Application of carboxymethyl cellulose to mixed pulp slurries for wood-containing paper production

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ABSTRACT: A pulp modification technique using carboxymethyl cellulose (CMC) at the wet end was applied to mixed pulp slurries containing softwood bleached kraft pulp (SBKP), deinked pulp (DIP), and hydrogen peroxide-bleached thermomechanical pulp (TMP). Introduction of anionic sites by adsorption of the added CMC molecules on the fibers was confirmed by an increase in negative charge of the mixed pulp fibers. Sizing degree of the handsheets prepared with 2% aluminum sulfate and 0.2% rosin dispersion size was clearly improved by 0.1% CMC addition. On the other hand, we observed no significant differences in rosin size content between the handsheets prepared with and without CMC. These results indicate that some mechanisms other than enhancement of rosin size retention may have brought about the clear improvement of sizing performance by the CMC addition. Changes in distribution of rosin size components or some structural changes of rosin size components in the handsheets by the CMC addition may be candidates for sizing development. The CMC addition technique at the wet end is, therefore, also applicable to mixed pulps containing DIP and TMP.

Application: Sizing performance of wood-containing grades with alum and rosin dispersion size can be improved by 0.1% CMC addition at the wet end.

As paper machine speeds and the recovery ratio of white water have been increasing, so have accumulations of anionic trash and inorganic ions in the process water. This, in turn, reduces the ability of wet-end chemicals to improve paper properties and papermaking runnability [1-3].

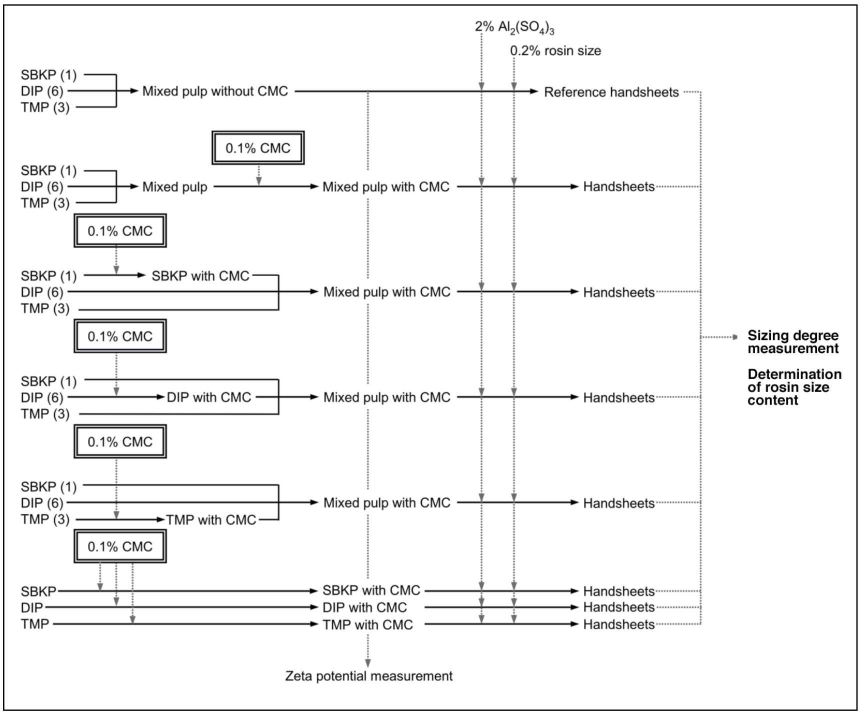
Electrostatic interactions are the main forces driving retention of wet-end chemicals. Carboxyl groups in pulp fibers play an important role as anionic sites for the adsorption of wet-end chemicals onto pulp fibers [4,5]. Many studies have been conducted to introduce carboxyl groups to pulp fibers or to increase their anionic charges by some chemical modifications of pulp fiber surfaces. Barzak et al. [6] carried out carboxymethylation of chemical pulps to improve specific bond strength of paper sheets. Kitaoka et al. [7,8] applied 2,2,6,6-tetramethyl piperidine-1-oxy radical (TEMPO)-mediated oxidation to chemical pulps under aqueous and mild conditions. Retentions of polyamideamine-epichlorohydrin (PAE) resin, a wet-strength additive, and rosin dispersion size were improved by using the TEMPO-oxidized pulps.

