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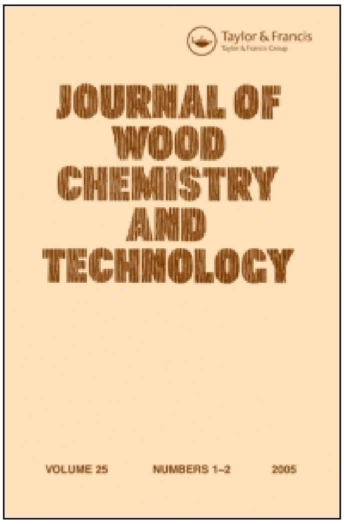

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Spectroscopic Study of Tempo-Oxidized Deinked Pulp

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Abstract: Deinked pulps are not currently used in value-added paper manufacturing. To implement their use, both strength and optical properties must be improved. TEMPO oxidation has been shown to improve strength properties of thermomechanical and deinked pulps. However, a significant reduction of the pulp brightness results due to yellowing of mechanical fibers. Spectroscopic techniques were used to investigate the effect of TEMPO oxidation on deinked fiber properties. Fourier transform infrared (FTIR) spectroscopy and UV/VIS spectrum showed that oxidation conditions are driving important chemical reactions that affect optical properties. Results indicated that ortho-quinone compounds as well as carboxylic groups are generated depending on oxidation conditions resulting in pulp brightness decrease. Spectroscopic studies also revealed that residual ink detachment from fiber surfaces is occurring during oxidation contributing to improve pulp brightness.

Keywords: Deinked fibers, FTIR, optical properties, oxidation, tempo, UV-visible spectroscopy

INTRODUCTION

Deinked pulps are mainly used for the production of newsprint, boards, and tissue papers. However, they are not commonly used for the production of value-added papers such as printing and writing grades, coated and supercalendered

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papers due to an unsuitable deinked pulp quality. Three main quality issues must be overcome. Bonding potential and optical properties must be significantly increased, while residual contaminant levels must be reduced. Various approaches have been studied to improve deinked pulp properties. However, none of them are satisfactory enough to achieve the suitable quality level required for value-added papers.

It is well known that paper strength is strongly correlated to fiber bonding.[1,2] Studies have shown that fiber bonding is dependent on carboxylic group's content on fiber surfaces through their impact on fiber swelling, which increases the fiber plasticity and the bonded area.[3,4] Catalytic and selective oxidation of primary hydroxyl groups of pulp fibers using TEMPO has received much attention in recent years to improve pulp strength by introducing additional carboxylic groups on the fiber surface.[5–8] TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy radical) is a water-soluble, stable, and commercially available nitroxyl radical reagent. It is used as a catalytic oxidant with NaBr and NaOCl for conversion of primary hydroxyl groups of cellulose into carboxylic groups under aqueous conditions. The couple NaOCl/NaBr is a co-oxidizer system that allows the regeneration of the TEMPO. The cellulose is treated with those chemicals under alkaline conditions (pH around 10 and 11), yielding carboxylic acid sites on the cellulosic chain.[5] However, those studies were mainly focusing on chemical and to a lower extent on mechanical pulps. In a recent study, Leroux et al. have studied the effect of TEMPO oxidation on deinked pulp strength improvement because they are containing both types of pulps.[9] They have shown that TEMPO oxidation conditions improved deinked pulp strength, but decreased significantly the brightness. However, this brightness loss was totally recovered by carrying out a bleaching stage with hydrogen peroxide after the oxidation step. Results also showed that residual ink particles were removed after a flotation stage as shown by a reduction of the effective residual ink concentration (ERIC values). However, it was not possible to clearly establish a correlation between oxidation and ink removal.

To further understand the impact of oxidation and deinking operations on pulp optical properties, spectroscopic techniques were used to help determine the role of chemical reactions involved by TEMPO oxidation and peroxide bleaching. Fourier transform infra-red (FTIR) spectroscopy and UV/Visible reflectance spectroscopic techniques were used to establish the role of chemical reactions involved by TEMPO oxidation and their effects on optical properties of deinked pulps. They are well suited to examine chemical modifications of cellulose and lignin with chemicals under various experimental conditions.[10–14] Therefore, the aim of this study was to analyze the effects of TEMPO oxidation on deinked pulp optical properties, mainly brightness and residual ink content using spectroscopic techniques.

