Selective TEMPO-Mediated Oxidation of Thermomechanical Pulp

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Carboxylic acid groups were introduced onto thermomechanical pulp (TMP) long fiber surfaces by 2,2,6,6,- tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation in the present study. The number of introduced carboxylic groups was closely related to the NaClO dosage, and more flexible fibers with lower curl and kink index were generated. Lignin was dissolved during the TEMPO-mediated oxidation, and its content was 24.2% with a carboxylic content of 1444 mmol/kg, in contrast to the control, which had 33.6%. Meanwhile, significant decreases in uncondensed lignin and β-O-4 lignin were observed during the TEMPO-mediated oxidation. The generation of carboxylic acid groups enhanced both the tensile and burst strengths of oxidized TMP significantly, and the value was 70% higher than the control with a carboxyl content of 1444 mmol/kg. However, side reactions during TEMPO-mediated oxidation led to a decline in intrinsic fiber strength, which may have contributed to the decline in paper tear strength.

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INTRODUCTION

Mechanical pulp, such as thermomechanical pulp (TMP), is characterized by its high bulk, high light-scattering coefficient, and low cost factors that have contributed to its widespread use within the papermaking industry (Hu *et al.* 2004). However, in contrast to bleached chemical pulp, the inter-fiber bonding capacity of mechanical pulp is quite poor (Law 2006). It is known that acidic groups can be generated during pulping and bleaching, and these acidic groups can increase fiber swelling and fiber-to-fiber bonding (Scallan 1983). Therefore, the introduction or generation of carboxylic acid groups on fiber surfaces, and within the cell walls of fibers (Sbiai *et al*. 2011), is a potential way to enhance paper strength. Past research in carbohydrate chemistry has indicated that acidic groups, such as carboxylic groups or aldehyde groups, can be generated by oxidizing cellulose primary alcohols. Recently, a 2,2,6,6-tetramethyl-piperidine-1-oxyl radical (TEMPO)-mediated oxidation system, which is composed of TEMPO, NaBr, and NaClO, was found to effectively convert the primary alcohols to carboxylic acid groups with high selectivity (de Nooy *et al.* 1995; Leroux *et al.* 2006). This TEMPO-mediated oxidation has recently been exploited to enhance the strength of bleached chemical pulp (Dang *et al.* 2007), deinked pulp (Leroux *et al.* 2007), and mechanical pulp (Law *et al.* 2007; Ma *et al.* 2010; Ma *et al.* 2012a).

The TMP refining process retains most of the lignin, resulting in very poor swelling capacity and inter-fiber bonding potential of the TMP fibers. In particular for

long TMP fibers, the inter-fiber bonding capacity is extremely poor due to its low specific surface area and scarcity of functional groups, contributing to low strength properties. Therefore, to widen the application of TMP in value-added products, it is necessary to enhance the quality of TMP, in particular for the long fiber fraction. In the present study, attempts to ameliorate the poor bonding capacity of TMP long fibers by means of TEMPO-mediated oxidation to create more carboxylic groups were made, and the fiber morphology and chemical composition of the TMP long fibers were also investigated.

EXPERIMENTAL

Materials

A low-freeness (~90 mL) TMP as a mixture of eastern Canadian spruce and balsam (70%:30%) was obtained from the Kruger paper mill in Trois-Rivières, Quebec, Canada. It was fractionated into long-fiber and short-fiber fractions by means of an unusual technique. More precisely, the sample pulp (25 g per batch, o.d. basis) was first disintegrated in a standard pulp disintegrator using hot water (~95 °C) for 5 min (~1.3% consistency), about 10 g (o.d. basis) of which was washed by dipping and shaking repeatedly in a bucket of water (~20 L) using a 20-cm–wide stainless steel kitchen strainer of ~22-mesh size. The washing, performed in batches, was continued until small fibers passed through the strainer. This process permitted us to recover all fines with less effort as compared with a Bauer McNett classifier. The long fibers (LF), fibers retained on the strainer, represented ~66%, while the short fibers (SF), fibers passed through the strainer, represented ~34%.