Laine et al. [9,10] reported that carboxymethyl cellulose (CMC) with a low degree of substitution (DS) was irreversibly attached onto kraft pulp fibers (even though CMC molecules and kraft pulps both have anionic charges) when pulp fibers and CMC were treated in water at high temperatures and high electrolyte concentrations. Retention of PAE was improved by using the CMC-attached pulps, resulting in wet-strength improvement of the sheets. Recently, an efficient CMC attachment system has been proposed to take advantage of the high temperatures and high electrolyte concentrations during kraft cooking, which are preferable for CMC attachment [11]. Another method to attach CMC onto kraft pulp fibers has been developed by Blomstedt et al. [12], where CMC with low DS dissolved in 2.5 M sodium hydroxide was added to pulp slurries at 60°C with continuous stirring for 1 h.

Watanabe et al. [13] reported that CMC molecules can be irreversibly adsorbed onto hardwood and softwood kraft pulps by wet-end addition of CMC to pulp slurries at around 40°C during papermaking. CMC retention ratios on pulp fibers at 0.1% CMC addition increased with decreasing DS of CMC and increasing electrical conductivity of pulp slurries, and reached more than 90% using CMC with a DS of 0.46 under suitable wet-end conditions. Sizing degrees of handsheets prepared with 2% aluminum sulfate and 0.2% rosin dispersion size were clearly improved by the 0.1% CMC addition to hardwood bleached kraft pulp slurries under usual papermaking conditions. Therefore, this on-line pulp modification technique using CMC is already being applied to mill papermaking processes as an advanced wet-end system [14].

The adsorption of anionic CMC molecules onto anionic pulp fibers occurs through 1) reduction in electrical repulsions between anionic carboxyl groups of CMC molecules and those of pulp fibers in pulp slurries by increased electrical conductivity, and 2) enhancement of hydrophobic interactions and/or hydrogen bonds between pulp fibers and β-(1→4)-linked glucose chains partly present in the CMC molecules with low DS. Gondo et al. [15] used size-exclusion chromatography attached with a laser-light scattering detector to study the relationships between conformations of CMC molecules in water at various electrical conductivities and the adsorption behavior of CMC molecules on pulp fibers. They found that CMC molecules tended to have compressed conformations and to form aggregates in aqueous solutions with decreasing DS and increasing electrical conductivity. The results help explain the effectiveness of CMC attachment on pulp fibers during practical papermaking processes.

On the other hand, almost all commercial paper products consist of pulp mixtures, such as deinked pulp (DIP) and wood-containing pulps. Especially in the case of wood-containing papers, such as newsprints and base papers for light weight coated paper, weight ratios of DIP in mixed pulps containing thermomechanical pulp (TMP) and a small amount of softwood bleached kraft pulp (SBKP) have been increasing. For this report, the on-line pulp modification technique using CMC was applied to a mixed pulp containing DIP, TMP, and SBKP. The effect of CMC addition at the wet end on sizing degree and size retention was evaluated for handsheets prepared from the mixed pulp slurries with and without CMC. We also studied suitable CMC addition sequences.



1. Scheme of preparation of handsheets from mixed and single pulp slurries with and without carboxymethyl cellulose (CMC). SBKP = softwood bleached kraft pulp, DIP = deinked pulp, TMP = thermomechanical pulp.

EXPERIMENTAL

Materials

Throughout the investigation, we used the following pulps obtained from commercial pulp mills:

- SBKP with 570 mL CSF,
- DIP with 155 mL CSF,
- hydrogen peroxide (H_2O_2)-bleached TMP with 85 mL CSF (TMP-A), and
- another H_2O_2-bleached TMP with 105 mL CSF (TMP-B).

TMP-A and TMP-B were obtained from different sources, and detailed differences between them other than their CSF values were unknown. CMC was provided by Daiichi-Kogyo Seiyaku (Japan). DS of the CMC was 0.46, and viscosity at 2% aqueous CMC solution was 100 mPa. CMC was dissolved in deionized water to prepare 0.5% (w/w) CMC solutions. A commercial rosin dispersion size (AL1208, 50% solid content) was provided by Seiko PMC (Japan) and used after dilution to a 1% rosin size dispersion. Reagent grade aluminum sulfate ($Al_2[SO_4]_3 \cdot 16H_2O$), was purchased from Wako Pure Chemicals (Japan) and used as its 1% solution.

