Improved Strength of Peroxide-Bleached Deinked Pulp after TEMPO-Mediated Oxidation at Medium Consistency

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Deinked pulp was pretreated using the 4-acetamido-2,2,6,6,- tetramethyl-pipelidine-1-oxyl radical (TEMPO)/NaBr/NaClO system and then bleached using hydrogen peroxide to achieve a medium pulp consistency. The effect of the amount of oxidant NaClO addition on the peroxide bleaching of deinked pulp was studied. The treated pulp was characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM). The characterization of XRD and SEM showed that the treated pulp had a higher degree of crystallinity and more fibrillation than untreated pulp. Fiber quality analysis also revealed that the treated pulps had more fines and shorter fiber length than the untreated pulp. A handsheet test showed that the deinked pulps pretreated with the TEMPO system exhibited high tensile index values. The tensile index of the TEMPO pretreated pulp was 17% higher than that of the pulp bleached by hydrogen peroxide alone.

Keywords: TEMPO/NaBr/NaClO system; Deinked pulp; Hydrogen peroxide bleaching; Medium consistency

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INTRODUCTION

Currently, the Chinese pulp and paper industry mainly faces three problems: material shortage, an energy crisis, and environmental pollution. The ability to recycle and reuse wastepaper saves natural resources and helps protect the environment; thus it can alleviate some of the pressure on the Chinese pulp and paper industry. However, deinked fibers exhibit a lower bonding ability, resulting in lower strength properties in paper (Somwang *et al.* 2002; Diniz *et al.* 2004; Garg and Singh 2006). This occurs because the deinked fibers are subjected to various chemical and mechanical treatments during drying and in the course of the deinking and repulping processes, which may affect the fiber's physical properties (Hubbe 2007; Hubbe *et al.* 2007). This problem is especially true for waste newspaper deinked pulp, which exhibited increased hornification and lower bonding ability, owing to the shorter collecting cycles and increased reusability. Therefore, it is more difficult to meet the demand for newsprint paper concerning favorable strength properties for pulp from deinked wastepaper. In addition, newsprint manufacture requires more chemicals to compensate for the inadequate strength.

The TEMPO/NaBr/NaClO oxidation system has attracted attention in recent years because of its highly selective conversion of the primary hydroxyl groups into carboxylate compounds in aqueous solution (De Nooy *et al.* 1995a; Tahiri and Vignon 2000; Isogai *et al.* 2011). Benhamou *et al.* (2014) demonstrated the control and optimized preparation of

nanofibrillated cellulose (NFC) from the date palm tree by varying the TEMPO-mediated oxidation time. Rodionova *et al.* (2013) applied the TEMPO-mediated system to Norway spruce and eucalyptus pulps to obtain nanofibers and nanofiber dispersions. The TEMPO-mediated oxidation system also can be applied to native wood celluloses to obtain individual nanofibers and to hemp fibers for obtaining high added value products (Milanovic *et al.* 2012; Saito *et al.* 2012; Kuramae *et al.* 2014). Leroux *et al.* (2010) applied the TEMPO/NaBr/NaClO oxidation system to deinked pulp, and results yielded significant improvements in tensile and burst properties. However, the deinked pulp consistency of the TEMPO treatment was controlled at 2%, which resulted in more wastewater for the following hydrogen peroxide bleaching at a medium pulp consistency. Deinked pulp is usually bleached using hydrogen peroxide at a medium pulp consistency to reduce environmental pollution and water consumption. To improve the strength properties of deinked pulp after the hydrogen peroxide bleaching, a pretreating process using the TEMPO system at medium pulp consistency was employed. The objective of this study is to ascertain the effects of hydrogen peroxide bleaching on deinked pulps when using a pretreatment with the TEMPO system, at a medium pulp consistency.

EXPERIMENTAL

Materials

The sodium bromide, hydrogen peroxide, and other chemicals and solvents were laboratory grade reagents. They were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China) and used without any further purification. The TEMPO (4-acetamido-2,2,6,6-tetramethylpiperidine-1-oxyl radical) and sodium hypochlorite (7.5 to 8.0% as active chlorine) solutions were commercial grade and purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Deinked pulp (DIP) was provided by a southern Chinese paper mill. The pulp was produced from a mixture of 90% old newspapers (ONP) and 10% old magazines (OMG). The carboxylic acid group content was determined using conductimetric titration (141 mmol /kg o.d pulp).

