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Carbohydrate Polymers 70 (2007) 310–317
Carbohydrate Polymers
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Characterizing TEMPO-mediated oxidation of ECF bleached softwood kraft pulps

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Received 24 February 2007; received in revised form 11 April 2007; accepted 18 April 2007
Available online 30 April 2007

Abstract

Elementally chlorine-free (ECF) bleached softwood (SW) kraft pulp was catalytically oxidized with the 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO)–KBr–NaClO system. The carboxyl group content of the fibers was improved with increasing NaClO charge whereas, the carbonyl group content of fibers approached a maximum when a charge of 0.85 mmol NaClO/g o.d. fibers or higher was employed. The degree of polymerization of fibers drastically decreased from 2416 to 688 depending on the increase of NaClO charge during the TEMPO-mediated oxidation. Scanning electron microscopy (SEM) images of the original fibers and the oxidized fibers showed that TEMPO-mediated oxidation is able to remove the primary wall of SW kraft fibers. The optimum reaction temperature and pH for TEMPO-mediated oxidative generation of carboxyl groups was found to be 23 °C at a pH of 9.10. Oxidized fibers were shown to exhibit 62.9% higher water retention values (WRV) than the original fibers. Due to the enhanced carboxyl group content after oxidation, physical strength studies of paper test sheets indicated that the tensile index of the oxidized fibers is 13.8% greater than that of the original fibers. The individual fiber strength of the oxidized fibers was 17.0% lower than that of the original fibers as determined by zero-span strength measurements.
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Keywords: Carbonyl; Carboxyl; Copper number; NMR; SEM; TEMPO; Tensile; Viscosity; WRV; Zero-span

1. Introduction

A number of cellulosic fiber modification strategies have been developed to enrich carboxyl groups of cellulosic fibers over the last few decades. It has been well established that carboxyl groups of fibers influence several key physical properties of fibers including: the swelling of wet fibers, water absorption, fiber flexibility, and fiber–fiber bonding (Barzyk, Page, & Ragauskas, 1997; Dang, Elder, & Ragauskas, 2006; Duarte et al., 2006; Katz & Scallan, 1983; Laine & Stenius, 1997; Lindström & Carlsson, 1982; Scallan & Grignon, 1979).

Recently, the catalytic oxidation of polysaccharides by 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO)–NaBr–NaClO has been reported to effectively convert C6 primary hydroxyl groups to carboxylates via a reactive aldehyde-intermediate (Bragd, van Bekkum, & Besemer, 2004; de Nooy, Besemer, & van Bekkum, 1995; Isogai & Kato, 1998; Jiang & Ragauskas, 2005; Kato, Matsuo, & Isogai, 2003; Kitaoka, Isogai, & Onabe, 1999). The mechanism of TEMPO–NaClO–NaBr oxidation of polysaccharides is summarized in Fig. 1 (Kato et al., 2003).

In a study by de Nooy et al. (1995), the optimum pH for TEMPO-mediated oxidation of water-soluble glucans was found between 10 and 11. Their studies also indicated that pullan was oxidatively depolymerized. This pathway was pH dependent, with minimum depolymerization in the pH range of 9.2–9.7 (de Nooy, Besemer, van Bekkum, van Dijk, & Smit, 1996). Tahiri and Vignon (2000) investigated the TEMPO-oxidation of cellulose, and their results showed that the experimental conditions for minimizing the depolymerization of amorphous cellulose occurred employing a solution pH 10 at 4 °C. Isogai and Kato

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0144-8617/$ - see front matter Published by Elsevier Ltd.
doi:10.1016/j.carbpol.2007.04.014

