Characterization of TEMPO-Oxidized and Refined Pulps

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Abstract
Catalytic oxidation using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) can be used to selectively convert primary hydroxyl groups in accessible regions of cellulose and hemicellulose molecules in pulp fibers into aldehyde and carboxy groups. Clear improvement of the wet tensile strength of handsheets prepared from a TEMPO-oxidized pulp (TOP) was previously demonstrated without the use of any wet strengthening agent. Moreover, the paper chemical contents added at the wet end and retained in the handsheets increased. However, the practical use of TOPs as raw materials in papermaking has not yet been sufficiently studied. In this study, the effects of refining TOPs on the resultant fiber morphologies and properties were investigated. TOPs with carboxy group contents of 0.42 and 0.86 mmol/g were prepared and refined to various levels using a PFI mill. The average fiber lengths of the TOPs decreased and their fines contents increased with increasing number of PFI revolutions; these results were similar to those for the original pulp. However, the freeness remarkably decreased and the water retention value significantly increased with increasing number of PFI revolutions compared with those of the refined original pulp. Moreover, the fibrillation behavior of the TOPs with refinement clearly differed from that of the original pulp in terms of the changes in pulp morphology and the amount of functional groups.

Keywords: TEMPO, beating, refining, fiber morphologies, fiber properties, freeness, water retention value

1. Introduction
Anionic carboxy groups on pulp surfaces play an important role in the adsorption of paper chemicals (e.g., paper strengthening agent and sizing agent)\(^1\). The retention of these chemicals increases with increasing carboxy group concentration on the pulp surface. Furthermore, the presence of carboxy groups on the pulp surface also improves the sheet strength because these groups increase the fiber–fiber bonding strength\(^2\). However, the carboxy group concentration of kraft pulp is less than 0.08 mmol/g\(^3\) and that on the pulp surface is only 0.03 mmol/g\(^4\). Therefore, pulp surface modification techniques have been developed to increase the carboxy group concentration.

Pulp surface modification techniques can be roughly classified into direct and indirect methods. For the direct methods, oxidation techniques using \(\text{N}_2\text{O}_4\) and partial carboxymethylation have been proposed by Bjellfors et al.\(^5\) and Barzyk et al.\(^2\), respectively. The former technique has been used to produce medical gauzes but re-
quires the use of the organic solvent CH₃Cl, and the latter technique requires the use of the high-risk organic solvent CH₂ClCOOH. Therefore, it is difficult to apply these techniques to pulpking and papermaking processes, which are closed and non-solvent processes. Furthermore, for the latter method, changes in the cellulose crystal structure are unavoidable because of the use of high-concentration NaOH.

The adsorption of carboxymethyl cellulose (CMC) on a pulp surface has been proposed as an indirect method by Gondo et al. Easy and irreversible adsorption of CMC on the pulp surface can be achieved by adjusting the conductivity or pH. This method has resulted in the improvement of the retention of paper chemicals in the papermaking process. However, the carboxy group concentration only reached a maximum of 0.003 mmol/g using this method because of the limited amount of CMC that can adsorb on the pulp surface.

Recently, Isogai et al. proposed the direct oxidation of the C6 hydroxyl groups of the cellulose surface using 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a catalyst. Fig. 1 shows the reaction mechanism of the TEMPO/NaBr/NaClO system in water at pH 10-11. In the TEMPO/NaBr/NaClO system, NaBr works as a co-oxidant agent and NaClO works as the main oxidant agent. The formation of N-oxoammonium ions mediates the oxidation of the primary hydroxyl group of the cellulose surface. This oxidation method proceeds in water at room temperature under atmospheric pressure and can be applied in the pulp bleaching process because an organic solvent is not required. Furthermore, it has been reported that TEMPO oxidizes the C6 hydroxyl group selectively with the TEMPO-oxidized pulp (TOP) maintaining its original pulp morphology and cellulose crystal structure. The amount of carboxy groups introduced by the TEMPO-mediated oxidation is controlled by the NaClO dosage. For hard wood bleached kraft pulp (LBKP), an increase of the concentration of carboxy groups up to 1.69 mmol/g has been reported. Thus, TEMPO-mediated oxidation offers several advantages compared with previously reported pulp surface modification techniques.