Methods

TEMPO-mediated oxidation of TMP long fibers

The TEMPO-mediated oxidation conditions are given in Table 1; the detailed procedures were similar to those described by Law *et al.* (2007). The experiment was conducted in a 2-L glass reactor at 21 °C. The long fibers of 30 g (o.d. basis) were first diluted to a 1.5% consistency in deionized water, to which a predetermined amount of 4-acetamido TEMPO, sodium bromide, and sodium hypochlorite were then added gradually.

Table 1. TEMPO-Mediated Oxidation Conditions of TMP Long Fibers

Exp. No.	Time (min)	Fiber (g)	TEMPO (g/30g fiber o.d)	NaBr (mmol/g fiber o.d)	NaClO (mmol/g fiber o.d)	Temp. (°C)	Carboxyl Content (mmol/kg. fiber o.d)
1	50	30	0.05	6	0.7	21	167
2	50	30	0.05	6	2.0	21	415
3	50	30	0.05	6	4.0	21	935
4	50	30	0.05	6	6.0	21	1272
5	50	30	0.05	6	8.0	21	1444

The pH of the system was maintained at 10.5 using a NaOH or an HCl solution. The pulp suspension was continuously agitated by means of an electric stirrer. At the end of the predetermined reaction time (50 min), the fibers were drained, washed, and filtered; then the pH of the fiber suspension was adjusted to 5.0. The pulp was again drained, washed, and filtered at least four more times prior to the measurement of the carboxylic content in accordance with the technique described by Katz *et al.* (1984).

Fiber morphology

The morphologies of TMP long fibers, including fiber length, curl index, and kink index, were determined using an Optest FQA (Fiber Quality Analyzer) in accordance with TAPPI T232 cm-01.

Water retention value (WRV)

The measurement of WRV was in accordance with the method described by Allender and Waterhouse (1986). A fiber mat was obtained onto a 100-mesh wire as 70 mL TMP slurry with 3.43% consistency was centrifuged at 2500 rpm for 20 min by Centra GP8 (Thermo Electron Corp.). This fiber mat was weighted before and after drying overnight at 105 °C, and the WRV was calculated as the following equation: $WRV = (W_1 - W_2)W_2$, where W_1 is the fiber mat weight before drying and W_2 is the fiber mat weight after drying.

Chemical composition

The holocellulose content of TMP long fibers was measured in accordance with TAPPI T249 om-00. Klason lignin and acid-soluble lignin contents were determined in accordance with TAPPI methods T222 om-02 and T13 wd-74, respectively. The sum of the Klason lignin and acid-soluble lignin was considered the total lignin content.

Nitrobenzene oxidation and ozonation

The lignin aromatic and side chain structures were analyzed by alkaline nitrobenzene oxidation (NO) and ozonation, respectively. NO was conducted according to the procedure described by Funaoka and Abe (1983), and ozonation was handled in accordance with the method of post-treatment protocol modified by Akiyama *et al.* (2002).

Scanning electron microscopy (SEM)

Handsheets used for SEM study were formed by a standard British handsheet former and couched with a standard roll, but without the standard pressing stage. The sheets were placed between drying rings and dried for 24 h in a conditioning room at 23 °C and 50% relative humidity. The surfaces of 1-cm-diameter samples were coated with gold palladium and examined using a JEOL SEM (model JSM-5500, JEOL, Tokyo, Japan).

Paper sheet properties

Standard handsheets of 60 g/m^2 for physical and optical properties analysis were prepared by means of a British sheet-mould according to PAPTAC Standard Testing Methods C.4 and C.5, respectively. The paper density was measured according to TAPPI T258 om-02. Tensile strength, burst strength, tear strength, and zero-span tensile strength were tested in accordance with TAPPI T404 wd-03, TAPPI T403 om-02, TAPPI T414 OM-98, and TAPPI T258 om-02, respectively.