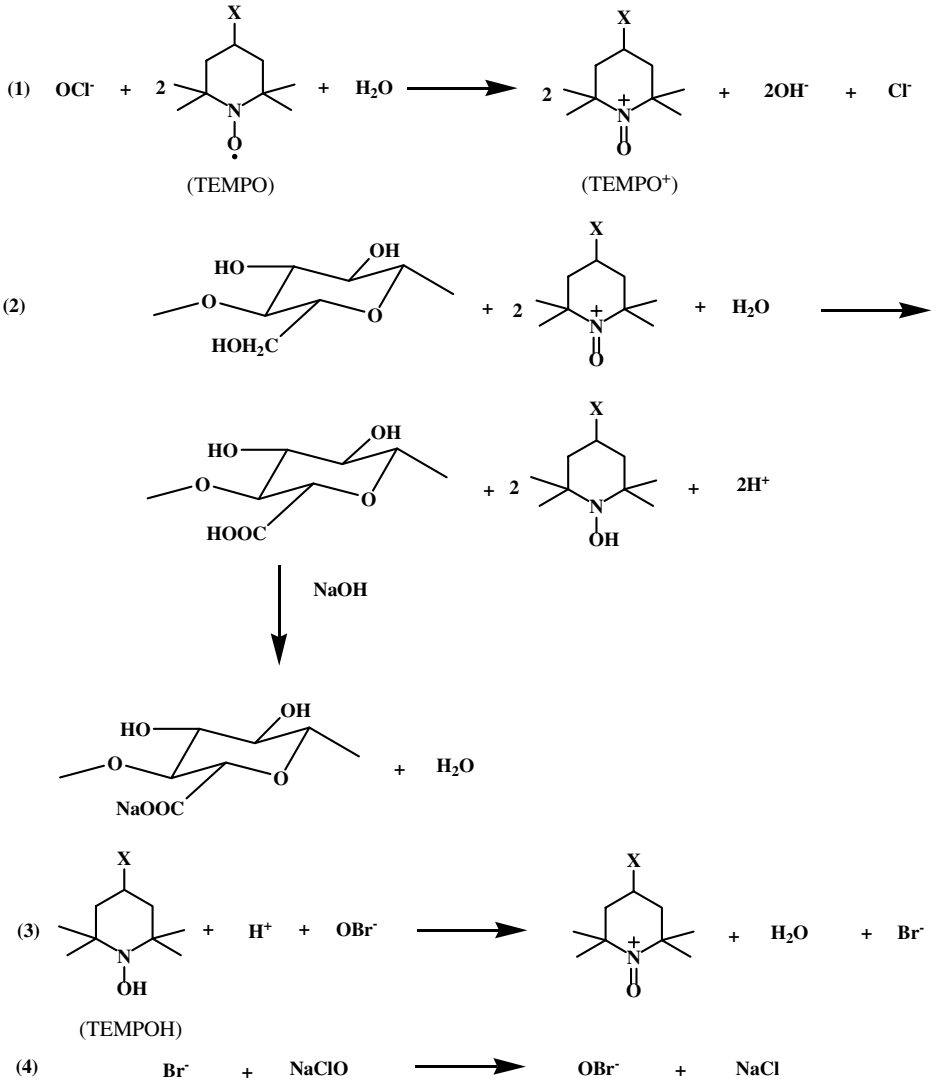

Fig. 1. The mechanism of TEMPO-mediated oxidation of the C6 hydroxyl group of cellulose (Kato et al., 2003).

(1998) applied TEMPO–NaBr–NaClO oxidation at room temperature to increase the carboxyl group content of several different cellulosic samples. For regenerated, or mercerized cellulose, their studies showed that almost all C6 primary alcohol groups could be converted to carboxyl group and the charge of TEMPO, reaction time, and temperature were the key factors controlling the depolymerization of cellulose. For softwood and hardwood bleached kraft pulps, bacterial cellulose, and microcrystalline cellulose powder, Isogai and Kato (1998) demonstrated that TEMPO-oxidation of these substrates was less efficient.

The depolymerization of polysaccharides during TEMPO-mediated oxidization has been attributed to sodium hypochlorite oxidation of polysaccharides, which leads to 2,3-scission of glucose unit; resulting in the formation of dialdehyde and dicarboxylic structures (Besemer, 1993). The presence of carbonyl groups at C-2, C-3 in glucose unit facilitates depolymerization of celluloses via β-alkoxy fragmentation in alkaline medium (Calvini, Conio, Lorenzoni, & Pedemonte, 2004). In addition, depolymerization can occur via β-elimination (Bragd, Besemer, & van Bekkum, 2001; de Nooy et al., 1996; Isogai & Kato, 1998; Kitaoka et al., 1999). Interestingly, a bromide-free TEMPO-mediated oxidation of starch has been reported to proceed with high selectivity and limited depolymerization (Bragd, Besemer, & van Bekkum, 2000). Kitaoka et al. (1999) applied the TEMPO-mediated oxidation system to enrich carboxyl groups of a commercial bleached hardwood kraft pulp. The carboxyl groups of the fibers was shown to be increased from 0.06 mmol/g o.d. pulp to the maximum value of 0.47 mmol/g o.d. pulp depending on the charge of oxidant employed. Saito and Isogai (2005) increased fiber charge by a factor of 1.5 for a hardwood bleached kraft pulp using TEMPO-mediated oxidation with 0.30 mmol NaClO/g o.d. pulp. The dry and wet tensile index of treated sheets was shown to increased by 38% and 208%, respectively. Duarte et al. (2006) also studied the TEMPO-mediated oxidation of a hardwood

bleached kraft pulp and found that the oxidized pulp exhibited an increase of 33% in the tensile strength, 48% in tear index and 60% in hand sheet internal cohesion properties.