Handsheets

When a mixed pulp was used, SBKP, DIP, and either TMP-A or TMP-B were mixed at a weight ratio of 1:6:3, respectively. This ratio of three pulps is similar to those of commercial wood-containing papers. Pulp consistencies in slurries were adjusted to 2%, and their electrical conductivities before wet-end additions were fixed to 200 mS/m by adding sodium sulfate. To the mixed pulp slurry at 40°C, 0.1% CMC (on dry weight of the total pulp) was added under continuous stirring. After the slurry was stirred for 1 min, 2% aluminum sulfate and 0.2% rosin dispersion size (based on dry weight of the total pulp) were added in this order to the pulp slurry. Handsheets with a basis weight of 40 g/m^2 were prepared from the CMC-modified pulp slurries with tap water, according to TAPPI T 205 om-88, “Forming handsheets for physical tests of pulp.” The webs were wet-pressed, and dried at 105°C for 2 min using a rotary drum dryer. Reference handsheets were prepared from the mixed pulp slurry without CMC. As alternative procedures, 2% pulp slurries of SBKP, DIP, and either TMP-A or TMP-B were prepared separately, and 0.1% CMC (based on dry weight of the total mixed pulp) was added at once to one of the three pulp slurries at 40°C. After the pulp slurry was stirred for 1 min, this CMC-added pulp slurry and the other two pulp slurries without CMC were mixed to fix the SBKP, DIP, and TMP ratio of 1:6:3, respectively, followed by the 2% aluminum sulfate and 0.2% rosin dispersion size additions under continuous stirring at 40°C. In other experiments, 0.1% CMC, 2% aluminum sulfate, and 0.2% rosin dispersion size were added to SBKP, DIP, and TMP pulp slurries, and the corresponding SBKP, DIP, and TMP handsheets were prepared from each pulp slurry. **Figure 1** illustrates these handsheet-making procedures. The handsheets thus prepared were conditioned at 23°C and 50% relative humidity for more than one day, and then measured for sizing degree and rosin size content.

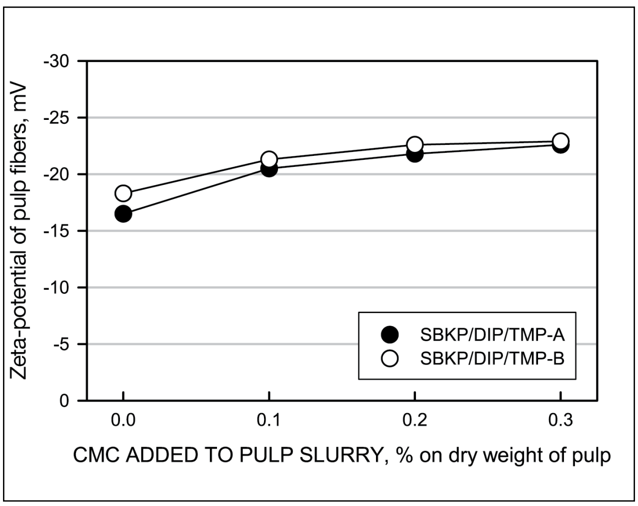
Measurements

Zeta potentials of the pulp fibers were determined using an electrophoretic light scattering apparatus (Zetasizer 2000; MALVERN Co., Ltd., United Kingdom). The pulp slurries were filtered through a 150-mesh wire, and the zeta potential of the filtrates, mainly consisting of fines fractions of the pulps, were measured at room temperature and about 0.02% solid content. Rosin size content of the handsheets was determined by pyrolysis-gas chromatography-mass spectroscopy (CG-MS; Py-2020id of Frontier LAB, Ltd. and GCMS-SP2010 of Shimadzu Co., Japan) combined with the on-line methylation method using a 25% tetramethylammonium hydroxide/methanol solution (Aldrich Co., USA) [16]. Sizing degree of the handsheets was measured according to TAPPI UM-596, "Water absorbency of non-bibulous paperboard."