RESULTS AND DISCUSSION

Fiber Morphology

Table 2 shows the fiber morphology properties of oxidized TMP long fibers. The fiber length was increased to 1.657 mm from 1.576 mm when the carboxyl content of the TMP long fibers was increased from 67.8 mmol/kg to 1444 mmol/kg. Meanwhile, the fiber curl index reduced to 0.023 from 0.063. Similarly, the fiber kink index declined to 0.24 mm^{-1} from 0.036 mm^{-1}. These phenomena reveal that the introduction of carboxylic groups on TMP long fibers was positive for fiber swelling, and it can be easily deduced that these more flexible fibers were beneficial in improving the inter-fiber bonding capacity.

Table 2. Fiber Morphology of TMP Long Fibers with Different Carboxyl Contents

Carboxyl Content mmol/kg	67.8	167	415	935	1272	1444
Mean length[a], mm	1.576	1.594	1.615	1.639	1.642	1.657
Mean curl[b]	0.063	0.035	0.029	0.026	0.024	0.023
Mean kink[c], mm^{-1}	0.36	0.34	0.32	0.29	0.26	0.24

[a,b,c], Length weight mean
The standard deviation of the mean length for oxidized TMP was 0.02 mm^{-1}
The standard deviation of the mean curl index for oxidized TMP was 0.05 mm
The standard deviation of the mean kink index for oxidized TMP was 0.002

Water Retention Value

The WRV of oxidized TMP long fibers are shown in Table 3. WRV reflects the capacity of the fibers to hold water, and generally, the higher WRV reveals the better swelling of the fibers. The WRV increased to 8.96 g/g from 1.40 g/g with the ascending carboxyl content from 67.8 mmol/g to 1444 mmol/g. More small internal pores were widened, and delaminations of microfibrils occurred with the rising WRV, which in turn generated more flexible fiber. The better swelling of the oxidized fibers with more acid groups provided the potential to give a stronger paper (Scallan 1983).

Table 3. WRV of TMP Long Fibers with Different Carboxyl Contents

Carboxyl Content mmol/kg	67.8	167	415	935	1272	1444
WRV, g/g	1.40	1.71	2.45	5.87	7.42	8.96

The standard deviation for WRV was 0.03 g/g

Chemical Composition

The variables of the TMP long fibers' chemical composition during TEMPO-mediated oxidation are shown in Fig. 1. TMP is rich in lignin, and the lignin content of the TMP decreased remarkably with increasing fiber carboxyl content (Fig. 1), which indicates that a large amount of lignin was degraded and dissolved from the cell wall and that a higher NaClO charge resulted in lower lignin content in the oxidized TMP (Sbiai *et al*. 2011; Ma *et al*. 2012b). NaClO alone could react with the lignin, and the addition of TEMPO-mediated oxidation system promoted the dissolution of lignin (Ma *et al*. 2012b). In turn, the removal of lignin during TEMPO-mediated oxidation led to higher holocellulose content with increasing carboxyl content, and it can be seen that the lignin removal

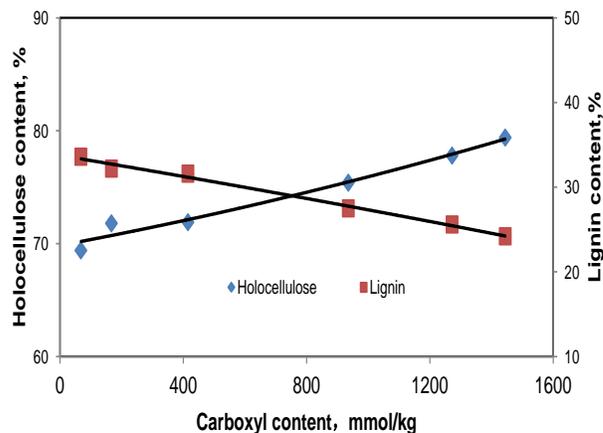during TEMPO-mediated oxidation was beneficial for inter-fiber bonding capacity as well.

