The mechanism of wet-strength development of cellulose sheets prepared with polyamideamine-epichlorohydrin (PAE) resin

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Abstract

The mechanism of wet-strength development of cellulose sheets prepared with typical wet-strength additive, polyamideamine-epichlorohydrin resin (PAE), was studied by some analytical techniques. PAE-containing sheets were prepared from cellulose fibers with different carboxyl contents by either internal addition of PAE to slurries of cellulose fibers or soaking treatment of once-dried cellulose sheets with aqueous PAE solutions. The results showed that carboxyl groups in cellulose fibers behaved as anionic retention sites of cationic PAE molecules for both internal addition of PAE in the sheet-making process and soaking treatment of cellulose sheets with PAE solutions. Moreover, wet-tensile strength of the PAE-containing sheets was clearly improved by heating treatment of the sheets at 110 °C for 10 min, when the cellulose fibers of the sheets clearly had carboxyl groups. FT-IR analysis of PAE films showed that ester bond formation between carboxyl groups at the end of polyamideamine chains in PAE and azetidinium groups of PAE, i.e. within PAE molecules, are possible to occur at least in heated PAE films. PAE-containing cellulose sheets were then subjected to cellulase treatment to obtain PAE-rich fractions in the sheets by removing most of cellulose and hemicellulose fractions without any interactions with PAE. The cellulase-treated residues obtained in the yields of about 1% were analyzed by FT-IR. The result revealed that significant amounts of ester bonds formed between azetidinium groups of PAE and carboxyl groups of cellulose fibers were present in the PAE-containing cellulose sheets, and that these ester bonds increased by heating treatment of the sheets. Thus, it was concluded that wet-strength development of PAE-containing cellulose sheets is primarily ascribed to the ester bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers, i.e. the covalent bond formation.

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1. Introduction

Wet strength is one of the most significant properties especially for tissue paper, paper towel, liquid packaging base paper etc, and defined as tensile strength of cellulosic paper sheets re-wetted with water. Polyamideamine-epichlorohydrin resins (PAE) are commonly used wet-strength additives for this purpose [1–5]. PAE is synthesized from polyamideamine chains by reacting with epichlorohydrin, resulting in the formation of the unique four-membered 3-hydroxy-azetidinium ring at about 80% of each amideamine repeating unit together with partial cross-linking between polyamideamine chains through 2-hydroxypropane bridges originating from the attached epichlorohydrin [6]. Thus, PAE molecules in commercial PAE/water solutions are cross-linked and highly dense polymers with, for example, weight and number average molecular mass values of 1,140,000 and 27,000, respectively, and polydispersity of 42 [7].

The mechanisms of wet-strength development of cellulose sheets prepared with PAE have been extensively studied [2,3,8–10], and the reinforcement and protection mechanisms have been proposed [8]. The former is the so-called reaction mechanism between azetidinium groups of PAE and carboxyl groups of cellulose fibers, which are present as minor functional groups. The latter is the formation of water-insoluble PAE networks, which inhibit fiber-bond detachment of PAE-treated cellulose sheets re-wetted in water. Wågberg and Björklund reported from the results obtained by FT-IR analysis of PAE-treated sheets prepared from a carboxymethylated cellulose with degree of substitution of 0.069 that ester bonds were formed between azetidinium groups of PAE and carboxyl groups of the carboxymethylated cellulose and these covalent bonds...
directly contributed to wet-strength development of the sheets [9]. In a series of our PAE studies, we have developed new analytical methods of more detailed chemical structures of PAE by NMR [6] and absolute molecular mass values by size-exclusion chromatography attached with a multi angle-laser light scattering detector [7]. Moreover, the roles of azetidinium groups and molecular mass values of PAE in wet-strength development of cellulose sheets prepared with PAE were studied [11,12]. The cationic quaternary ammonium groups of azetidinium rings primarily contribute to retention of PAE molecules in cellulose sheets by electrostatic interactions in the sheet-making process [2,3,9,11]. The azetidinium groups of PAE allow to bring about cross-linking reactions of PAE molecules by heating treatment of PAE-treated cellulose sheets to increase in molecular mass values of PAE, which is necessary for wet-strength development of PAE-treated cellulose sheets [7].