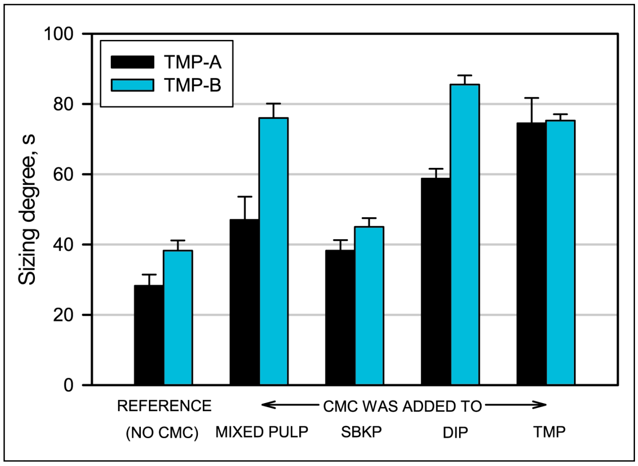
RESULTS AND DISCUSSION

Modification of pulp fibers of SBKP/DIP/TMP mixture with CMC

When hardwood bleached kraft pulp was used, CMC with a DS of 0.46 and pulp slurries at 200 mS/m electrical conductivity gave the highest adsorption ratio of CMC on the pulp fibers [13,14]. The same conditions were applied to the SBKP/DIP/TMP-mixed pulp slurries for wood-containing paper production. The introduction of anionic charges on the mixed pulp fibers was evaluated on the basis of their zeta potentials (**Fig. 2**), where 0-0.3% CMC was added to the mixed pulp slurry consisting of SBKP, DIP, and either TMP-A or TMP-B, with a weight ratio of 1:6:3, respectively. Because 150-mesh-passed



2. Relationships between carboxymethyl cellulose (CMC) addition and zeta potential of pulp fibers. Pulp slurry was composed of softwood bleached kraft pulp (SBKP), deinked pulp (DIP), and thermomechanical pulp (TMP) with a weight ratio of 1:6:3, respectively. Electrical conductivity of the slurry was 200 mS/m. CMC (degree of substitution [DS] 0.46) was added to the pulp slurry and stirred for 1 min at 40°C.



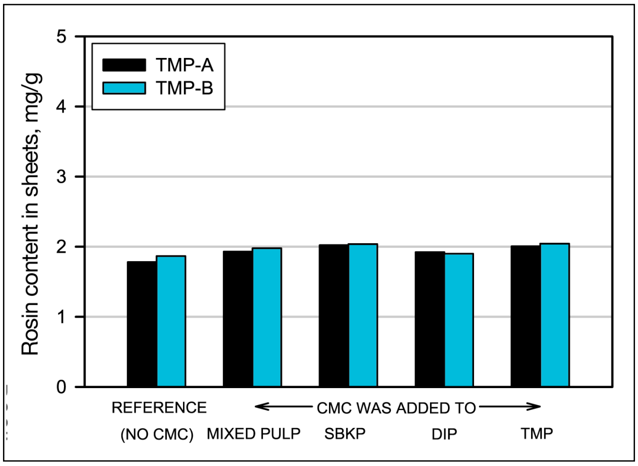
3. Sizing degrees, determined using 5 µL-water drops, of handsheets prepared from mixed pulp slurries with 2% aluminum sulfate and 0.2% rosin dispersion size under various handsheet-making procedures. The carboxymethyl cellulose (CMC) addition level was 0.1% on the total weight of dry pulp. Pulp slurry was composed of softwood bleached kraft pulp (SBKP), deinked pulp (DIP), and thermomechanical pulp (TMP) with a weight ratio of 1:6:3, respectively.

filtrates of the pulp slurries were subjected to the zeta potential measurement, we evaluated changes in zeta potentials of fines fractions in the mixed pulp by the CMC addition. The zeta-potentials of the fines became more negative with CMC addition, and thus, anionic charges were introduced onto at least the fines fractions of the mixed pulp fibers by the CMC addition.

Effect of CMC addition to mixed pulp slurries on sizing degree

The effect of the pulp modification with CMC on sizing degree of the handsheets was studied by measuring adsorption time of 5 µL water drop put on a handsheet prepared with aluminum sulfate and rosin dispersion size. This sizing test is often applied to newsprints and base papers for lightweight coated paper to evaluate their water-absorption behavior during offset printing. The leftmost four bars in **Fig. 3** show the sizing degrees of the handsheets prepared from the mixed pulp using either TMP-A or TMP-B, with and without CMC. In both systems using TMP-A and TMP-B, sizing degree of the handsheets was remarkably improved by the addition of CMC to the mixed pulp slurry. Which of the pulps in the slurry most adsorbed the CMC molecules was not determined.