Methods

TEMPO system pretreatment of deinked pulp

Deinked pulps (15.0 g, o.d) were suspended in distilled water (135.0 mL) in an airtight bag to form a 10% consistency slurry. The TEMPO (15.0 mg, 0.1% in mass percent of o.d pulp) and sodium bromide (NaBr) (0.15 g, 1.0% in mass percent of o.d pulp) solutions were added as the catalysts (De Nooy *et al.* 1995b). The amounts of the two catalysts were determined to be optimal based on preliminary work, considering the very expensive price of TEMPO. The amount of sodium hypochlorite (NaClO) was determined according to the pH of the slurry. However, when the pulp slurry consistence is controlled at 10%, it is not easy to make the chemicals disperse very well in the medium pulp slurry and to detect the pH values of the medium pulp slurry. When the amount of NaClO was varied from 0 mL to1.5 mL, the pH values of the slurry ranged from 10.50 to 11.36. The pH value of the sample without NaClO was adjusted to 10.50 by adding 0.1 M NaOH. Briefly, the portions of NaBr and NaClO (Table 1) were first mixed in distilled water and added to the pulp slurry. Then, the ingredients were uniformly mixed by hand. Lastly, a constant amount of the TEMPO solution was added to the pulp slurry and sealed in an airtight bag. The pretreatment was processed for 1 h at 25 °C, and the pulp slurry was

mixed uniformly every 10 min during the reaction process. After the pretreatment, the pulp slurry was bleached using hydrogen peroxide (H_2O_2).

Table 1. Experimental Conditions and the Chemicals Compositions

samples	TEMPO system pretreatment[1]			H_2O_2 bleaching[2]		
	TEMPO	NaBr	NaClO	H_2O_2	Na_2SiO_3	NaOH
1[3]	0.0	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	2.0%	1.2%	0.5%
3	0.1%[4]	1.0%	0.0	2.0%	1.2%	0.5%
4	0.1%	1.0%	0.5%	2.0%	1.2%	0.5%
5	0.1%	1.0%	1.0%	2.0%	1.2%	0.5%
6	0.1%	1.0%	1.5%	2.0%	1.2%	0.5%
7	0.1%	1.0%	2.0%	2.0%	1.2%	0.5%
8[5]	0.0	0.0	2.0%	2.0%	1.2%	0.5%

[1] TEMPO system pretreatment conditions: 25 °C, pulp consistency 10%, 1 h
[2] H_2O_2 bleaching conditions: 85 °C, pulp consistency 10%, 1.5 h
[3] Untreated deinked pulp
[4] The amount of chemicals added was reported in mass percent of the oven-dried deinked pulp
[5] The sample was treated with NaClO only in the pretreatment stage and then bleached in the same way to other samples.

Bleaching process

Both the pretreated deinked pulps and the untreated deinked pulps were bleached using a hydrogen peroxide bleaching process. In both cases, the bleaching was carried out at 10% pulp consistency using 1.2% sodium silicate, 2.0% hydrogen peroxide, and 0.5% sodium hydroxide. All of the reagents were mixed uniformly in the pulp slurry by hand. Then, the bag was sealed and transferred into a thermostat bath maintained at 85 °C for 90 min. The pulp slurry was mixed every 10 min during the bleaching process. After bleaching, the deinked pulp was washed thoroughly with distilled water and stored at 4 °C for further detection.

Determination of carboxylate contents

The carboxylate contents of the deinked pulps were determined using the electric conductivity titration method (Araki *et al*. 2001).

Brightness and physical strength

Deinked pulps treated with the TEMPO system and/or hydrogen peroxide were prepared according to the ISO 5269/1 standard (2005). The strength properties of pulp handsheets were examined according to TAPPI T 220 om-88 standard (1994). The pulp ISO brightness was measured using a CM-3630 Bench-top Spectrophotometer (Konica Minolta Inc., Tokyo 100-7015, Japan).