In this study, therefore, the mechanism of wet-strength development of cellulose sheets by PAE was studied by FT-IR analysis of cellulose-treated residues of PAE-containing cellulose sheets to make clear whether or not the covalent bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers occurs in cellulose-containing sheets prepared at usual addition levels of PAE. The influence of heating of the PAE-containing sheets on wet-strength improvement was also studied in terms of the covalent bond formation. Because cellulase treatments removed most of cellulose and hemicellulose fractions without any interactions with additives, such as sizing agents used in papermaking, in the sheets under mild conditions [13–16], the PAE-rich fractions containing PAE/cellulose fiber interfaces were expected to be obtained by the cellulase treatment. In addition, the influence of carboxyl contents in cellulose fibers on PAE retention as well as wet-strength development of PAE-treated cellulose sheets [7].

2. Experimental

2.1. Materials

A commercial hardwood bleached kraft pulp (HBKP), HBKP whose carboxyl groups were mostly converted to methylamide groups using methylamine and water-soluble carbodiimide in a HBKP/water suspension [17], linter pulp (Ashless linter pulp: Advantec Toyo, Ltd., Japan) and TEMPO (2,2,6,6-tetramethylpyridine-1-oxy radical)-oxidized linter pulp [18] were used in making cellulose sheets. α-Celullose contents of HBKP and linter pulp were about 90% and 99%, respectively. Carboxyl contents of these cellulose pulps are listed in Table 1. A commercial PAE/water solution (solid content of 12.5%) was kindly provided by a supplier. This PAE contained carboxyl and amino groups of 0.27 and 3.27 mmol/g, respectively [11]. A commercial crude cellulase (Onozuka R-10, Yakult Corp., Japan) was used to remove cellulose and hemicellulose fractions of PAE-containing cellulose sheets. Sodium azide and other solvents and reagents were of reagent grades (Wako Pure Chemicals, Japan), and used without further purification.

<table>
<thead>
<tr>
<th>Table 1: Carboxyl content (mmol/g) of hardwood bleached kraft pulp (HBKP), methylamidated HBKP, linter pulp and TEMPO-oxidized linter pulp</th>
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<tbody>
<tr>
<td>HBKP[^a^]</td>
</tr>
<tr>
<td>Methylamidated HBKP[^a^]</td>
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<tr>
<td>Linter pulp[^a^]</td>
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<tr>
<td>TEMPO-oxidized linter pulp[^b^]</td>
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[^a^] Determined by the titration method using methyl red as an indicator [17].
[^b^] Determined by the conductometric titration [15].

2.2. Cellulose sheet making

Handsheets were made from HBKP, methylamidated HBKP, linter pulp and TEMPO-oxidized linter pulp with or without PAE using tap water at pH 7.8 according to TAPPI Test Method [19]. The cellulose sheets prepared without PAE were then soaked in PAE solutions with various concentrations for 10 s, followed by pressing the wet sheets using a mangle (cylinder press) having two rollers to control the pick-up weight of the PAE solution in the base sheets. Each wet sheet was placed between a metal plate and three blotters, and additionally pressed at 3.43 kPa for 5 min. Unheated cellulose sheets were prepared by drying the wet sheets at 23 °C and 50% relative humidity for more than 1 day. Some of these unheated sheets were then heated at 110 °C for 10 min in an oven, and then conditioned at 23 °C and 50% relative humidity for more than 1 day.

2.3. Preparation of PAE film

The original PAE solution was diluted to 2.5% solid content by water, and the PAE solution was cast on a polyethylene plate. PAE films were obtained by drying the PAE solution on the plate at room temperature for several days. Some of the PAE films were then heated in an oven at 110 °C for 10 min.

2.4. Cellulose treatment of PAE-containing cellulose sheets

The cellulose sheets prepared from slurries of cellulose fibers by internal addition with 0.3% (on dry weight of cellulose) PAE were cut into pieces smaller than 0.5 cm × 0.5 cm. These piece sheets of about 10 g were suspended in de-ionized water (500 mL) in a 1 L Erlenmeyer flask. Cellulase (0.5 g) and sodium azide used as a preservative (0.015–0.215 g) were added to the suspension. This suspension was stirred at room temperature for 2.5–3.5 months. Then, the suspension was centrifuged, and the powder-like residue was thoroughly washed with de-ionized water by centrifugation followed by freeze-drying.