Fig. 1. Holocellulose and lignin content of TMP fibers with different carboxyl contents

Lignin Structure

Different from previous TEMPO-mediated oxidation studies on chemical pulp, the lignin content of TMP is relatively high, and it was degraded during the TEMPO-mediated oxidation. Therefore, to better understand the influences of TEMPO-mediated oxidation on lignin, the lignin aromatic ring and side chain structures of oxidized TMP with different carboxyl contents were analyzed by nitrobenzene oxidation (NO) and ozonation, respectively; the changes in lignin structure are shown in Table 4. Interestingly, the NO yield decreased to 20.2% from 33.5% (untreated long fibers), which revealed that more lignin condensation took place during TEMPO-mediated oxidation, resulting in the significant drop in the NO yield. However, only a slight drop in the NO yield was observed when the carboxyl content increased from 935 mmol/kg to 1444 mmol/kg, which illustrated that no more lignin condensation occurred when the carboxyl content increased to some extent during TEMPO-mediated oxidation.

Table 4. Lignin Aromatic Ring and Side Chain Structures of TMP with Different Carboxyl Contents

Carboxyl Content, mmol/kg	Aromatic Ring	Lignin Side Chain	
	NO, %	E+T, %	E/T
67.8	33.5±0.5	20.1±0.4	1.07
935	20.2±0.4	16.0±0.3	0.75
1444	19.6±0.4	15.7±0.3	0.73

Similarly, lignin side chain structures varied during TEMPO-mediated oxidation. The total (E+T) of erythronic (E) and threonic acids (T) gives information about the total β-O-4 content, and E/T gives the erythro/threo ratio of β-O-4 structures (Fujimoto *et al.* 2005). The (E+T) and E/T of untreated long fibers were 20.1% and 1.07, and they declined to 16.0% and 0.75%, respectively, when the carboxyl content increased from 67.8 mmol/kg to 935 mmol/kg, which indicated that β-O-4 lignin was degraded during

TEMPO-mediated oxidation and that the etherified erythro β-O-4 structures were degraded more rapidly than the threo β-O-4 structures (Miksche 1972). Moreover, increasing the carboxyl content from 935 mmol/kg to 1444 mmol/kg did not generate noticeable changes in either (E+T) or E/T.

SEM

High-magnification observation by means of an SEM revealed that TEMPO-mediated oxidation somewhat modified the smoothness of the surfaces of the oxidized TMP long fibers. More pronounced ridges on the surfaces of the oxidized long fibers (Fig. 2B) were found in terms of number and dimension than on the control (Fig. 2A). These ridges might be induced by drying and subsequent transversal shrinkage of micro-fibrils in the S2 layer of the secondary cell wall (Law *et al.* 2007) and may be attributed to the dissolution of the degraded lignin and carbohydrates that existed in the fiber cell wall.
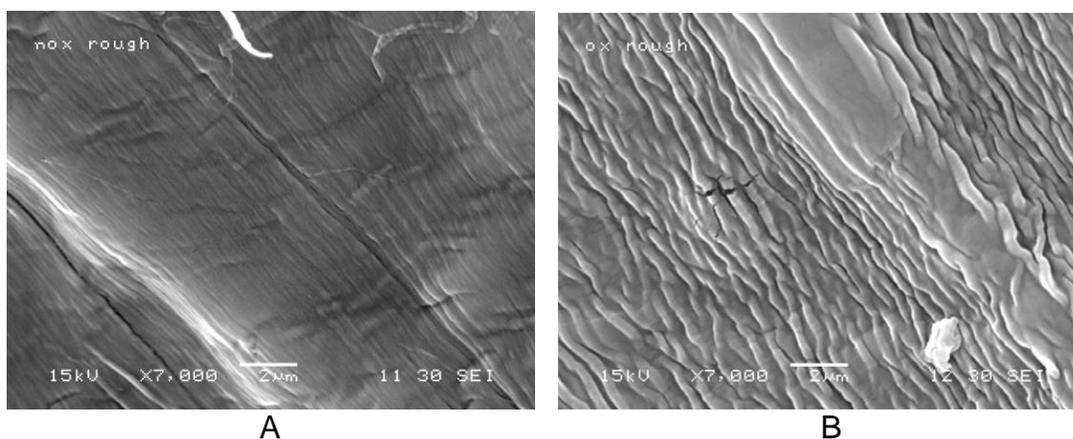