X-ray diffraction (XRD)

X-ray diffraction measurements were performed on a D8 ADVANCE diffractometer (Bruker Corp., Germany) with a Ni-filtered Cu Kα radiation (λ = 0.154 nm) at 40 kV and 40 mA in a 2θ range between 4° and 60°. The crystallinity index was calculated from the X-ray diffraction patterns according to the conventional methods (Segal *et al.* 1959).

Scanning electron microscopy (SEM)

A Merlin Scanning Electron Microscope (ZEISS, Oberkochen, Germany), operated at 2 keV, was used to image deinked pulp samples. Samples were coated with Au using a vacuum sputter-coater (KJ-1100X-SPC-16M, Zhengzhou Kejia Furnace Co., Ltd., China) to improve the conductivity of the samples, thus the quality of the SEM images.

Fiber quality analysis

0.2 g (o.d) pulps were dispersed uniformity in 1L water and then diluted to suitable concentration to be analyzed with a Kajaani FS300 device (Metso, Finland).

RESULTS AND DISCUSSION

Recovery Ratio and Brightness of Deinked Pulps

Figure 1 shows the effects of the amount of NaClO on the recovery ratio and the brightness of deinked pulps. The results showed that the hydrogen peroxide bleaching had a remarkable effect on pulp brightness, with an approximate 10 points promotion from an initial 45.7% ISO to 55.0% ISO between sample 1 (untreated deinked pulp) and sample 2 (treated with hydrogen peroxide only). Besides, the brightness of the deinked pulp pretreated with the TEMPO system (sample 7, 55.2% ISO) was a little higher than that pretreated with NaClO only (sample 8, 54.2% ISO), indicating that the brightness was promoted when NaClO was used with TEMPO and NaBr. The alkaline conditions during the pretreatment produced an alkali darkening effect on the brightness of the deinked pulp. However, the bleaching treatment was able to recover the brightness loss during the pretreatment process (Niskanen 1998). Therefore, the brightness of the deinked pulps treated with 1.5% (sample 6, 55.1% ISO) and 2.0% (sample 7, 55.2% ISO) NaClO was nearly identical to that of the pulp treated with hydrogen peroxide only (sample 2, 55.0% ISO). The result corresponded to the research of Leroux *et al.* (2010), in which they also treated deinked pulp with the TEMPO system and the hydrogen peroxide. But the pulp consistency of the TEMPO oxidation and the peroxide bleaching was controlled at 2% and 12%, respectively, in their experiment, while both of the two stages in the present work were controlled at 10%. Their highest brightness of the pulp treated with the TEMPO system and the hydrogen peroxide (main chemical dosages: TEMPO 0.042 %w/w; NaBr 7.9 %w/w; NaClO 2.5 %v/v; hydrogen peroxide 5 %w/w) was promoted by ~4.8% from ~62% ISO to ~65% ISO toward the pulp treated with peroxide only. The brightness of the pulp treated with peroxide only promoted ~6% ISO from ~56% ISO to ~62% ISO toward the untreated pulp, which was lower than our result (~9.3% ISO promotion). So their better effect on the brightness promotion of the treated pulp may be attributed to the TEMPO oxidation, especially at the higher oxidant NaClO dosage. In addition, their starting material was produced from a mixture of 70% old newspapers (ONP) and 30% old magazines (OMG), while the furnish used in the present work was produced from a mixture of 90% old newspapers (ONP) and 10% old magazines (OMG). So the different properties of the two experimental materials may also lead to the different results.