2.5. Analyses

FT-IR spectra of PAE films and the cellulase-treated residues of PAE-containing cellulose sheets were collected by the direct film method and KBr disk technique, respectively, using a MAGNA-IR 860 model (Nicolet, USA). PAE contents in the sheets were calculated from their nitrogen contents, which were determined by an elementary analyzer (FLASH EA1112, Amoco Co., Italy) [8,9]. Carboxyl content of the celluloses
used in sheet making was determined according to TAPPI Test Method using methyl red as an indicator [20] or the conductometric titration [18]. Wet-tensile strength of the sheets was measured by a slightly modified method of TAPPI Test Method [21]. Soaking time of the specimen strips with 15 mm width in de-ionized water was set to 30 min, and excess water of the strips was removed by blotters. The wet strips were then immediately subjected to tensile strength measurement with a span of 10 cm. Wet-tensile strengths were expressed as wet-strength indices according to the method for the dry-tensile strengths of paper samples [22]. Six specimen strips were measured for each sample to obtain an average wet-strength index.

3. Results and discussion

3.1. The effect of carboxyl groups in cellulose on wet strength of cellulose sheets prepared by internal addition of PAE

In the case of internal addition, retention of PAE is the first significant step to develop wet strength of PAE-containing cellulose sheets. Cationic PAE molecules added to slurries of cellulose fibers are primarily retained in sheets during the filtration, couching and pressing processes in papermaking by electrostatic interactions or formation of ionic bonds with anionic cellulose fiber surfaces in water [2,3,9,11]. Hence, carboxylic groups, a part of which intrinsically behave as anionic sites on cellulose fiber surfaces in water, are likely to play a significant role in the PAE retention. Fig. 1 shows the results of PAE retention in the sheets, when three celluloses having different carboxyl contents were used. Expectedly, the higher the carboxyl content of the cellulose, the more PAE was retained in the sheets; carboxyl groups in cellulose fibers are the predominant retention sites of cationic PAE molecules.

Even though the linter pulp had nearly no carboxyl groups, when determined by the titration method using methyl red as the indicator [19], about 0.47 mg PAE per gram of the sheet or about 16% of the added PAE was retained in the linter pulp sheets at the 0.3% PAE addition level. Moreover, the PAE content in the linter pulp sheets increased to 0.62 and 0.75 mg/g with increasing the PAE addition level to 0.6% and 0.9%, respectively. Thus, not only electrostatic interactions between cationic PAE molecules and anionic cellulose fibers but also some other interactions might contribute to the PAE retention, although this PAE retention mechanism is not predominant. Similar results were obtained also for the methylamidated HBKP sheets. Because the methylamidation adopted in this study could not completely block the carboxyl groups of HBKP, the PAE contents retained in the HBKP sheets were higher than those for the linter pulp sheets.

As described in the previous paper [6,7], PAE is a highly cross-linked polymer consisting of polyamideamine chains and 2-hydroxypropane bridges. Each PAE molecule has a small amount of carboxyl groups at the end of polyamideamine chains. $^1$H NMR analysis revealed that the commercial PAE used in this study contained carboxyl and amino groups of 0.27 and 3.27 mmol/g, respectively [11]. The carboxyl groups of PAE molecules may have some chances to form ionic linkages with cationic sites of other PAE molecules by electrostatic interactions, resulting in the formation of large PAE polyion complexes, which may be entrapped in the cellulose fiber matrices of the wet webs during filtration process of the sheet making. This is one of the hypotheses to explain the increases in PAE contents in the linter pulp sheets and methylamidated HBKP sheets with increasing the PAE addition level in Fig. 1.

The relationships between PAE content in the sheets and their wet-tensile strengths are depicted in Fig. 2. In both heated and unheated sheets, wet strength of the sheets roughly increases with increasing their PAE contents, showing that PAE content in the sheets nearly governs the resultant wet strengths. However, when the data in Fig. 2 is carefully observed, there is a gap of wet strength even at the similar PAE content (see the dotted line in Fig. 2). Particularly in this case, (1) some interactions...
between carboxyl groups in HBKP and PAE molecules may have improved wet strength for the PAE-containing HBKP sheets, or (2) the structures of PAE molecules adsorbed on the methylamidated HBKP, e.g. large PAE complexes, may have brought about lower wet strength for the PAE-containing methylamidated HBKP sheets.

Moreover, Fig. 2 shows that wet strength of the sheets prepared from HBKP and methylamidated HBKP with PAE was clearly improved by the heating treatment. The ester bond formation between aditidinium groups of PAE and carboxyl groups of cellulose fibers is, of course, one of the plausible candidates to explain the wet-strength improvement by heating of the PAE-containing sheets. As described previously, because each PAE molecule has carboxyl groups at the end of polyamideamine chains, intra- and inter-molecular ester bond formation to become more cross-linked PAE or PAE having higher molecular mass values in the sheets is also plausible by heating.