Increased retention of paper chemicals has been reported for TOP. It has also been reported that the wet strength of sheets prepared from TOP increases without the need for a wet strengthening agent. The increase of the wet strength may be caused by the formation of a hemiacetal linkage between pulp fibers via hydroxyl and aldehyde groups. These aldehyde groups are formed as intermediate structures during the TEMPO-mediated oxidation of C6-OH groups of cellulose in the pulp. At domestic paper making mills, polyamide epichlorohydrin resin (PAE) is used as a wet strengthening agent. Although PAE effectively increases the wet strength of sheet over a wide pH range, it contains absorbable organic halides (AOXs), which are generated as by-products during PAE manufacturing. PAE containing less AOXs has been developed by modifying the manufacturing process, but AOX-free PAE has not yet

Fig. 1  Mechanism for oxidation of primary hydroxyl groups of cellulose by TEMPO/NaBr/NaClO system in water at pH 10-11.
been produced. Other wet strengthening agents such as polyvinylamine (PVAm)\textsuperscript{13} and dextran aldehyde\textsuperscript{14} have been developed; however, these chemicals have not yet replaced PAE because of stability issues. Therefore, the use of TOPs is expected in the development of a new wet strengthening system.

Since the method of pulp oxidation using TEMPO was developed, TOP has been used to elucidate the paper chemical adsorption behavior to pulp and the expression mechanism of paper chemicals with any other modified pulp, playing an important role in establishing the theory of wet-end chemicals for the papermaking process. Among these studies, useful properties of TOP such as improvement of chemical retention and increase of the wet strength as described above have been observed. However, studies concerning the application of TOP as a raw material for paper are limited. For example, previous studies have used small TOP concentrations of less than 0.5 mmol/g. In addition, few studies have examined the application of TOP in the actual papermaking process. In this study, two TOPs containing carboxy group contents of 0.42 and 0.86 mmol/g were prepared and refined using a PFI mill as a laboratory-scale beater. After refining the TOPs, their fiber morphologies and characteristics as papermaking materials were investigated to study the effect of refining, which is generally performed in the papermaking process.

2. Material and Methods

2.1 Preparation of TOPs

A commercial dried LBKP sheet (carboxy and aldehyde groups contents of 0.07 and 0.03 mmol/g, respectively) was disintegrated following JIS P 8220 and then suspended in distilled water to prepare a 1 wt% pulp slurry. TEMPO (0.1 mmol/g based on dry pulp; Kanto Chemicals Co., Japan) and NaBr (1 mmol/g based on dry pulp; Wako Pure Chemical Industries Ltd., Japan) were stirred into the LBKP slurry. It has been reported that TOP containing more than 1 mmol/g carboxy groups can be easily integrated into nanofibers\textsuperscript{15}. Therefore, in this study, two TOPs with carboxy group contents of 0.42 and 0.86 mmol/g were prepared by adjusting the NaClO addition because the preparation of the nanofibers was not the main objective of this work (Table 1). The TEMPO-mediated oxidation was performed under atmospheric pressure, and the pH was maintained at 10 ± 0.3 using 1 N NaOH (Wako Pure Chemical Industries Ltd., Japan). After the consumption of 1 N NaOH stopped, the pulp slurry was filtered and washed with distilled water.

The original LBKP and the two TOPs (TOP-A and TOP-B) were diluted with distilled water to concentrations of 10 wt%. Using TAPPI Test Method T248 wd–97, the original LBKP was refined using 10,000, 20,000, and 40,000 PFI revolutions. TOP-A and TOP-B were refined using 10,000 and 20,000 PFI revolutions.

2.2 Analysis of pulp morphologies

The fiber length (contour length) and width and fines contents of the pulps were measured using Kajaani Fiber Lab V3.5 (Metso Automation Co., Finland) according to TAPPI Test Method T233 cm–95. The pulp fibers after refining with the PFI mill were suspended in water, and their morphologies were examined using differential interference microscopy (Olympus BX50; Olympus Corporation, Japan).

2.3 Measurement of small fiber content

Information about the small fiber content such as that of nanofibers could not be obtained from the Kajaani Fiber Lab V3.5 or differential interference microscopy measurements. Therefore, the supernatant concentration after centrifugation was measured and used as an index of the small fiber content. First, 20 g of each pulp was diluted to 1 wt% with distilled water and subjected to centrifugation. Saito et al. reported that nanofibers prepared from TEMPO-oxidized pulp were not precipitated by centrifugation at 12,000 \(\times g\) for 30 min\textsuperscript{8}. In this study,

<table>
<thead>
<tr>
<th>Table 1 Differences in properties of original pulp and TOPs</th>
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<tr>
<td>NaClO added in oxidation (mmol/g)</td>
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<tr>
<td>Carboxylate content (mmol/g)</td>
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<tr>
<td>Aldehyde content (mmol/g)</td>
</tr>
<tr>
<td>Average fiber length (mm)</td>
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<tr>
<td>Average fiber width (μm)</td>
</tr>
<tr>
<td>Fines content (wt%)</td>
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<tr>
<td>Ratio of water-soluble fraction (wt%)*</td>
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<tr>
<td>DPv</td>
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*: centrifugation at 2000 × g
Results and discussion