Softwood and hardwood kraft pulps are often used for absorbency materials. However, softwood fibers are judged to have much better water absorbency property than hardwood fibers (Hillman, 1990). Therefore, they are often preferably used as absorbency materials (Martin, Wiesemann, & Shoemaker, 2000). The objective of this study is to investigate TEMPO-mediated oxidation of an ECF bleached softwood kraft pulp which has not been previously examined. The effect of the oxidation parameters on carboxyl group content, copper number, water absorbency, and intrinsic viscosity of SW bleached kraft pulp were examined. NMR analyses and SEM images were employed to study the crystallinity index and surface morphology of oxidized fibers, respectively.

2. Materials and methods

2.1. Materials

A never-dried industrially generated ECF bleached softwood kraft pulp was used in this study. The pulp was washed with distilled water until the effluent pH was neutral. The washed pulp was filtered and stored at 2 °C. This pulp had a carboxyl group content of 3.98 mmol/100 g o.d. pulp, Tappi brightness of 84.5 (TAPPI, 1996), copper number of 0.43, and intrinsic viscosity of 672 ml/g. The sodium hypochlorite solution contained 10% available chlorine and had a density of 1.206 g/ml. All chemicals used in this study were purchased from Aldrich, JT Baker, and Fisher as analytical grade and used as received.

2.2. The procedure of TEMPO-mediated oxidation

The oxidation procedure was based on the literature methodology (Kitaoka et al., 1999; Saito & Isogai, 2005). In brief, a never-dried ECF bleached softwood kraft pulp (20.00 g over-dried), TEMPO (0.050 g, 0.320 mmol), and KBr (0.500 g, 4.202 mmol) were mixed with deionized water (1840 ml). Subsequently, a NaClO solution containing 10% available chlorine was added into the slurry. There were five levels of NaClO charge employed in this study, which were 1.70, 3.40, 8.50, 17.01, and 34.01 mmol, respectively. If the initial pH after adding NaClO was lower than 10.5, then the pH value was adjusted to 10.5 by adding 1.00 N NaOH. Generally, the TEMPO-oxidation reactions were performed at the room temperature (23 °C) for 2.0 h.

An additional series of TEMPO-oxidations were conducted at 4–80 °C, with a constant 0.85 mmol NaClO/g o.d. pulp. The effect of pH on the oxidation was examined using the same conditions described above, except that the reaction pH was varied from 7.10 to 10.00. When the reaction started, pH value decreased because of the formation of carboxyl group of fibers. Once the reaction pH value decreased to the targeted value, it was kept constant by adding 1.00 N NaOH.

2.3. Analytical methods

The carboxyl group content was determined using a conductometric titration methodology (Lloyd & Horne, 1993). Copper number was determined following Tappi standard method T 430 (TAPPI, 1996). Both the carboxyl group content and copper number were conducted in duplicate for each sample and the results had an error less than ±3% and ±5%, respectively. The intrinsic viscosity was determined according to ASTM standard D-1795-62 (American Society for Testing & Materials, 2003). The typical error for intrinsic viscosity is ±5 ml/g of the average number. Tensile strength (TAPPI, 1996) and zero-span strength (TAPPI, 1996) were measured to investigate the paper physical properties with an error less than ±5%.

2.4. ^{13}C CP/MAS NMR and SEM analysis of oxidized bleached pulps

Four samples were analyzed by solid-state NMR, which consisted of the untreated ECF bleached SW kraft pulp and oxidized pulps (see Table 1). The ^{13}C CP/MAS NMR spectra were recorded at room temperature on an instrument Bruker Advance/DMX-400 operating at 100.06 MHz using an MAS 4 mm probe and ZrO_2 rotors. The MAS spin rate was 5 kHz. Acquisition was performed with a CP pulse sequence using 4.5 μs pulse, 2.0 ms contact pulse and 3.0 s delay between repetitions. 5000 scans were accumulated for each sample.