Figure 1 also shows that all of the recovery ratios of deinked pulps were decreased by varying degrees after the TEMPO system pretreatment, under different NaClO additions. The recovery ratio of deinked pulps pretreated with the TEMPO system at the highest amount of NaClO (sample 7, 83.5%) decreased by approximately 1.8% in contrast to the pulp treated with hydrogen peroxide alone (sample 2, 85.3%). The loss may be attributed

to the lignin, hemicelluloses, and a part of cellulose, which were removed as water-soluble compounds (Mao *et al*. 2008). Besides, some material from the deinked fibers might be degraded into soluble molecules (*e.g.*, monosaccharides) during the oxidation by the TEMPO system, and these products may be lost during the washing process (Saito and Isogai 2003; Saito *et al.* 2006). According to Ma *et al.* (2012), delignification was promoted when TEMPO was used with NaBr and NaClO. Maybe that is the reason why the recovery ratio of the deinked pulp pretreated with the TEMPO system (sample 7, 83.5%) was lower than that pretreated with NaClO only (sample 8, 84.7%). In Leroux *et al.*'s work, the dosages of the sodium hypochlorite were varied from 1.25% (% v/v, approximately 9.24 mmol/g) to 8.3% (% v/v, approximately 61.4 mmol/g), and the yield was not given. However, a large drop in yield occurred when the dosage of sodium hypochlorite was 6.0 mmol/(g of fiber) or higher (Mao *et al.* 2008; Okita *et al.* 2009).

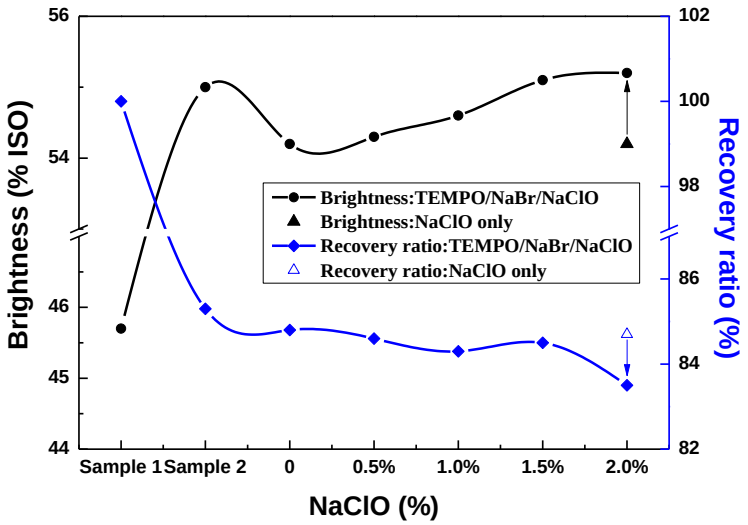

Fig. 1. The effect of NaClO (%) on the recovery ratio and the brightness of deinked pulps

Strength Properties of Handsheets

Figure 2 shows the association between the NaClO (%) additions and the carboxylate content of the treated pulps, as well as the tensile index of the handsheets. According to the previous research, the TEMPO-mediated oxidation of native cellulose at pH 10 to 11 was optimum for shortening the oxidation time (Saito and Isogai 2004). Therefore, the starting pH of the pulp slurries (sample 3~8) during the pretreatment stage was controlled at 10.50, 10.50, 10.87, 10.92, 11.36, and 11.36, respectively. Results showed that more carboxylate groups were generated at the surface of deinked fibers as the NaClO (%) addition was increased. When the NaClO (%) addition was 2%, the carboxylate content was 198.2 mmol/kg (sample 7) and 186 mmol/kg (sample 8), which was promoted by ~7% and ~0.4%, respectively, compared with the pulp treated with peroxide only (sample 2, 185.2 mmol/kg), indicating that TEMPO and NaBr were good catalysts to NaClO in converting primary hydroxyl groups into carboxyl ones. But the carboxylate content did not increase after the TEMPO system oxidation. The reason might be that part of the oxidant NaClO was consumed by the lignin or even the hemicellulose dissolution (Okita *et al.* 2009; Ma *et al.* 2012). In addition, similar effects were observed with the tensile index.

The tensile index is mainly dependent on fiber-to-fiber bonding, as well as hydrogen bonding. As the number of carboxylate groups generated increases, this increases the number of hydrogen bonds that are formed; thus, the oxidative treatments can be expected to yield higher tensile strengths of handsheets. When the amount of NaClO added reached 2%, the tensile index of the handsheets increased to 47.0 N·m/g (sample 7) and 43.3 N·m/g (sample 8), increasing by 17% and 7.7%, respectively, compared with that of the handsheets treated with hydrogen peroxide only (sample 2, 40.2 N·m/g). According to Leroux *et al.* (2010), the breaking length of their treated pulp increased ~23% from 4.8 km (treated with peroxide only) to 5.9 km (treated with 0.042 %w/w TEMPO, 7.9 %w/w NaBr, 2.5 %v/v NaClO and 5 %w/w hydrogen peroxide). Their better tensile strength might be attributed to their higher oxidant NaClO dosages.