Table 1. Properties of the deinked pulp

ONP (%)	OMG (%)	Tensile (km)	Burst (kPa-m^2/g)	Tear (mN-m^2/g)	Brightness (%)	ERIC (ppm)
70	30	3.64	2.04	9.0	58.0	216

EXPERIMENTAL

Materials

The 4-Acetamido TEMPO, sodium bromide, and other chemicals and solvents were of laboratory grades. They were purchased from Aldrich and used without any purification. Sodium hypochlorite was of commercial grade (5.5–6% active chlorine).

Deinked pulp (DIP) was provided by an Eastern Canadian paper mill. The pulp was produced from a mixture of 70% old newspapers (ONP) and 30% old magazines (OMG). This pulp was selected because it is widely used for the production of newsprint and easily available. Table 1 presents the properties of the deinked pulp.

Methodology

Figure 1 presents a schematic diagram of the procedures involved for experimentation.

Oxidation of Pulp

Oxidation of deinked pulp was carried out by mixing 60 g o.d. in 3 L of deionized water to make a 2% slurry consistency. The pH was adjusted to 10.5 with NaOH. The TEMPO was first diluted in water and added to the mixture according to the dosages required as indicated in Table 2. The appropriate amounts of sodium bromide and sodium hydroxide (see Table 2) were first

Table 2. Chemical dosages for TEMPO oxidation of deinked pulps

Charge TEMPO (%)	TEMPO (%w/w)	NaBr (%w/w)	NaOCl (%v/v)
100	0.17	32.0	8.3
50	0.083	15.8	5.0
25	0.042	7.9	2.5
12.5	0.021	3.96	1.25

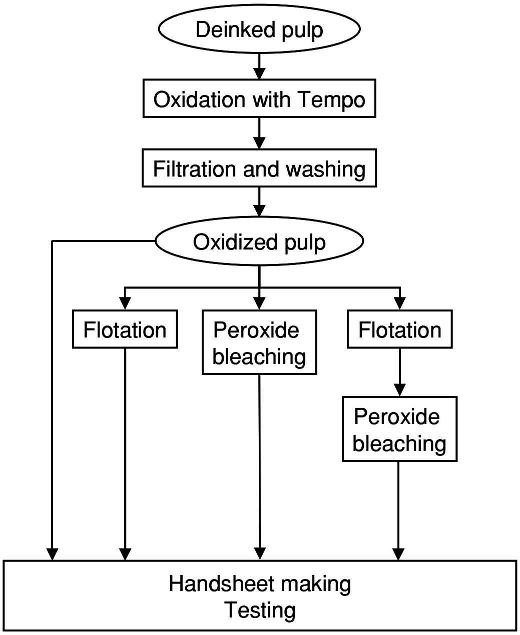

Figure 1. Schematic diagram of the methodology.

mixed and then added slowly to the pulp slurry maintained under agitation in a mixing container. During chemicals addition, the pH of the slurry was kept constant at 10.5 using a pH controller and 0.1 M solutions of HCl or NaOH. The reaction was carried out for two hours. Finally, the reaction was stopped by adding 20 mL of ethanol to the slurry. The pulp was then filtered and reslushed. Then, the pH of the pulp slurry was decreased to 5.5 using HCl (1 M). The pulp was filtered again and washed three times with deionized water to remove any residual chemicals. The carboxylic acid groups content was determined by conductimetric titration according to the method developed by Katz et al.[15] (110 mmol/kg o.d. pulp).

Flotation

A sample of the oxidized pulp was diluted to 0.5% consistency using deionized water. The pH was adjusted to 9.5 using NaOH 1 M solution, and the temperature was adjusted to 50°C using hot water. The free calcium ion content was then measured by titration with EDTA. Then, the free calcium ion was adjusted to 100 mg/L by adding the corresponding amount of calcium chloride in the pulp slurry. A surfactant (sodium oleate) was then added to the pulp slurry. The amount was 0.5% based on the dry fiber content. The slurry was stirred for 5 minutes and transferred to a Leeds flotation cell (6.5 L). The slurry in the flotation cell was agitated at 1200 rpm, and then air was injected at a flow rate of 3 L/min. Flotation was carried out during 5 minutes. The froth was continuously collected in a beaker during the flotation. After the flotation stage, the cleaned pulp remaining in the cell was recovered; the pH was adjusted to 5.5, and filtered on a büchner funnel. A sample of the thickened pulp was then used to make handsheets.