3.2. The effect of carboxyl groups in cellulose on wet strength of cellulose sheets prepared by soaking treatment with PAE solutions

As shown in Figs. 1 and 2, the amounts of PAE retained in the sheets are quite small, when the cellulose fibers having low carboxyl contents are used for the internal addition of PAE in sheet making. This is because electrostatic interactions between cationic PAE molecules and anionic cellulose fibers are the predominant retention mechanism in slurries of cellulose fibers. In this section, therefore, PAE molecules are compulsorily impregnated into the base sheets prepared beforehand without any additives by the soaking treatment with PAE solutions, in order to make clear the effect of carboxyl groups in the sheets on wet-strength improvement of the PAE-containing cellulose sheets.

Fig. 3 shows the relationships between the PAE content calculated from the pick-up weight of PAE solutions in the sheets by the soaking treatment and that obtained from the nitrogen content of the PAE-treated sheets after drying. When the sheets prepared from the linter pulp were used in the soaking treatment, PAE contents were nearly the same levels as those calculated from the pick-up weight. On the other hand, when the sheets prepared from HBKP and the TEMPO-oxidized linter pulp were used in the soaking treatment, PAE contents were much higher than those calculated from the pick-up weight of PAE solutions. The HBKP and TEMPO-oxidized linter pulp sheets have significant amounts of carboxyl groups, whereas the linter pulp sheets do not (Table 1). Ionic bonds may be formed between cationic PAE molecules and anionic carboxyl groups in the sheets during the PAE soaking treatment, resulting in partial prevention for PAE molecules to move from wet cellulose sheets to blotters during the pressing process. Thus, even in the soaking treatment, interactions between cationic PAE molecules and anionic sites due to carboxyl groups in the base sheets play a significant role in improving retention of PAE.

The relationships between PAE content and wet-tensile strength of the sheets prepared by the internal addition of PAE to HBKP slurries and the soaking treatment of the once-dried HBKP sheets with PAE solutions are depicted in Fig. 4. Even though the number of plots is not so many, wet strength of the sheets is roughly governed by their PAE contents in both internal addition and soaking treatment. There must be no significant differences in the mechanisms of wet-strength development of cellulose sheets between the two application methods of PAE.

Fig. 5 depicts the relationships between PAE content and wet-tensile strength of the sheets prepared by the soaking treatment of the linter pulp and TEMPO-oxidized linter pulp sheets with PAE solutions. Because fiber morphologies, degrees of fibrillation and hemicellulose contents of the linter and TEMPO-oxidized linter pulps are quite different from those of HBKP, absolute wet-strength values in Fig. 5 are far lower than those for the PAE-treated HBKP sheets in Fig. 4 even at the same PAE content. It is noticeable, however, that the TEMPO-oxidized linter pulp sheets had clearly higher wet strength than that of the linter pulp sheets at the similar PAE content. Moreover, wet strength was remarkably improved by the heating treatment for the TEMPO-oxidized linter pulp sheets soaked in PAE solutions, in a similar manner to that for the HBKP sheets in Fig. 4.
In contrast, when the linter pulp sheets were used for the soaking treatment, no clear differences in wet strength were observed between the heated and unheated sheets, indicating that the wet-strength development of PAE-treated cellulose sheets by heating is associated with some interactions between carboxyl groups in the sheets and PAE molecules. The ester bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers in the sheets by heating is the most probable candidate to explain these results. In other words, interactions or ester bond formation within PAE molecules, even if such interactions are possible for PAE molecules retained in the sheets, have nearly no contribution to wet-strength development at least at the PAE addition levels studied. Thus, again the ester bond formation between azetidinium groups of PAE and carboxyl groups in cellulose fibers is likely to be the predominant driving force for the wet-strength development of PAE-treated sheets especially by heating treatment.

3.3. FT-IR analysis of PAE films

It is expected to concentrate the fractions of PAE/cellulose fiber interfaces by cellulase treatment of PAE-containing sheets; the cellulase treatment may efficiently remove the abundant cellulose and hemicellulose fractions having no interactions with PAE in the sheets under mild conditions. If such PAE-rich fractions in the sheets can be obtained, FT-IR analysis of the cellulase-treated residues would provide information about whether or not ester bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers occurs in the sheets.

As a preliminary experiment, the heated and unheated PAE films were subjected to FT-IR analysis to see whether any structural changes of PAE molecules in the films occurred by the heating treatment (Fig. 6). The once-dried PAE films were swollen but no longer soluble in water, indicating the formation of some inter-molecular cross-linking during the drying process. Both heated and unheated PAE films had typical amide I and II absorption bands at 1643 and 1550 cm$^{-1}$, respectively [23]. The absorption band at 1728 cm$^{-1}$ due to C=O stretching vibration of ester bonds, which were formed between carboxyl groups at the end of polyamidamine chains and azetidinium groups in PAE, was detected in both heated and unheated PAE films.