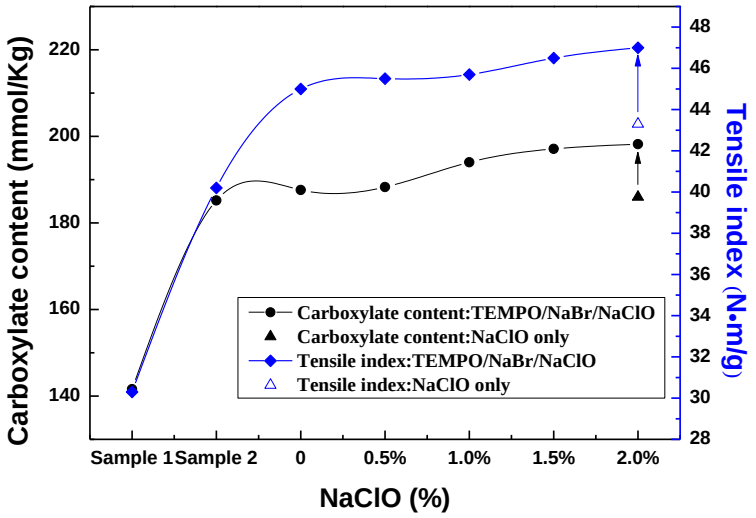

Fig. 2. The effect of the NaClO (%) addition on the carboxylate content and the tensile index of the handsheets

The burst and tear indices of the handsheets were affected by the NaClO (%) additions. The results are shown in Fig. 3. The pretreatment with the TEMPO system had a slight effect on the burst of the handsheets; these handsheets (burst indices varied from 2.44 kPa·m^2/g to 2.53 kPa·m^2/g) were similar to those of the handsheets bleached using hydrogen peroxide only (burst index: 2.48 kPa·m^2/g). However, the tear strength was reduced after the pretreatment with the TEMPO system, and the reduction was more notable as the amount of NaClO (%) was increased. When the amount of NaClO (%) was 2.0%, the tear index of the handsheets decreased 8.6% from 6.13 mN·m^2/g (sample 7) to 5.6 mN·m^2/g (sample 2). And when the deinked pulp was pretreated with NaClO only (sample 8), its burst and tear were 2.45 kPa·m^2/g and 5.65 mN·m^2/g, respectively. Both of them were almost the same as sample 7 (2.48 kPa·m^2/g, 5.6 mN·m^2/g). The burst was associated with the fiber-to-fiber bonding and the length of fibers, while the tearing resistance was largely dependent on fiber length only. Generally, more carboxylate groups were formed, meaning that the ability of fiber-to-fiber bonding was stronger after the oxidation with the TEMPO system. However, depolymerization was also inevitable, and would result in shortened fiber length (Shibata and Isogai 2003). Therefore, the burst strength of the handsheets almost remained the same, while the tear was reduced after the pretreatment with the TEMPO system. In comparison, Leroux *et al.* (2010) reported an

increase of 37% on burst from 2.7 kPa·m^2/g (pulp treated with peroxide only) to 3.7 kPa·m^2/g (pulp treated with 0.042 %w/w TEMPO, 7.9 %w/w NaBr, 2.5 %v/v NaClO and 5 %w/w hydrogen peroxide) and a decrease of 20% on tear from 9.0 mN·m^2/g (pulp treated with peroxide only) to 7.2 mN·m^2/g (pulp treated with 0.042 %w/w TEMPO, 7.9 %w/w NaBr, 2.5 %v/v NaClO and 5 %w/w hydrogen peroxide). The burst increase was much higher than in the present work, while the tear was reduced more significantly in the cited work.

