattern of Fig. 2a was almost identical to that of the original low-DP-cellulose, resonances derived from ASA components appeared at about 0.85 and 1.25 ppm due to their methyl and methylene protons, respectively, suggesting the presence of unextractable ASA components in the acetone-insoluble fraction. However, these resonances were detected in all $^1$H-NMR spectra of the acetone-insoluble fractions examined so far, and the relative resonance areas between methylene protons of ASA components and C1-protons of the low-DP-cellulose were almost constant for all acetone-insoluble fractions, that were prepared at 20-105 °C for 30-120 min by the model experiment (A). Therefore, the small resonances due to ASA components in $^1$H-NMR spectra of the acetone-insoluble fractions are likely to originate from ASA components physically entangled in the low-DP-cellulose sample without forming ester linkages.

As shown in Fig. 2b and 2d, $^1$H-NMR spectrum of the acetone-soluble fraction was almost identical to that of ASAcid, except for the range of 0.95-1.15 ppm; almost all ASA components extracted with acetone from the mixture had the structure of ASAcid. Thus, hydrolysis of ASA proceeded predominantly during the drying process of the mixture in the presence of water rather than the ester formation with cellulose-OH. The pattern of resonances at about 0.95-1.15 ppm in Fig. 2b due to methyl protons, that are linked to carbons with double bonds, suggests that isomerization of double bonds occurs in ASA components during the heating treatment.

The results of the model experiment (B) were similar to those obtained by the model experiment (A); no ester linkages were formed between ASA and the low-DP-cellulose even under non-aqueous conditions.

Fig. 3d and 3e show IR spectra in carbonyl ranges of
Table 1 Sizing Degrees of ASA-Sized Handsheets after Solvent Extractions

<table>
<thead>
<tr>
<th>Handsheet samples</th>
<th>Original</th>
<th>CHCl₃</th>
<th>H₂O-acetone</th>
<th>DMSO</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 0.2% ASA</td>
<td>19</td>
<td>28</td>
<td>10</td>
<td>+0</td>
</tr>
<tr>
<td>B: 0.2% ASA</td>
<td>25</td>
<td>32</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.04% PAE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C: 0.2% ASA</td>
<td>39</td>
<td>50</td>
<td>23</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>1.0% Alum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D: 0.2% ASA</td>
<td>46</td>
<td>54</td>
<td>30</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.04% PAE</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.0% Alum</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Percentages of additives: their addition levels on dry weight of pulp to pulp suspension.

Table 3 IR spectra of ASA (a), ASAcid (b), ASAcid methyl ester (c), ASA emulsion (ASA + cationic starch + water) dried at 105 °C for 30 min (d), acetone-insoluble fraction of the sample (e), and cationic starch (f).

3.2 Extractions of ASA-Sized Handsheets

Table 1 shows sizing degrees of four ASA-sized handsheets. Their sizing degrees increased by the Soxhlet extraction with chloroform, as reported by Roberts and Daud [2]. They hypothesized that appearance of sizing features is brought about by ASA components chemically linked to cellulose-OH, assuming that most of ASA components physically entangled in pulp fibers were extractable by Soxhlet extractions. They speculated also that, after the solvent extractions, hydrophilic ASAcid, a by-product of ASA, was removed by the solvent extractions and thus sizing degrees improved. However, as shown in Table 1, the pre-treatment of the handsheets with water for swelling resulted in decreases in sizing degrees after the extraction with acetone. Furthermore, extraction with DMSO at 90 °C brought about very low sizing degrees for these handsheets, although they had nearly no weight-loss by the extraction procedure. Therefore, ASA components even physically entangled in pulp fibers of handsheets can not be extracted completely with such solvents as chloroform, which could not swell cellulose pulp fibers at all [7].