SEM images of the original ECF bleached SW kraft pulp and the fibers treated with a charge of 1.70 mmol NaClO/g o.d. pulp were acquired using a LEO 1530 thermally-assisted field emission (TFE) microscope at 10 kV. The coated quartz slide and the smooth side of the paper test sheets were gold coated prior to analysis.

2.5. PEG treatment of pulp fibers

PEG (1.00 g, MW 3350 or 10,000) was dissolved in deionized water (99.00 ml) which has been acidified to pH 2.00 with 1.00 N hydrochloric acid. The solution was

Table 1
Crystallinity index results from ^{13}C CP/MAS NMR analysis of original ECF bleached SW kraft pulp fibers and TEMPO-mediated oxidized fibers

Sample ID	Crystallinity index
Original ECF bleached SW pulp fibers	0.52
Oxidized fibers (0.43 mmol NaClO/g o.d. pulp charge)	0.52
Oxidized fibers (0.85 mmol NaClO/g o.d. pulp charge)	0.53
Oxidized fibers (1.70 mmol NaClO/g o.d. pulp charge)	0.54

mixed until the dissolution of PEG was visually complete. Cellulosic fibers (2.00 g oven-dried) were then immersed in the solution for the ester cross-linking of the cellulosic hydroxyl groups/carboxyl groups with PEG-hydroxyl end groups. The fibers was treated for 15 min and then filtered without washing. Thereafter, the sample was cured at 105 °C for 30 min. It was then disintegrated and immersed in pH 8 NaOH aqueous solution for 1 h. Subsequently, four equivalents of solution were prepared and each contained 0.250 ± 0.050 g o.d. cross-linked fibers for water retention value measurements.

2.6. Water retention value (WRV) of fibers

Pulp water retention values were determined using Tappi Useful Method 256 Water Retention Value (TAPPI, 1991). This methodology employs a pulp mat formed by draining a dilute pulp slurry on a fine mesh screen, in a centrifuge cup. The pulp mat is prepared at a fixed basis o.d. weight of 0.250 ± 0.050 g. The pulp pad is then centrifuged at 900 g for 30 min. The wet pad, after centrifuging, is weighed, dried at 105 °C, and then reweighed. The WRV is calculated as the amount of water by weight retained in the pad after centrifuging per o.d. weight of fibers (Eq. 1).

$$\mathrm{WRV} = \frac{W_\mathrm{w} - W_\mathrm{d}}{W_\mathrm{d}} \times 100\% \quad (1)$$

W_w is the weight of the wet sample after centrifuging, and W_d is that of dry sample. The tests were done in quadruplicate, and standard deviation of 95% confidential level was used for the experimental error evaluation.

3. Results and discussion

3.1. The effect of charge of NaClO on carboxyl group content, carbonyl group content, intrinsic viscosity of fibers after TEMPO-mediated oxidation

Fig. 2 presents the carboxyl group content, carbonyl group content, and intrinsic viscosity of pulp fiber after treatment with different levels of NaClO charge. These results indicate that the carboxyl group content increased from 3.98 to 23.1 mmol/100 g o.d. fibers in a near linear relationship of NaClO addition. The change in the degree of cellulose polymerization was monitored by intrinsic viscosity measurement. These results are in agreement with recent studies by Kitaoka et al. (1999) and Saito and Isogai (2005). Evans and Wallis (1989) developed an equation relating the degree of polymerization (DP) to the intrinsic viscosity $[\eta]$ of the carbohydrates (Eq. 2). The DP of the control ECF bleached fibers was estimated as 2416, while the DP of the TEMPO oxidized fibers after 1.701 mmol NaClO/g o.d. pulp charge was 688.

$$\mathrm{DP}^{0.9} = 1.65 \times [\eta] \quad (2)$$

The copper number ($\mathrm{Cu}^{\#}$) is an indication of aldehyde groups in fibers and the analysis for the TEMPO oxidized pulps is presented in Fig. 2. Röhrling et al. (2002) reported a linear relationship between the carbonyl group content and copper number shown in Eq. 3. In this study, this