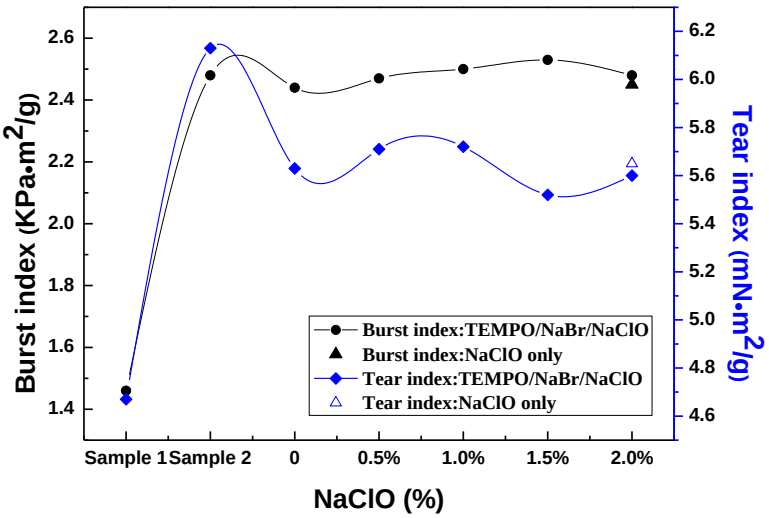

Fig. 3. The effect of NaClO (%) additions on the burst and tear indices of handsheets

Changes in Crystallinity of Deinked Fibers

An XRD analysis was performed to determine changes in the crystallinity of the deinked pulp samples (Fig. 4).

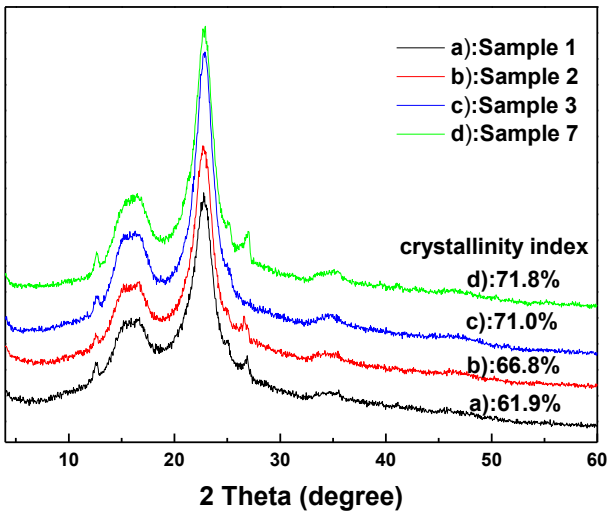

Fig. 4. The XRD analysis of samples: a) untreated deinked pulp, b) deinked pulp bleached with H_2O_2, c) 0.1%TEMPO+1.0%NaBr+0%NaClO+H_2O_2, d) 0.1%TEMPO+1.0%NaBr+2.0%NaClO+ H_2O_2

Results showed that the X-ray diffraction patterns were nearly unchanged after the hydrogen peroxide bleaching or the TEMPO system oxidation, indicating that the carboxylate groups formed in the treated deinked pulps are selectively present on the cellulose microfibril surfaces and in disordered regions (Okita *et al.* 2009). However, the crystallinity indices of the deinked pulps after TEMPO system oxidation or peroxide bleaching were higher than that of untreated pulp. The lignin, hemicelluloses, and amorphous cellulose, in the deinked pulps are preferably degraded by the TEMPO-mediated oxidation and the peroxide bleaching, and then were removed as water-soluble compounds in the washing process, while the original crystalline regions are mostly remained in the water-insoluble treated deinked pulp fraction. Thus, the crystallinity indices were relatively increased after the oxidation. The results corresponded to those of Okita *et al.* (2009).