Handsheets also were prepared by adding the total amount of CMC to one of the three pulp slurries and then mixing the CMC-added pulp slurry and the other two pulp slurries without CMC before the additions of aluminum sulfate and rosin dispersion size (see Fig. 1). Sizing degrees of these handsheets are depicted as the rightmost six bar graphs in Fig. 3. Even when the total amount of CMC was added to only one of the three pulp slurries, sizing degrees of all handsheets were higher than those of the reference handsheets prepared without CMC. However, sizing degrees varied, depending on the pulp to which the total amount of CMC was added. When CMC was added to SBKP before mixing the pulps, sizing degrees slight-



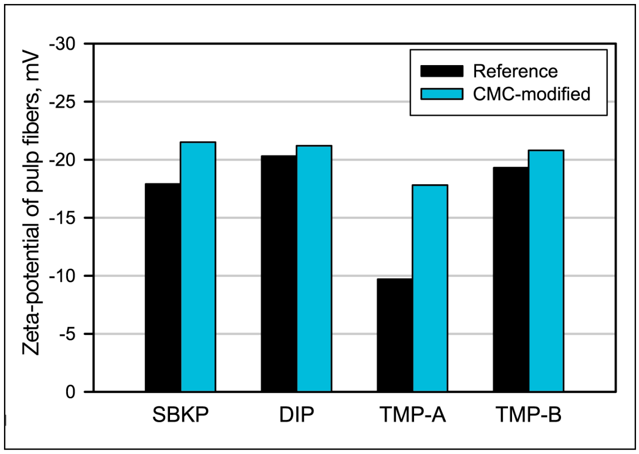
4. Rosin size contents in the handsheets corresponding to those in Fig. 3. CMC = carboxymethyl cellulose, SBKP = softwood bleached kraft pulp, DIP = deinked pulp, TMP = thermomechanical pulp.

ly increased in comparison with the reference handsheets. Sizing degree improved more significantly when CMC was added to either DIP or TMP before mixing the three pulps. Adding the total amount of CMC to TMP-A was especially effective in improving sizing degree of the handsheets. When the TMP-B was used, sizing degree was similar to that of the handsheets prepared by the addition of CMC to the mixed pulp or DIP. Thus, the CMC addition is effective in improving sizing degree of the handsheets for pulp slurries containing DIP and TMP, and the addition point of CMC significantly influences the resultant sizing degree of the handsheets.

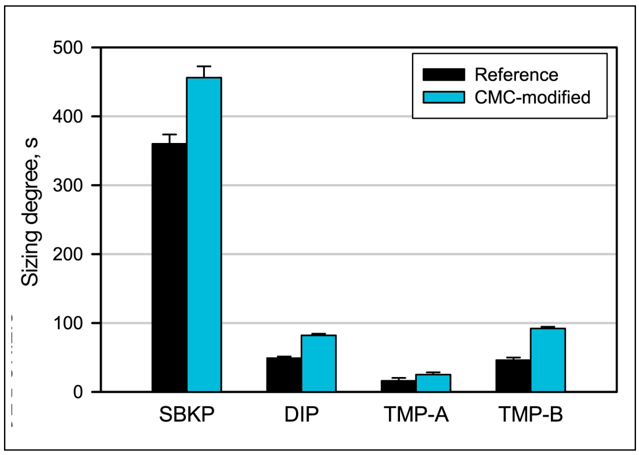
Figure 4 shows rosin size content in the handsheets, which corresponds to those in Fig. 3. Unexpectedly, we observed nearly no clear differences in rosin size content between the handsheets prepared from pulp slurries containing DIP and TMP by different procedures. These results indicate that more even distribution of rosin size components or preferable structural changes in rosin size components with, for example, aluminum compounds in the handsheets have resulted in higher sizing degree of the handsheets prepared from pulp slurries containing DIP and TMP by CMC addition. On the other hand, the CMC addition might contribute few if any improvements in rosin size retention of the handsheets, when the mixed pulp containing DIP and TMP is used. Thus, even though the CMC addition to pulp slurries is effective in improving sizing degrees of the handsheets for hardwood bleached kraft pulp and the mixed pulp containing DIP and TMP, the mechanisms to improve sizing degree of the handsheets by CMC addition might be different between the two systems.