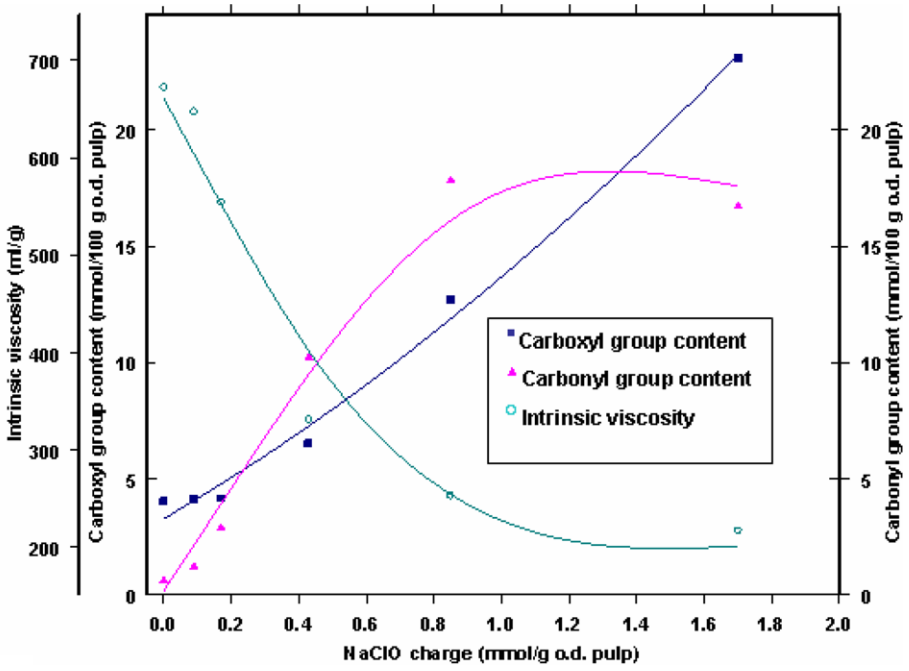

Fig. 2. Carboxyl group content, carbonyl group content, and intrinsic viscosity of ECF bleached SW kraft pulps prepared with varying NaClO charge on pulps during TEMPO-mediated oxidation.

equation was applied to convert $Cu^{\#}$ to carbonyl group content.

$$\text{Carbonyl group content (mmol/100 g o.d. pulp)} = (Cu^{\#} - 0.07)/0.6 \quad (3)$$

The aldehyde group is generated by oxidizing C6 hydroxyl group during TEMPO-mediated system. The results of carbonyl group content measurements are summarized in Fig. 2. This data shows that the aldehyde groups enhanced with increasing NaClO charge approaching a maximum value of 17.8 mmol/100 g o.d. pulp with NaClO charge of 0.85 mmol/g o.d. fibers. These results suggest that the TEMPO-oxidation process is not yet fully optimized for the formation of acid groups.

3.2. ^{13}C CP/MAS NMR spectra of the oxidized fibers

^{13}C CP/MAS NMR analysis of the starting and TEMPO oxidized pulp were recorded, and the crystallinity index was determined following a literature method (Lennholm, Larsson, & Iversen, 1994). As summarized in Table 1, these results indicate that there was a minor increase in the crystallinity for the oxidized fibers. This suggests that the amorphous regions in fiber are slightly more prone to oxidation.

3.3. SEM images of the oxidized fibers

Fig. 3 illustrates the SEM images of the original ECF bleached SW kraft pulp fibers and TEMPO-mediated oxidized pulps (NaClO charge of 1.70 mmol/g o.d. pulp). Fig. 3a provides a clear illustration of the primary wall of a fiber. The fibrils inside the fibers can be clearly seen from Fig. 3b. This result suggests that the primary wall or even the S1 sublayer, i.e. the outer layer of second wall, of the fibers were partially peeled by the alkaline TEMPO-mediated oxidation.

3.4. The effect of temperature during TEMPO-mediated oxidation on carboxyl group content and intrinsic viscosity of fibers

As discussed previously, hypochlorite degrades carbohydrates which results in the loss of fiber viscosity. Usually, hypochlorite bleaching of kraft pulps is limited to high alkalinity (pH ~ 10) and low temperature (Gullichsen & Fogelholm, 2000). To investigate the effect of reaction temperature on carboxylate content and fiber viscosity, the TEMPO-oxidation was conducted at varying reaction temperatures with a fixed charge of 0.85 mmol NaClO/g o.d. pulp (see Fig. 4). These results show that the carboxyl group content of SW bleached fibers reaches a maximum value at 23 °C. The intrinsic viscosity of fibers after TEMPO-oxidation at 23 °C was found to be the lowest.