Bleaching

In two series of experiments, a peroxide bleaching stage was carried out using either the oxidized pulp or the oxidized/floated pulp samples (see Figure 1). In both cases, the bleaching was carried out at 12% pulp consistency using 3% sodium silicate, 0.05% magnesium sulphate, 5% hydrogen peroxide, and a total alkali ratio of 0.8. All chemicals were introduced in the pulp contained in a plastic bag and mixed for 2 minutes. The pulp was then preheated in a microwave oven. Then, the bag was sealed and transferred in a thermostatic bath maintained at 70°C for 90 minutes. After bleaching, the remaining peroxide in the pulp sample was neutralized using sodium metabisulphite until the pH was reduced to 5.5. The bleached pulp sample was filtered and used to make handsheets.

Handsheet Formation and Testing

Standard handsheets (60 g/m^2) of pulp samples after any treatments were made using a British handsheet machine according to PAPTAC Standard Testing Method C.4. Optical properties (PAPTAC Standard Testing Methods E.1, E.8P) were determined from these handsheets.

Spectroscopy

UV/Visible

UV/Visible spectroscopy was carried out on handsheets using a Cary 5000 spectrometer (Varian) equipped with integral Labsphere integrating sphere. Spectra from handsheets containing oxidized pulp were determined in total reflectance mode at wavelength ranging from 300 and 600 nm. The signal/noise ratio of the spectra were then optimized at every TEMPO concentration by adjusting the proper incidence angle into the integrating sphere and spectra difference between each optimized spectra were also obtained from spectroscopic data. From these data, Kubelka-Munk (KM) units differences were calculated for the data range observed.

FTIR

FTIR spectroscopy was also carried out on each handsheet using Perkin Elmer 2000 FTIR equipment. The diffuse reflectance infrared Fourier transform (DRIFT) method was used. The wavelength range was varied between 2000 and 1500 cm^{-1}. Only spectra at 12.5 and 100% TEMPO were analyzed. From these data, Spectra differences in Kubelka-Munk units were determined.

RESULTS AND DISCUSSION

Effect of TEMPO on Pulp Brightness

Figure 2 presents the effect of TEMPO dosages on pulp brightness. It is clear that TEMPO oxidation had a dramatic effect on pulp brightness with approximately 10 points brightness drop between the blank without any TEMPO and the trial at 12.5% TEMPO. This was attributed to the alkali darkening effect resulting from the alkaline conditions prevailing during oxidation. The effect was less important at higher TEMPO dosages but the brightness drop was still significant (compare bar 1 in each series of experiments). To compensate for this effect, a bleaching stage with peroxide at a constant dosage of 5% was carried out (bar 3 in each series). Results show that the bleaching stage was able to recover more than the brightness lost during the oxidation process. The

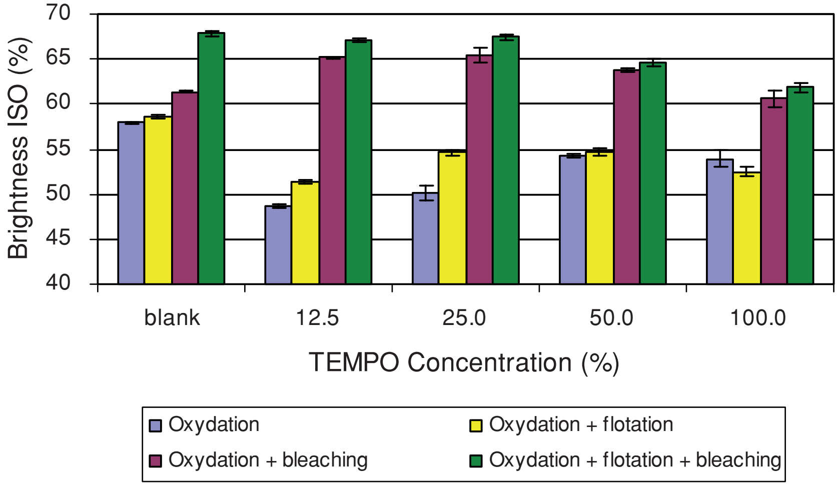

Figure 2. Effect of TEMPO concentration on pulp brightness after oxidation, bleaching, or flotation.