Effect of CMC addition on sizing degree

Figure 5 shows differences in zeta potential of each pulp before and after 0.1% CMC addition. Although negative zeta potentials more or less increased for all pulps by the CMC addition, TMP-A had the largest increase in the negative zeta potential by CMC addition. In other words, although the original zeta potential of TMP-A was only about –10 mV, which was far from those of the other three pulps, the CMC addition



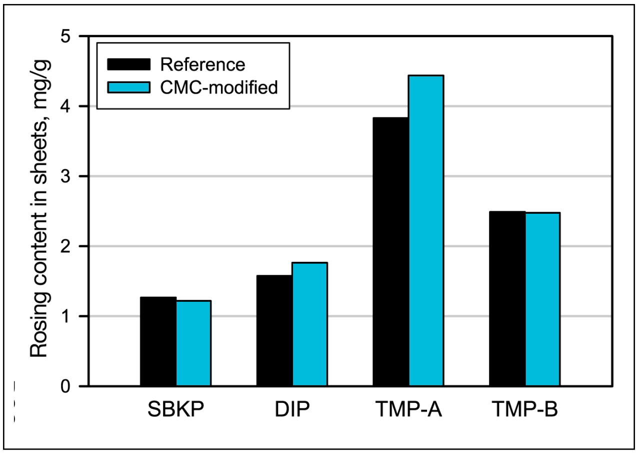
5. Zeta-potentials of each pulp with or without carboxymethyl cellulose (CMC), where CMC was added to each pulp slurry, which was then stirred for 1 min at 40°C. SBKP = softwood bleached kraft pulp, DIP = deinked pulp, TMP = thermomechanical pulp.



6. Sizing degrees, as determined with 5 μL-water drops, of handsheets prepared from each pulp slurry with or without carboxymethyl cellulose (CMC). Each pulp slurry had 2% aluminum sulfate and 0.2% rosin dispersion size added. The CMC addition level was 0.1% on dry weight of each pulp. SBKP = softwood bleached kraft pulp, DIP = deinked pulp, TMP = thermomechanical pulp.

to the TMP-A slurry increased the anionic charge nearly as much as those of other pulps, i.e., approximately –17.5 mV. Some differences in bleaching conditions between the two TMP samples probably led to the differences in zeta potential between them.

Handsheets were prepared from each pulp slurry, with 0.1% CMC, 2% aluminum sulfate, and 0.2% rosin dispersion size. In all cases examined, CMC addition to each pulp slurry increased sizing degree (**Fig. 6**). However, absolute sizing degrees of the handsheets prepared from DIP and TMP slurries were remarkably lower than those of the SBKP handsheets. The DIP and TMP-B handsheets had similar sizing degrees, while the TMP-A handsheets had the lowest sizing degrees. **Figure 7** shows the size contents of the handsheets



7. Rosin size contents in the handsheets corresponding to those in Fig. 6. CMC = carboxymethyl cellulose, SBKP = softwood bleached kraft pulp, DIP = deinked pulp, TMP = thermomechanical pulp.

in Fig. 6. Clear increases in rosin size content by CMC addition were observed for the TMP-A handsheets, while only slight improvements in rosin size retention by CMC addition were observed for SBKP, DIP, and TMP-B handsheets. In this rosin size determination experiment using pyrolysis-GC-MS, abietic acid present in the handsheets was used as the marker. The abietic acid content of the original DIP and TMP varies according to the residual rosin size in DIP and wood extractives in TMP, depending on the origins of DIP, recycling history of DIP, washing conditions of TMP, wood species for TMP production, and other factors. This is why the rosin size contents of the handsheets prepared from TMP-A and TMP-B exceeded the amount of rosin size added at the wet end (0.2% on dry weight of the pulp). However, the rosin size retention was clearly improved for TMP-A by the CMC addition.

Because sizing degrees are influenced by size content in sheets and by many other factors -- such as sheet structures, surface areas of pulp fibers constituting the sheets, retention of aluminum components and their distribution on pulp fiber surfaces, fines content, and concomitant components present in the pulps -- comparison of absolute sizing degree between the handsheets prepared from different pulps in Fig. 6 may be irrelevant. However, we can conclude that 1) the CMC addition at the wet end is effective in improving sizing degree of the handsheets prepared from not only SBKP, but also DIP and TMP in the alum-rosin sizing system, 2) the improvement of sizing degree for the SBKP and TMP-B handsheets by the CMC addition cannot be explained in terms of rosin size content in the handsheets, and 3) a clear increase in rosin size content is observed for TMP-A by CMC addition.