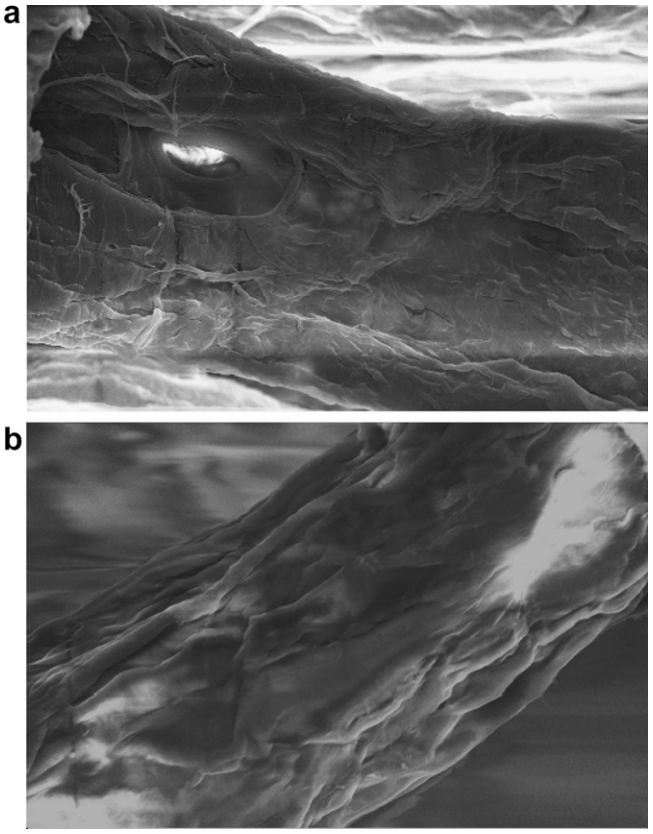

Fig. 3. (a) SEM image of original ECF bleached SW kraft pulp fibers. (b) SEM image of TEMPO-mediated oxidized ECF bleached SW kraft pulp fibers (1.70 mmol NaClO/g o.d. pulp charge).

3.5. The effect of pH value during TEMPO-mediated oxidation on carboxyl group content, carbonyl group content, and intrinsic viscosity of fibers

It's been reported that the solution pH value has an impact on the TEMPO-mediated oxidation with respect to the formation of carboxyl group and the reaction rate (Bragd et al., 2001). To evaluate this effect for SW bleached kraft pulp, five reaction pH values were examined including 7.10, 8.00, 8.60, 9.10, and 10.00. The remaining experimental conditions were kept constant including a 1.33% solution consistency, reaction temperature of 23 °C, 2.0 h reaction time, and 0.85 mmol NaClO/g o.d. pulp. Fig. 5 shows the results of carboxyl and carbonyl group content, and intrinsic viscosity of fibers after the ECF bleached SW kraft pulp was oxidized by the TEMPO-mediated system with 0.85 mmol NaClO/g o.d. pulp. In terms of the formation of carboxyl group content of fibers, the optimal result was obtained at pH 9.10. At this pH value, the carbonyl group content was the lowest, and the intrinsic viscosity was next to the highest value observed.

3.6. The effect of PEG addition on water retention value of fibers after TEMPO-mediated oxidation

Pulp water retention values characterize the swelling capability of pulps (Katz, Beatson, & Scallan, 1981). It is