3.1 Effect of TEMPO-mediated oxidation on pulp morphologies

Table 1 lists the pulp properties of the original LBKP, TOP-A, and TOP-B. Only the water-soluble fractions after centrifugation at 2,000×g are listed in Table 1 because the values were almost the same for the different relative centrifugal forces. The fiber lengths and widths of the TOPs were longer and larger than those of the original LBKP, indicating that swelling of the TOPs occurred. Fiber swelling has been reported to be affected by the osmotic pressure of the internal fiber and charge repulsion between microfibrils. In this study, the increase of the carboxy group content may have caused the increase of the osmotic pressure of the internal fiber and charge repulsion between microfibrils, resulting in the swollen TOP fibers.

The fines content and water-soluble fraction after centrifugation increased slightly after the TEMPO-mediated oxidation, indicating that small fiber fractions are generated during TEMPO-mediated oxidation. Dang et al. reported the possibility of delamination of the cell wall outer layer during TEMPO-mediated oxidation, which may have occurred in this study, possibly resulting in the increase of the fines content.

As reported by Shinoda et al., the DPv values decreased compared with that of the original LBKP. The decrease of DPv may have been caused by β-alkoxy elimination and/or the presence of radical species as a by-product of the TEMPO-mediated oxidation. Dang et al. reported the possibility of delamination of the cell wall outer layer during TEMPO-mediated oxidation, which may have occurred in this study, possibly resulting in the increase of the fines content.

3.2 Effect of refining on pulp morphologies

Figs. 2~4 present the fiber length, fines content, and water-soluble fraction results after centrifugation and refining of each pulp, respectively. For all the pulps, the
fiber length decreased and the fines content and water-soluble fraction after centrifugation increased with increasing number of PFI revolutions. The behaviors of the TOPs were similar to that of the original LBKP. Although the generation of a large small-fiber fraction was expected because TOP is easily disintegrated into nanofibers, the deterioration of the fiber length was not significant for either TOP-A or TOP-B.

Each pulp fiber refined using 10,000 PFI revolutions was suspended in water and examined using a differential interference microscope to investigate the difference in the pulp morphologies. Many external fibrils were observed on the original LBKP surface (Fig. 5 a). However, the two TOPs had lower external fibril contents (Fig. 5 b–c), indicating that the fibrillation behavior of the TOPs differed from that of the original LBKP. Because the trends of the small fiber fractions were similar for the original LBKP and TOPs, external fibrillation may hardly occur for TOPs and fibrils produced by refining may easily peel off from the pulp. Nelson and Kalkipsakis reported that the sheet strength of carboxymethylated pulp containing many carboxy groups hardly increased with refining\(^{20,21}\). A similar result was reported by Cadenas et al. for hexenuronic-acid-containing and hexenuronic-acid-free pulp\(^{22}\). In both reports, it was concluded that the carboxy groups led to an increase of water retention and that water molecules may have a relaxing effect in the refining process. The water retention values of the two TOPs were higher than that of the original LBKP, indicating the interference of the refining process on the fibrillation behavior. The water retention results will be discussed in further detail in Section 3.4.

The fiber morphologies of the TOPs containing less than 0.86 mmol/g carboxy groups were maintained after refining, and the refined TOPs could be applied as raw materials for the papermaking process. However, the generation of external fibrils by refining was less likely for the TOPs. Because external fibrillation contributes to increasing the sheet strength similar to internal fibrillation\(^{23}\), the increase of the sheet strength by external fibrillation for TOPs compared with that for the original LBKP is expected to be small.

### 3.3 Amount of functional groups on pulp surface

Figs. 6 and 7 present the results for the carboxy and aldehyde group contents on the pulp surface. Both the carboxy and aldehyde group contents increased with increasing number of PFI revolutions. The increased amount of carboxy groups for the TOPs was higher than...
that for the original LBKP for the same number of PFI revolutions (Fig. 8). An increase in the amount of functional groups by refining has also been confirmed in hard and soft wood bleached kraft pulp: fiber cutting as well as external and internal fibrillation during refining have been shown to increase the specific surface area, resulting in an increase of the amount of functional groups exposed on the pulp surface. In Section 3.2, it was suggested that external fibrillation of TOPs hardly occurs during refining and that the increase in the specific surface area was smaller than that for the original pulp. In addition, the TOPs contain a large amount of functional groups and a high density of carboxy groups. Therefore, even though the increase in the specific surface area by refining was inferior for the TOPs, the increase in the amount of functional groups may be high. Because an increase in the carboxy group content on the pulp surface leads to improvement of the paper strength and chemical retention, the use of refined TOPs may impart improved functionality to the sheet.