Then, ASA components were extracted with aqueous acetone from handsheets in fibrous form, for swelling of pulp fibers as possible, under neutral and alkaline conditions. Ester linkages between ASA and cellulose-OH, if they are present in handsheets, are stable in the neutral extraction, whereas they are cleaved completely in the alkaline extraction. As shown in Fig. 4, no sizing feature appeared on the handsheets prepared with the old ASA emulsion, whose ASA component was ASAcid. Two ASA-sized handsheets both had differences in the amounts of ASA components extracted between neutral and alkaline conditions, although the differences between them were smaller than 0.2 mg/g. These differences may have corresponded to the amounts of ASA components chemically
linked to cellulose-OH in the handsheets. On the other hand, similar difference was observed for the handsheets prepared with the old ASA or ASAcid emulsion, which had no chances to form ester linkages with cellulose-OH. A part of ASAcid, even physically entangled in pulp fibers, must be, therefore, unextractable with aqueous acetone under neutral conditions. Swelling of pulp fibers and/or partial formation of ASAcid sodium salt with aqueous NaOH may enhance the extractability of ASAcid from pulp fibers of handsheets. These results indicate that the differences in the amounts of ASA components extracted between neutral and alkaline conditions for the ASA-sized handsheets were not due to the ASA components chemically linked to cellulose-OH but were due to difference in extractability of ASAcid between the two conditions. Therefore, the results of these fibrous-form extractions were negative to the hypothesis that ester linkages between ASA and cellulose-OH are present in ASA-sized papersheet; ASA components must be present in handsheets as the structure of ASAcid without forming ester linkages with hydroxyl groups of pulp fibers.

### 3.3 Curing Treatments of ASA-Sized Handsheets

Sizing degrees of ASA-sized papersheet generally increase by curing or thermal treatments. So far, these phenomena have been explained by increases in the ester linkages between ASA and cellulose-OH during the curing treatments, on the basis of the hypothesis that sizing degrees correspond to the amounts of the ester linkages in ASA-sized papersheet. Table 2 shows effects of curing on sizing degrees of ASA-sized handsheets. When the handsheets were cured at the next day after the handsheet-making, sizing degrees increased for all samples examined. However, even after one year's condition-

![ amounts of ASA components extracted from ASA-sized handsheets in fibrous form under neutral (N) and alkaline (A) conditions. Percentages of ASA, PAE and alum are their addition levels on dry weight of pulp to pulp suspension.](image)

**Table 2** Effects of Curing Treatments on Sizing Degrees of ASA-Sized Handsheets

<table>
<thead>
<tr>
<th>Handsheet samples</th>
<th>One day after handsheet-making</th>
<th>One year after handsheet-making</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before curing . After curing</td>
<td>Before curing . After curing</td>
</tr>
<tr>
<td>A: 0.2% ASA</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>26</td>
<td>27</td>
</tr>
<tr>
<td>B: 0.2% ASA 0.04% PAE</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>32</td>
<td>35</td>
</tr>
<tr>
<td>C: 0.2% ASA 1.0% Alum</td>
<td>39</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>35</td>
</tr>
<tr>
<td>D: 0.2% ASA 0.04% PAE 1.0% Alum</td>
<td>46</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>58</td>
<td>42</td>
</tr>
</tbody>
</table>

Percentages of additives: their addition levels on dry weight of pulp to pulp suspension.
ing, sizing degrees increased by the curing treatments for
ASA-sized handsheets prepared without alum. Since ASA
is unstable to water or moisture, all ASA molecules must
have been already transformed to non-reactive ASAcid in
the handsheets during one year’s conditioning. Thus, the
increase in sizing degrees by curing treatments after one
year’s conditioning must be explained by some mecha-
nisms other than the ester linkage formation. Re-distribu-
tion of ASA components in pulp fibers may be one
reason for the increase in sizing degrees by curing treat-
ments, as observed for AKD and rosin sizes. The in-
crease in sizing degrees of ASA-sized handsheets after
Soxhlet extraction with chloroform at about 50–60 °C
(Table 1) also may be due to this re-distribution effect.
Therefore, the curing effects are not necessarily ex-
plained in terms of the simple mechanism of the ester
linkage formation in ASA-sized paper sheet. The differ-
ence between handsheets prepared with and without
alum in Table 2 can not be interpreted at this point, and
these curing effects should be further studied from the
aspects of re-distribution of size components in pulp fi-
bers.