phenomenon was similar at all TEMPO dosages. Of course the brightness gain was not significant for the blank experiments because no TEMPO was used. Deinked pulp generally contains mechanical and chemical fibers. Both types of fibers will react differently to oxidizers used. TEMPO is decreasing the brightness compared to the blank. However, the bleaching stage with peroxide is recovering more than the brightness loss during oxidation with TEMPO. This could be attributed to different chemical reactions involved by both oxidizers on both types of fibers. Chemical pulps mainly contain cellulose with very low level of residual lignin while mechanical fibers are mainly constituted by lignin. In both cases, oxidizers will react with alcohol groups on cellulose or lignin to generate carbonyl and carboxylic groups depending on the full completion of the reaction. Carbonyl groups on cellulose and lignin (quinones) are colored compounds or chromophores that will reduce pulp brightness while carboxylic groups are uncolored. It is thus required that the full reaction occurs to improve brightness of both pulps. Therefore, a balance between the formation of carboxyl groups and chromophores on lignin can be achieved depending on dosages of both chemicals. Our results showed that adding a peroxide bleaching stage to oxidized pulps shifted the reaction to form carboxylic groups from carbonyl. Therefore, this improved the brightness of the pulp by consuming the colored chromophores mainly generated on lignin. However, at high TEMPO dosages ($>50\%$) the brightness started to drop. Another explanation based on the chemistry and the dosages used in TEMPO oxidation with NaBr and NaOCl is also possible. It is suspected that the presence of bromide ions in the oxidation reaction could affect pulp brightness because bromide ions could be fixed to phenolic groups on the lignin to generate bromolignin compounds.[16] As the dosage of TEMPO is increased, the dosage of NaBr is also increased (see Table 2), thus providing a higher concentration of bromide ions in the system and the possibility of forming higher amounts of bromolignin compounds. Therefore, the presence of bromolignin compounds could be partly responsible for the drop in pulp brightness.

The UV-Visible reflectance spectra of oxidized handsheets containing various TEMPO concentrations were taken between 300 and 600 nm, corrected for the baseline of untreated pulp, and are presented in Figure 3A. Figure 3B shows the difference spectra where the result from a given concentration is corrected from the result of the previous one. Thus, the 12.5-BL shows the difference between 12.5 and the untreated pulp (which is thus the same as the one presented in Figure 3A), and 25–12.5 represents the difference observed when going from 12.5 to 25, and so on.

In Figure 3A, the 12.5 and 25 spectra (blue and red curves, respectively) show positive values of KM units for the whole spectra range. This indicates that chromophores are being created on lignin. On the other hand, the 50 and 100 spectra (green and purple, respectively) show negative values of KM units between 500 and 700 nm, and positive values below 500 nm. An important change is also observed between 350 and 440 nm for these curves. These

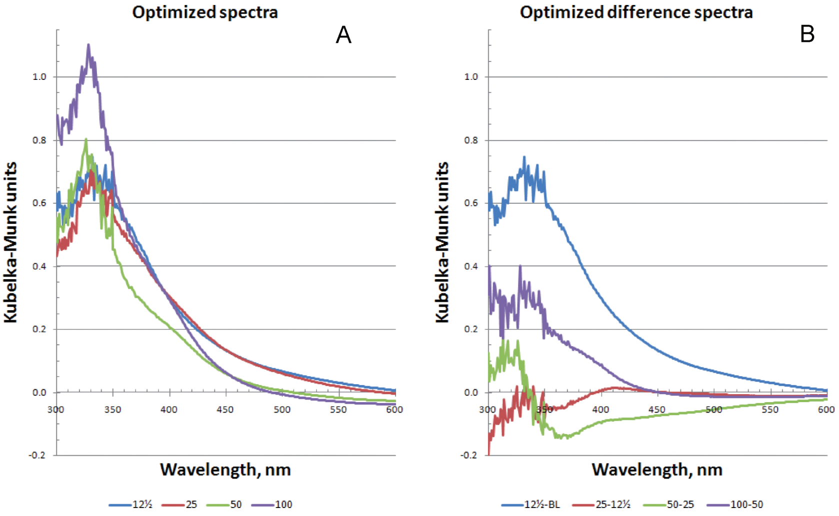

Figure 3. UV-Visible reflectance spectra at various TEMPO concentrations.

discrepancies can be explained by looking at the difference spectra shown in Figure 3B.

The difference spectra between 25 and 12.5 does not show significant modifications in the visible region (above 400 nm), but suggests that some chromophores absorbing in the UV region (340 to 390 nm) are removed or destroyed.