Because TOP-B contained many carboxy groups, it was expected that the amount of carboxy groups exposed on the pulp surface would increase with refining. However, the increased amounts of carboxy groups for TOP-A and TOP-B were almost the same (Fig. 7). Therefore, the increase of the specific surface area may have hardly occurred for the pulp containing many carboxy groups, suggesting that the carboxy groups interfere with the fibrillation during refining.

3.4 Drainage

Fig. 9 presents the freeness results. The freeness of the original LBKP and TOP-A decreased and that of TOP-B increased with increasing number of PFI revolutions. For TOP-B, the pulp concentration in the filtrate from the chamber was high compared with that for the original LBKP, which caused the increase of freeness (Fig. 10). Because the fiber length and fines content of TOP-B were almost the same as those of the original LBKP, the carboxy groups on the pulp surface may improve the dispersibility of the pulp slurry and liquidity, resulting in an increase of the filtrate concentration from the chamber.

The screen plate of the chamber was replaced with 80-mesh wire, and the freeness was remeasured because the difference in filterability could not be measured using the TAPPI method. The freeness of all the pulps decreased with increasing number of PFI revolutions (Fig. 11). The freeness values of the TOPs were lower than that of the original LBKP for the same number of PFI revolutions, and the freeness of the pulp with more carboxy groups was lower. Fig. 12 shows the relationship between the fines content and freeness. The relationship for each pulp differed, and the lower freeness of the TOPs could not be explained based only on the fines.
content. Similar results have been reported for partially carboxymethylated pulp (25), and these results demonstrate the effect of carboxy groups on the freeness. The decrease of freeness for the TOPs may result from the increase of the affinity with water because of the increase of the carboxy group content on the pulp surface and/or the formation of a high-density mat resulting from the increase of the pulp dispersibility. Based on the freeness results, when applying TOPs in the paper-making process, it is expected that excess refining may cause worse filterability at the wire part.

3.5 Water retention value

Table 2 presents the water retention values. The water retention value of each pulp increased with increasing number of PFI revolutions. The increase of the water retention value for the TOPs was greater than that for the original LBKP, and those refined using 20,000 PFI revolutions could not be measured because of the worse filterability during centrifugation. The water retention value of pulp has been reported to be related to fiber

<table>
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<tr>
<th>PFI revolution number</th>
<th>Original pulp</th>
<th>TOP-A</th>
<th>TOP-B</th>
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<tr>
<td>0</td>
<td>110</td>
<td>167</td>
<td>207</td>
</tr>
<tr>
<td>10000</td>
<td>147</td>
<td>255</td>
<td>302</td>
</tr>
<tr>
<td>20000</td>
<td>158</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>40000</td>
<td>183</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
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swelling, which is caused by loosening of bonds between microfibrils resulting from charge repulsion and/or osmotic pressure by ionic groups such as carboxy groups\(^{17}\).

Because swollen TOP fibers were observed in the fiber morphology analysis, fiber swelling caused by the carboxy groups may be responsible for the increase in water retention of the TOPs. The increase in water retention value of the TOPs by refining may be caused by reduced drainage rather than the water retention ability of the pulp itself because the water retention values of the TOPs for 20,000 PFI revolutions could not be measured because of reduced drainage. The drainage ability of TOPs due to refining was confirmed by the freeness measurements, and the increase in the hydrophilic groups on the surface of the pulp and formation of a higher-density sheet may have caused the increase of the water retention value. The water retention values for TOP-A and TOP-B for 10,000 PFI revolutions were as high as 1.7 and 2.1 times that of original LBKP, respectively. Based on the water retention results, when applying TOPs for the paper-making process, it is expected that excess refining will result in worse filterability at the wire part as well as an increase in the energy needed for drying.

4. Conclusion

Two TOPs with different carboxy group contents (0.42 and 0.86 mmol/g) were prepared and refined using a PFI mill, and the effects of refining on the fiber morphologies and raw material properties for paper making were investigated. The fiber morphologies of the TOPs were maintained even after refining, and the TOPs could be used as raw materials for the paper-making process. The behaviors of the fiber length and fines contents of the TOPs were similar to those of the original LBKP; however, external fibrillation hardly occurred during refining for the TOPs. Furthermore, the amount of functional groups on the pulp surfaces and the water retention values of the TOPs greatly increased and the freeness decreased compared with those of the original LBKP.

The increase in freeness and water retention may lead to a reduction of drainage on the wire of a paper machine and an increase in the necessary drying energy. However, the increase in water retention and increase in carboxy group content on the pulp surface may improve the sheet strength. The characteristics of sheet made from refined TOP will be investigated in future work.

References

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