SEM Observations and Fiber Quality Analysis of the Deinked Pulp Fibrils

Figure 5 shows the SEM images and fiber quality analysis of the fibrils of untreated deinked fibers (sample 1), hydrogen peroxide bleached deinked fibers (sample 2), and the TEMPO system oxidized and hydrogen peroxide bleached deinked fibers (sample 7). The SEM observations revealed that the surface of the fibrils pretreated with the TEMPO system had more fibrillation and fiber fragments. As the oxidation reaction continued, the introduction of carboxylate groups began primarily in the disordered regions and then progressed to crystal surfaces (Saito *et al.* 2006). The length-weighted fractions showed that the fines fractions in the treated deinked pulp (b-2: sample 2, 18.5% and c-2: sample 7, 20.5%) were higher than the untreated pulp (a-1: sample 1, 17.1%), while the fiber length (length-weighted mean) was slightly decreased after oxidation from 1.03mm (sample 1) to 1.02mm (sample 2) and 1.00mm (sample 7). The introduction of carboxylate groups made the oxidized deinked fibers more hydrophilic, and some of the cellulose may be degraded into smaller pieces (*e.g.,* monosaccharides), because of the oxidation process (Shibata and Isogai 2003). Thus, the fines fractions increased while the fiber length decreased after the oxidation.

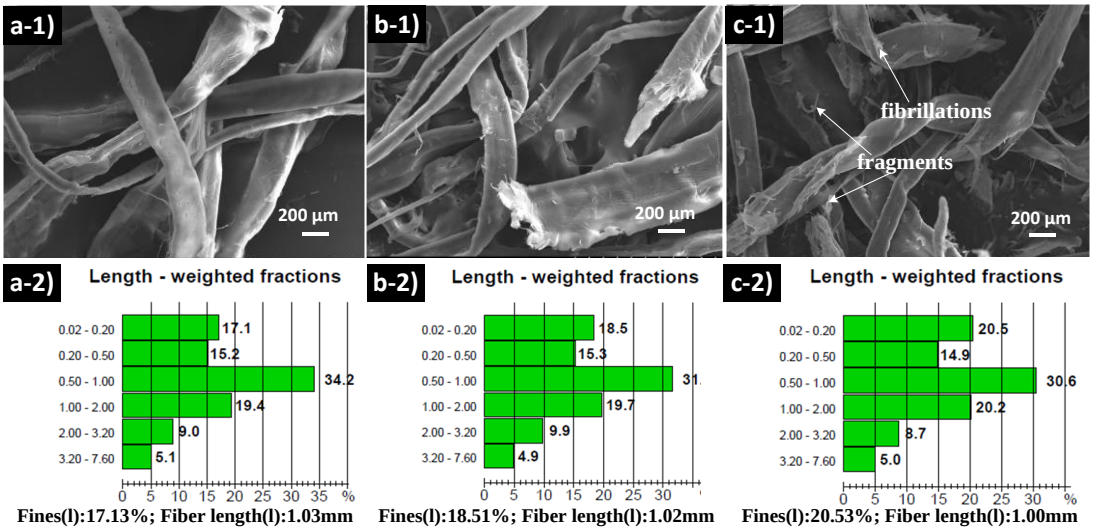

Fig. 5. The SEM images and fiber quality analysis of samples: a-1,2) fibrils of virgin deinked fibers, b-1,2) fibrils of deinked fibers bleached with H_2O_2, c-1,2) fibrils of deinked fibers treated with 0.1%TEMPO+1.0%NaBr+2.0%NaClO+H_2O_2

CONCLUSIONS

1. The TEMPO/NaBr/NaClO system pretreatment of deinked pulp at medium pulp consistency had a favorable effect on subsequent hydrogen peroxide bleaching, which was observed by the enhancement of the tensile property.
2. When applying a TEMPO-mediated oxidation with 2.0% NaClO charge at 10% consistency before the peroxide bleaching stage, it is possible to obtain a pulp with the same final brightness and an increase of 17% in tensile index and a decrease of 8% in tear index.
3. The deinked pulp pretreated with the TEMPO/NaBr/NaClO system and bleached with hydrogen peroxide maintained its crystalline form of cellulose and exhibited a higher crystalline index because of the partial remove of the disordered regions.
4. The TEMPO/NaBr/NaClO system pretreatment of deinked pulp and hydrogen peroxide bleaching at medium pulp consistency was demonstrated as a novel method to improve the tensile strength of newspaper.

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