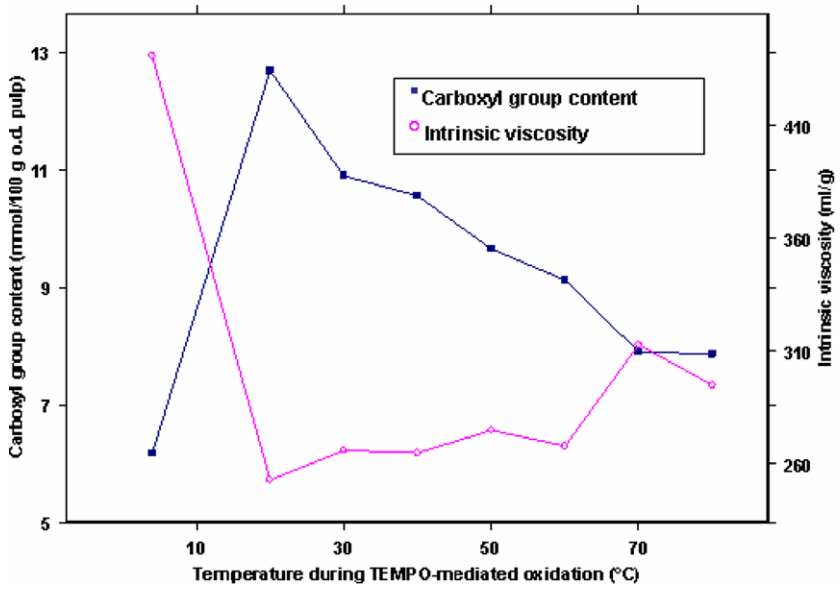

Fig. 4. The effect of temperature during TEMPO-mediated oxidation on carboxyl group content and intrinsic viscosity of ECF bleached SW kraft pulps at the condition of 0.85 mmol/g o.d. pulp NaClO charge.

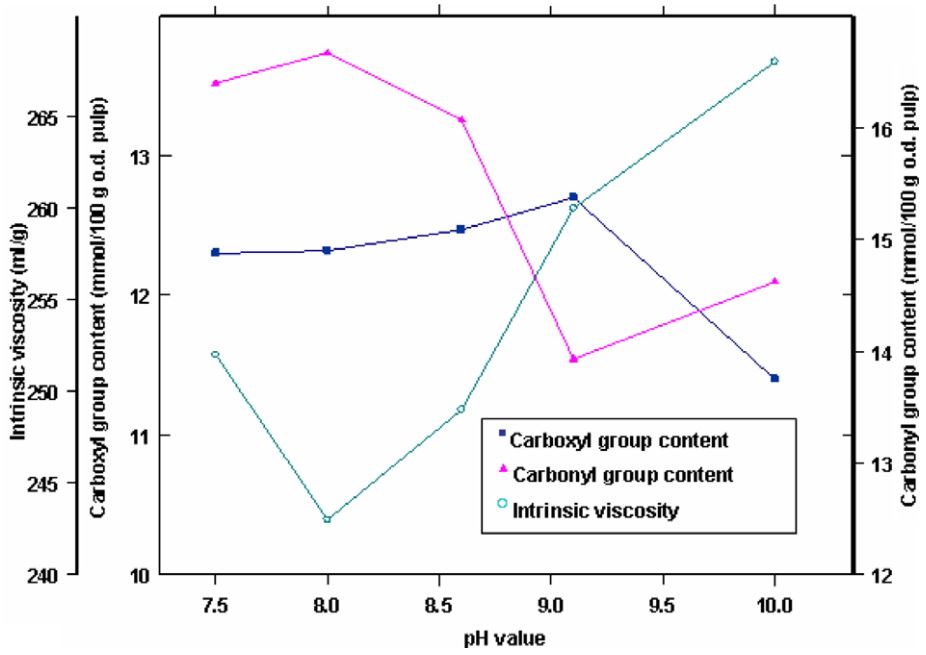

Fig. 5. The effect of pH value during TEMPO-mediated oxidation on carboxyl group content, carbonyl group content, and intrinsic viscosity of ECF bleached SW kraft pulps at the condition of 0.85 mmol/g o.d. pulp NaClO charge.

commonly acknowledged that enhanced fiber swelling relates to increased concentration of acid groups in the mechanical pulps (Katz et al., 1981; Katz & Scallan, 1983) and kraft pulp (Dang et al., 2006). In our previous study of the effect of carboxyl group content on WRV, it was found that there is a linear relationship between the carboxyl group content and WRV of the softwood kraft pulp (Dang et al., 2006).

PEG is widely used to cross-link pulp fibers to enhance the water absorbency property of fibers (Bajpai & Giri, 2002; Barcus & Bjorkquist, 1991). It has been reported that PEG-hydroxyl end groups can form ester cross-linking with cellulosic hydroxyl groups and carboxyl groups (Choi, 1993; Morris & Harper, 1995). Ibrahim, Abo-Shosha, Elnagdy, and Gaffar (2002) studied the addition of PEG in the citric acid treated cotton and reported that the carboxyl group content was decreased due to the esterification. The imparting of a more hydrophilic cross-linked structure leads to enhanced swellability of the cellulose structure and higher moisture absorption (Ibrahim et al., 2002). In addition, PEG treatment of textile fabric shows enhancement of the fabric properties including antistatic

Table 2
The results of water retention values of ECF bleached SW kraft pulps with and without cross-linking

Sample ID	Water retention value (g water/g o.d. pulp fibers)		
	Control	Cross-linked by PEG 3350	Cross-linked by PEG 10,000
Original ECF bleached SW pulp fibers	0.733	1.170	0.899
Oxidized fibers (0.85 mmol NaClO/g o.d. fiber)	1.194	1.410	1.230

behavior, wrinkle recovery, and abrasion resistance (Vigo & Bruno, 1989; Vigo, Lamb, Kepka, & Miller, 1991).