A stronger oxidation (50–25, green curve) results in a stronger lowering of the KM units between 400 and 600 nm, indicating a loss in chromophores. However, an even stronger oxidation (100–50, purple curve) induces the formation of new chromophores, over those that were removed/destroyed by the previous oxidation conditions (50–25).

An *ab initio* Hartree-Fock computation of unsubstituted *ortho*-benzoquinone using a 6-31G* basis set was performed using Spartan'06 software[17] to model the UV-Visible spectra of this molecule. As shown in Figure 4, it is clear that *ortho*-benzoquinone absorbs light in this spectral region. Numerous other calculations, using substituted quinone-type structures (not shown here) of the types encountered in the photoyellowing of paper in literature,[18–20] show similar absorption bands in this same region. Thus, because *ortho*-quinone type structures present in lignin are substituted in various ways, what we measure experimentally is a mixture of these compounds, and thus a mixture of these spectra.

FTIR spectroscopy confirms our UV-Visible observations. Figure 5 presents the DRIFT spectra in the 1500 to 1900 cm^{-1} fingerprint region for two conditions as in Figure 3A, (i.e., results corrected for baseline only). Only the 12.5 and 100 conditions are shown here for clarity.

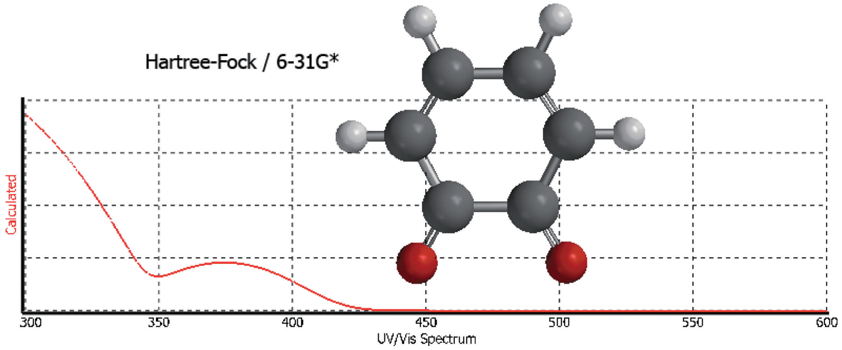

Figure 4. Molecular simulation of unsubstituted *ortho*-benzoquinone by *ab initio* (HF/6-31G*).

At 12.5%, an important band at 1600–1650 cm^{-1} attributed to the colored conjugated quinone structures appears, as well as another one between 1700 and 1800 cm^{-1} associated with colorless alkylated carboxylic acids. Using more oxidizing conditions, like 100%, produces more acids than quinones. This is in accordance with our results of carboxylic acids and ISO brightness measurements.

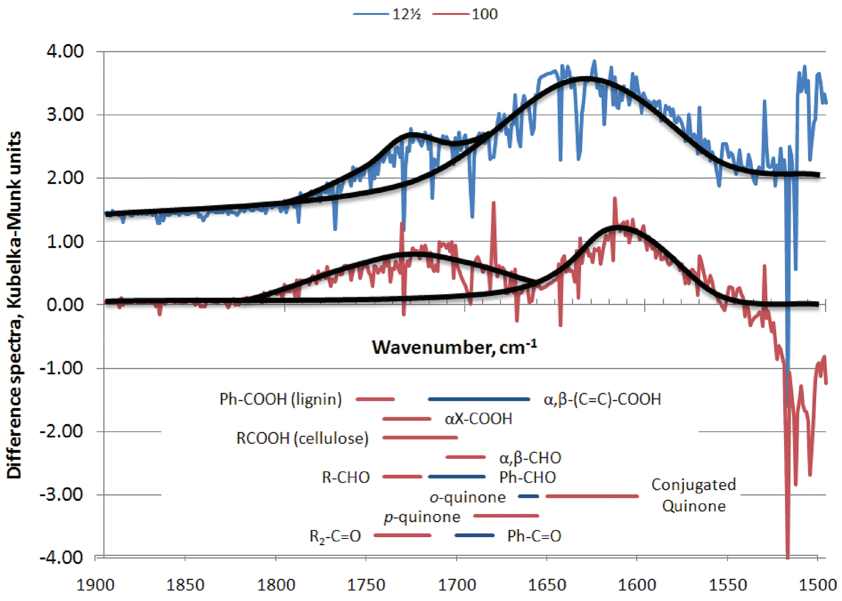

Figure 5. DRIFT FTIR spectra, Kubelka-Munk units.