3.4 Impregnations of ASA-Related Compounds into
Filter Papers

Table 3 shows sizing features of filter papers impreg-
nated with ASA-related compounds by their acetone
solutions. Although sizing mechanisms of ASA may be
somewhat different between the usual internal sizing and
the impregnation treatments, the possibility for ASA to
form ester linkages with hydroxyl groups of cellulose-\(\text{OH}\)
was examined also by the impregnation experiments.
When the filter paper was treated with ASA, sufficient
sizing feature appeared even after curing at 100 °C for
0.1 h. In contrast, non-reactive ASA-related compounds
such as ASAcid, ASAcid monomethyl ester and ASAcid
dimethyl ester gave no sizing feature to filter papers af-
ter the same curing treatment. This result may support
the hypothesis that sizing features of ASA-sized paper-

Table 3 Sizing Features of Filter Papers Impregnated with ASA-Related Compounds

<table>
<thead>
<tr>
<th></th>
<th>Curing conditions</th>
<th>Sizing features</th>
<th>After CHCl(_3)-extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp. (°C)</td>
<td>Time (h)</td>
<td>Original</td>
</tr>
<tr>
<td>ASA (20)(^a)</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ASA (20)(^a)</td>
<td>24</td>
<td>+ +</td>
<td>+ +</td>
</tr>
<tr>
<td>ASA</td>
<td>100</td>
<td>0.1</td>
<td>+ +</td>
</tr>
<tr>
<td>ASA</td>
<td>100</td>
<td>1</td>
<td>+ +</td>
</tr>
<tr>
<td>ASAcid</td>
<td>100</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>ASAcid</td>
<td>100</td>
<td>1</td>
<td>+ +</td>
</tr>
<tr>
<td>ASAcid-mMe(^b)</td>
<td>100</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>ASAcid-mMe(^b)</td>
<td>100</td>
<td>1</td>
<td>+ +</td>
</tr>
<tr>
<td>ASAcid-dMe(^c)</td>
<td>100</td>
<td>0.1</td>
<td>-</td>
</tr>
<tr>
<td>ASAcid-dMe(^c)</td>
<td>100</td>
<td>1</td>
<td>+ +</td>
</tr>
<tr>
<td>Hydrolyzed AKD (ketones)</td>
<td>100</td>
<td>0.1</td>
<td>+ +</td>
</tr>
<tr>
<td>Hydrolyzed AKD (ketones)</td>
<td>100</td>
<td>1</td>
<td>+ +</td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>100</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>100</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Succinic anhydride</td>
<td>100</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Phthalic acid</td>
<td>100</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>100</td>
<td>1</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^a\)No curing.
\(^b\)ASAcid monomethyl ester.
\(^c\)ASAcid dimethyl ester.
sheet are brought about by formation of ester linkages between ASA and cellulose-OH. However, as shown in Table 3, the curing treatment at 100 °C for 1 h resulted in appearance of sizing features on filter papers impregnated even with the non-reactive ASAcid and ASAcid methyl esters. When non-reactive hydrolyzed AKD (ketone mixture) was used for the impregnation treatment, sufficient sizing features appeared even after curing at 100 °C for 0.1 h. Acid anhydrides without alkenyl chains such as phthalic anhydride, maleic anhydride and succinic anhydride gave no sizing features to filter papers. Phthalic acid or succinic acid gave no sizing features, either. Thus, although it is true that the reactive ASA gives sizing features to filter papers more efficiently than non-reactive ASAcid or ASAcid methyl esters, all these ASA-related compounds have capability to give sizing features to filter papers. Furthermore, the results in Table 3 suggest that appearance of sizing features on papersheet is governed by distributed states of hydrophobic size components in hydrophilic pulp fibers. The results of these impregnation experiments also are negative to the hypothesis that sizing features of ASA-sized papersheet are brought about only by the formation of ester linkages between ASA and cellulose-OH.