The glycols used in this study to cross-link fibers were PEG with a MW of 3350 and 10,000. The water retention values of the original ECF bleached SW kraft pulp, TEMPO oxidized, and PEG cross-linked pulps were studied. Table 2 summarizes the results of water retention studies.

The WRV of oxidized fibers is greater than that of the original fibers by 62.9%. This result indicates that, the higher value of carboxyl group content, the higher is the water retention value of the fibers. Kitaoka et al. (1999) studied the chemical modification of bleached hardwood kraft pulp fibers by TEMPO-mediated oxidation. They reported that WRVs of pulps were roughly constant, even though these pulps had carboxyl contents from 0.06 to 0.47 mmol/g after TEMPO-oxidation. In comparison, the softwood kraft pulps in this study present an enhanced water absorbency property after TEMPO-oxidation.

The WRV of fibers after PEG cross-linking was increased compared to the untreated fibers. This is consistent with the study by Barcus and Bjorkquist (1991). As for the original fibers, the WRVs were increased by 59.6% and 22.6% after cross-linking by PEG 3350 and 10,000, respectively. However, they increased by 18.1% and 3.0% when the oxidized fibers were cross-linked by PEG 3350 and 10,000, respectively. Based on the performance of PEG 3350 and PEG 10,000 on fibers, the low molecular weight polymer appears to provide enhanced improvement of fiber WRV.

3.7. The paper physical properties of fibers after TEMPO-mediated oxidation

Tensile and zero-span strength of the paper test sheets prepared from the two oxidized pulp samples described in Section 3.6 were measured. The results are summarized in Table 3.

Due to the higher carboxyl group content, the tensile strength of the paper test sheet prepared from the oxidized pulp fibers was higher than that of the original pulp fibers. Zero-span index indicates the average ultimate strength of the longitudinal structure of individual fibers in a paper test sheet. The zero-span strength of the oxidized pulp fibers was lower than that of the original pulp fibers. Since the TEMPO-mediated oxidation drastically drops the intrinsic viscosity, it leads to the lower single fiber strength.

Table 3
The results of paper physical properties of original ECF bleached SW kraft pulp fibers and oxidized fibers

Sample ID	Paper physical strength	
	Tensile index (N m/g)	Zero-span index (N m/g)
Original ECF bleached SW pulp fibers	26.8	119.7
Oxidized fibers (0.85 mmol NaOCl/g o.d. fiber)	30.5	99.3

4. Conclusion

This study demonstrates the potential of the TEMPO–KBr–NaClO system to oxidize ECF bleached SW kraft pulp fibers providing a 480% increase in carboxyl group at the charge of 1.701 mmol NaClO/g o.d. pulp. In addition, at this high oxidative charge the carbonyl group content (i.e., Cu #) of pulp was increased by a factor of 28. A comparison of the SEM images between the original fibers and the oxidized fibers indicated that the primary wall can be peeled by TEMPO-mediated oxidation. In terms of the carboxyl group formation of fibers after TEMPO-mediated oxidation, the optimum temperature and pH value were found to be around room temperature, and 9.10, respectively. Water retention value of the oxidized fibers had higher value than the original fibers. Fibers after PEG cross-linking showed increased water retention value. The zero-span strength of the paper test sheets prepared from the oxidized pulp fibers were lower than the original bleached pulp fibers due to oxidatively induced changes in the fibers.

Acknowledgements

The authors thank the Institute of Paper Science and Technology at Georgia Institute of Technology endowment fund and NSF (EEC-0332554) whose financial support made this work possible. We wish to express our appreciations to Dr. Nan Jiang in the School of Chemistry and Biochemistry and Dr. Runqing Ou in the School of Materials Science and Engineering at Georgia Tech for their suggestions on TEMPO-oxidation and SEM applications, respectively. This work will be used by Z.D. for partial fulfillment of the degree requirement for his doctoral research.

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