The amide I band might partly overlap with the band around 1640 cm$^{-1}$ due to symmetric deformation vibrations of water molecules adsorbed on the PAE films. Thus, the ratio of absorption band area due to ester C=O to that due to the amide II N–H around 1550 cm$^{-1}$ was calculated by peak deconvolution using Gaussian functions. The absorption band ratio increased from 0.08 to 0.11 by heating the PAE film; the amount of ester bonds clearly increased by heating. The increased absorption band around 1260 cm$^{-1}$ for the heated PAE film may be due to C=O stretching vibration of ester groups [24], also suggesting the additional formation of ester bonds in the heated PAE film. The ester bonds detected in the film dried at room temperature may be formed during the PAE synthesis process and present in
the original PAE solution, and/or formed during the drying of the PAE film at room temperature.

3.4. FT-IR analysis of cellulase-treated residues of PAE-containing cellulose sheets

The heated and unheated sheets prepared from HBKP by internal addition of 0.3% PAE were subjected to the cellulase treatment at room temperature. The blank sheets prepared without PAE were also treated with cellulase under the same conditions. Fig. 7 shows FT-IR spectra of the cellulase-treated residues of the blank and PAE-containing HBKP sheets. Yields of the cellulase-treated residues were approximately 1%, and thus about 99% of cellulose and hemicellulose fractions without any interactions with PAE in the sheets were successfully removed by the cellulase treatment in de-ionized water.

Because the absorption band due to symmetric deformation vibrations of water molecules adsorbed on the cellulose-treated residues appears around 1640 cm\(^{-1}\), all the FT-IR spectra in Fig. 7 had this absorption band. The absorption bands due to ester C=O groups and amide II N–H groups at 1735 and 1550 cm\(^{-1}\) were clearly detected in the FT-IR spectra of the cellulose-containing residues of both heated and unheated PAE-containing HBKP sheets, while nearly no such absorption bands were observed in the FT-IR spectrum of the cellulose-treated residue of the blank HBKP sheets. Thus, the absorption bands due to ester C=O and amine N–H groups in the cellulose-treated residues clearly originate from PAE in the HBKP sheets. The ratio of absorption band area due to ester C=O to that due to the amide II N–H band was calculated by peak deconvolution using Gaussian functions. The absorption band ratio increased from 0.97 to 1.36 by heating the PAE-containing HBKP sheets; the amount of ester bonds increased by heating of the PAE-containing HBKP sheets. The increased absorption band around 1260 cm\(^{-1}\) also indicates the formation of ester bonds in the heated sheets.

The above absorption band ratios of 0.97 and 1.36 for the cellulase-treated residues of the PAE-containing cellulose sheets in Fig. 7 are remarkably higher than those for the PAE films in Fig. 6, i.e. 0.08 and 0.11. Thus, significant amounts of ester bonds can be regarded to form between azetidinium groups of PAE and carboxyl groups of HBKP fibers in the PAE-containing HBKP sheets. Moreover, the FT-IR results in Fig. 7 show that the ester bond formation is enhanced by the heating treatment of the PAE-containing HBKP sheets, which probably bring about the clear improvement of wet strength in Figs. 2 and 4. Reactions occurring between PAE and carboxyl groups, which were found in this study, are illustrated and summarized in Fig. 8.

4. Conclusions

1. Carboxyl groups in cellulose fibers behave as anionic retention sites of cationic PAE molecules for both internal addition of PAE in sheet-making process and soaking treatment of once-dried cellulose sheets with PAE solutions.
2. Wet-tensile strength of cellulose sheets containing PAE is improved by heating treatment, only when the sheets have carboxyl groups.
3. The ester bond formation between carboxyl groups at the end of polyamidoamine chains in PAE and azetidinium groups of PAE, i.e. within PAE molecules, are possible to occur in PAE films. However, these bonds within PAE have nearly no contribution to wet-strength development of PAE-containing cellulose sheets.

4. Azetidinium groups of PAE can form ester bonds with carboxyl groups of cellulose fibers in PAE-containing cellulose sheets, and the amount of these ester bonds increases by the heating treatment of the sheets.

5. Wet-strength development of PAE-containing cellulose sheets is primarily ascribed to the ester bond formation between azetidinium groups of PAE and carboxyl groups of cellulose fibers, i.e. the covalent bond formation.

References

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