The mechanism of improving sizing degree of handsheets by CMC addition

As shown, CMC addition is effective in improving sizing degree for handsheets prepared from DIP and TMP. However, it is difficult to explain simply all the results obtained in this study because many factors could affect the experimental results. Moreover, neither CMC retention values in the handsheets, their aluminum contents, nor distributions of rosin size in the handsheets could be determined in this study.

Because we observed no significant differences in sheet densities between the handsheets prepared with and without CMC, the 0.1% CMC addition might not have caused any clear enhancement of interfiber bonds in the sheets. Thus, the increases in sizing degree for the handsheets prepared with CMC (Figs. 3 and 6) cannot be explained by changes in sheet structures nor by changes in interfiber bonding level in the sheets.

For the mixed pulp containing TMP-A, however, some explanation of mechanisms may be plausible. As shown in Fig. 3, the CMC addition to the TMP-A pulp slurry before mixing with the other SBKP and DIP slurries resulted in the highest sizing degree of the handsheets. However, almost no significant difference in rosin size content was observed between the handsheets prepared by these two procedures (Fig. 4). Although the original TMP-A had the lowest negative zeta potential, it increased to the same level as those of other pulps by the addition of CMC. This increase in zeta potential of TMP-A by CMC addition resulted in a clear increase in rosin size content in the handsheets (Fig. 7), because additional anion sites are formed on the surfaces of TMP-A fibers and fines by CMC addition. Consequently, more even distribution of rosin size particles was probably achieved between the three different pulps in the mixed pulp slurry through the successive aluminum sulfate and rosin size additions, thus increasing the sizing degree of the handsheets.

CONCLUSIONS

The pulp modification technique using CMC at the wet end of papermaking is applicable also to mixed pulp slurries containing DIP and TMP. CMC addition led to the introduction of anionic sites onto pulp fibers, resulting in anionic charges increases in the mixed pulp fibers. The handsheets prepared from the mixed pulp slurries with CMC had higher sizing degrees than those prepared without CMC, when 2% aluminum sulfate and 0.2% rosin dispersion size were added to the pulp slurries. Because no significant differences in rosin size content were observed between the handsheets prepared with and without CMC, distribution of rosin size components in the handsheets might be changed by CMC addition. The results using TMP-A supported this hypothesis. Thus, the CMC addition technique is applicable to hardwood kraft pulp and to mixed pulp containing DIP and TMP for production of wood-containing paper. **TJ**

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INSIGHTS FROM THE AUTHORS

In a previous paper (Watanabe, et al., *TAPPI J.* 3[5]: 15[2004]), we reported that adding 0.1% CMC at the wet end to bleached kraft pulp slurries improved paper properties such as sizing degrees and dry strength. In this paper, the CMC pulp modification technique was applied to mixed pulp slurries containing DIP and TMP, which are more similar to practical papermaking systems producing commercial paper.

Our results showed that adding CMC at the wet end is also applicable to manufacturing wood-containing grades. The sizing behavior of handsheets, in particular, was improved by the CMC addition. However, because size content was almost the same for the CMC-modified and reference handsheets, some mechanisms other than improvement of size retention are needed to explain the results obtained in the mixed pulp systems. When simple systems using a bleached kraft pulp alone were used, the CMC addition to pulp slurries clearly improved retention values of rosin size.

Because large amounts of anionic colloidal and dissolved substances are present in the mixed pulp slurries containing DIP and TMP, the CMC molecules adsorbed on pulp fibers could not be determined by the colloidal titration method in this study. Accurate determination of the amounts of CMC adsorbed on the mixed pulp fibers is necessary to rationally explain the improved paper properties by the CMC addition and be a priority of future work.

When the mixed pulps were used, rosin size contents in the CMC-modified pulp sheets were almost the same as those of the reference sheets, even though sizing behavior was clearly improved by the CMC addition. Thus, the CMC addition to pulp slurries may participate in other factors influencing the performance of wet-end additives, such as distribution of the additives within one pulp fiber and between pulp fibers. CMC addition can be regarded as an efficient method to improve paper properties by wet-end additives.

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The addition levels of wet-end additives can be reduced to produce wood-containing paper with the same properties by the CMC addition, and thus this pulp modification technique using CMC is cost-effective in practical papermaking.

From a scientific aspect, determination of CMC molecules adsorbed on the mixed pulp fibers by some analytical method is a significant next step. As practical papermaking, we would like to expand the concept to use CMC at the wet end to other systems containing various pulps and more complicated white water-closed systems.

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