3.5 Cellulase Treatments of ASA-Sized Handsheets

As shown in Fig. 5, ASA-sized handsheets were treated with cellulase in an acetate buffer at pH=5 to remove cellulose and hemicellulose in the handsheets as possible. It was confirmed in preliminary experiments that the ester linkage of ASAcid monomethyl ester was stable under the conditions of the cellulase treatment; ester linkages between ASA and cellulose-OH, if they are present in handsheets, are not cleaved at all during the cellulase treatment. Yields of the cellulase-treated residues were 1.4, 0.7 and 1.1% for ASA-alum-sized handsheets, ASA-PAE-sized handsheets and PAE-treated handsheets, respectively. ASA contents in the residues A and B in Fig. 5 were about 10 and 15%, respectively, and thus ASA components in the handsheets were successfully concentrated by the cellulase treatments.

Fig. 6a, 6c and 6e show IR spectra of the cellulase-treated residues A, B and C in Fig. 5, respectively. Two absorptions due to carbonyl groups of amides in albumin (Fig. 6f) were present also in the spectra of Fig. 6a, 6c and 6e; a part of cellulase was adsorbed on the residues without being removed by washing with water. As shown in Fig. 6a and 6c, patterns of IR spectra were different between the cellulase-treated residues of handsheets prepared by ASA-alum and ASA-PAE systems. A clear absorption due to carbonyl groups of esters or free COOH of ASAcid was observed at about 1725 cm⁻¹ for the residue B (Fig. 6c). However, most of this absorption was removed by the extraction with aqueous acetone at 80 °C for 4 h (Fig. 6d), thus indicating that this absorption was mostly assigned to carbonyl groups of ASAcid. Although a small absorption due to esters or free COOH was still detected at about 1725 cm⁻¹ in Fig. 6d, IR spectrum of the residue C (Fig. 6e), which was obtained from handsheets prepared with PAE only, and that of freeze-dried PAE (Fig. 6l) also had absorptions at this range; the absorption at about 1725 cm⁻¹ in Fig. 6d must be due to carbonyl groups of PAE components present in the residue. The possibility for ASA to form esters with PAE in ASA-PAE-treated handsheets, as shown in Fig. 1, could not be confirmed from these IR spectra.

On the other hand, the residue A had a small shoulder absorption at about 1725 cm⁻¹ and had a large broad absorption at about 1650 cm⁻¹ (Fig. 6a). This absorption became slightly sharp by the extraction with aqueous acetone (Fig. 6b). Thus, some of ASA components in the
handsheets prepared by the ASA-alum system were present as ASAcid, whose carboxyl absorptions were shifted to lower wave numbers by forming strong hydrogen bonds probably with hydroxyl groups of pulp fibers. Furthermore, since Fig. 6a and 6b had broad absorptions at about 1550-1600 cm⁻¹, which were not observed in Fig. 6c and Fig. 6d, a part of ASAcid molecules may form aluminum salt in the handsheets. This absorption due to COOAI groups may be derived also from alumi- num salts of carboxyl groups originally present in pulp fibers.

These IR studies of the cellulase-treated residues show the following results: (A) most of ASA components do not form esters with cellulose-OH in ASA-sized handsheets, (B) in ASA-PAE-sized handsheets, most of ASA components are present as ASAcid molecules with somewhat isolated structures, (C) in ASA-alum-sized handsheets, ASA components are present as ASAcid molecules with strong hydrogen bonds with hydroxyl groups of pulp fibers and as ASAcid aluminum salts to some extent.

All the results obtained in this study show that most of ASA components are present as the structure of ASAcid in ASA-sized handsheets without forming ester link-ages with hydroxyl groups of pulp fibers; appearance of sizing features must be brought about by ASAcid mole- cules in ASA-sized papersheet. It is true, however, that ASAcid emulsions had no sizing effect and reactive ASA is necessary for efficient sizing of papersheet when used as a wet-end additive. Thus, paper-sizing with reactive ASA must be explained in terms of mechanisms other than the formation of ester linkages. These subjects of mechanisms of ASA sizing, i.e. roles of reactive ASA in internal paper-sizing will be reported in the following paper.

References