In summary, even a low oxidizing condition (12.5% TEMPO) produces oxidation of phenolic structures to quinones. Stronger oxidizing conditions reduce quinone structures even more by oxidizing these structures to carboxylic acids.

Effect of TEMPO on Effective Residual Ink Concentration (ERIC)

To further examine the effect of TEMPO on ink detachment, we have determined the level of residual ink on the fiber surface using the Effective Residual Ink Concentration (ERIC). Figure 6 shows the effect of TEMPO on ERIC values for the same experimental conditions. Results indicate that ERIC values decreased after each treatment. Flotation was particularly effective at reducing ERIC, especially after oxidation with TEMPO. However, it was also effective for the blank. Although a substantial reduction in ERIC values was observed after oxidation (compare bar 1 in each series of experiments), it is still unclear if the ERIC reduction can be attributed to the removal of detached ink particles from the oxidation process only. The same trend was observed for trials involving flotation followed by bleaching, except for trial at 100% TEMPO dosage.

UV-Visible spectroscopy has been used to study the possible effect of TEMPO concentration on ink detachment from the fibre surfaces during treatments. As shown previously, results indicate that part of the residual ink particles have been lost during oxidation. Two hypotheses can be proposed. First, the shearing action of stirrers used during oxidation in the reactor can be responsible for ink detachment. Second, ink detachment can be the result of

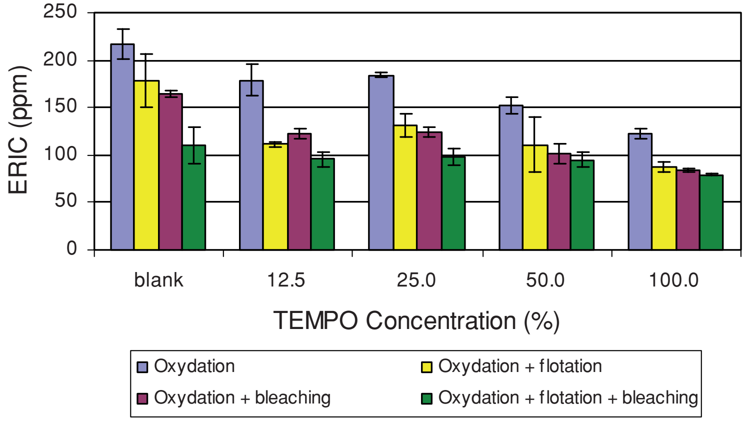

Figure 6. Effect of TEMPO concentration on ERIC values after oxidation, bleaching, or flotation.

surface oxidation achieved during treatment. Because oxidation is a surface phenomenon, it is probable that oxidation helped detach some remaining ink particles on the surface of the fibers. In fact, both phenomena could also be involved during pulp processing. Referring to Figure 3B, we can see that for the emission spectrum ranging from 475 to 600 nm, violet, red, and green curves show negative values of KM units. This means that for TEMPO concentration of 25% and higher, a significant amount of an absorbing compound is lost. Because the spectral modification covers the whole range of wavelength, this compound is certainly carbon black from remaining ink particles. This is in complete agreement with results obtained in Figure 6 where ERIC values are decreasing. Therefore, it can be concluded that oxidation helped to break ink/fiber bounds, resulting in further ink releasing from fiber surfaces during pulp processing. However, the exact mechanism is not known. It is suggested that the cellulose at the interface between carbon black particle and fiber surface is possibly weakened by the oxidation treatment, combined with the well-known effect of mixing/alkali conditions. The overall effect could thus be responsible for the increase in ink detachment and removal by the flotation stage.

CONCLUSIONS

FTIR and UV/Visible spectroscopic techniques were used to investigate the effect of TEMPO oxidation on deinked fiber properties and more specifically on pulp optical characteristics. The main observations are:

1. Oxidation conditions are driving important chemical reactions affecting significantly optical properties of deinked pulps.
2. FTIR and UV/Visible techniques are effective methods to determine the impact of oxidation conditions on fiber surface modifications affecting optical properties of deinked pulps.
3. TEMPO oxidation produces ortho-quinone compounds and carboxylic groups resulting in pulp brightness decrease.
4. Spectroscopic studies also revealed that residual ink detachment from fiber surfaces is occurring during oxidation that may contribute to the improvement of the overall visual appearance of deinked pulp.

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