Fig. 2. Fiber surface of untreated (control) (A) and oxidized (B) TMP long fibers

Paper Strength

The effects of carboxyl content on TMP long fiber tensile and burst strengths are shown in Fig. 3. The increase in carboxyl content had a significantly positive influence on the paper tensile strength. The paper tensile index was 64.31 N*m/g when the carboxyl content was 1444 mmol/kg, which was 75.0% higher than that of the control (36.75 N*m/g).

The generation of carboxylic acid groups on TMP fibers resulted in more flexible fibers. This should be the key point for the enhancement of TMP fibers. Besides, the aldehyde groups generated by TEMPO-mediated oxidation can form hemiacetal linkages between fibers, and these hemiacetal linkages have been shown to be effective to improve the wet strength (Saito and Isogai 2006; Brodin and Theliander 2012). It is known that the chemical hemiacetal linkages could supply stronger bonding capacity as compared to the hydrogen bonding. Hence, it can be proposed that the aldehyde groups might also be positive for the enhancement of TMP handsheets. Similar to the trend of increased tensile strength, the increase in carboxyl content was also beneficial for burst strength. The paper burst index was 3.76 kPa*m^2/g when the carboxyl content of the oxidized TMP long fibers was 1444 mmol/kg, which was 70.1% higher than the control (2.21 kPa*m^2/g).
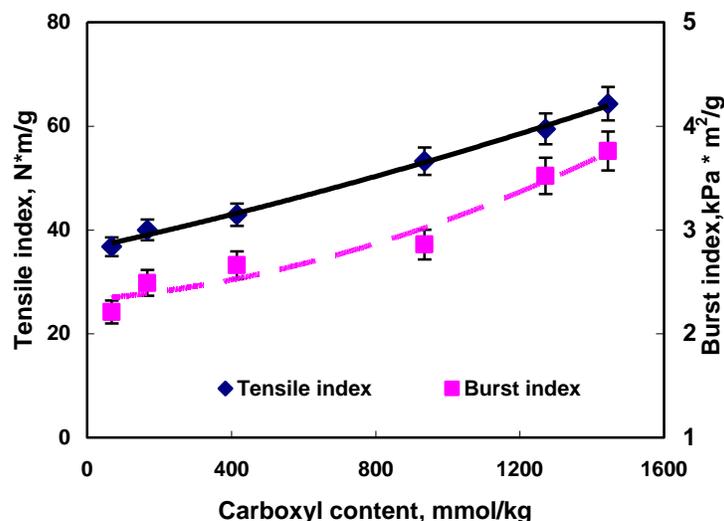
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Fig. 3. Effect of the carboxyl content of TMP long fibers on tensile and burst strengths

The relationship between paper density and tensile strength of oxidized TMP long fibers is shown in Fig. 4. The paper tensile strength of the oxidized TMP long fibers exhibited a close linear relationship with the paper density. This indicates that the higher carboxyl content was positive for generating more inter-fiber bonding areas and more contact points. In addition, the dissolution of lignin also provided more bonding areas between fibers, leading to higher paper density. This phenomenon should be responsible for the increase in paper tensile strength.
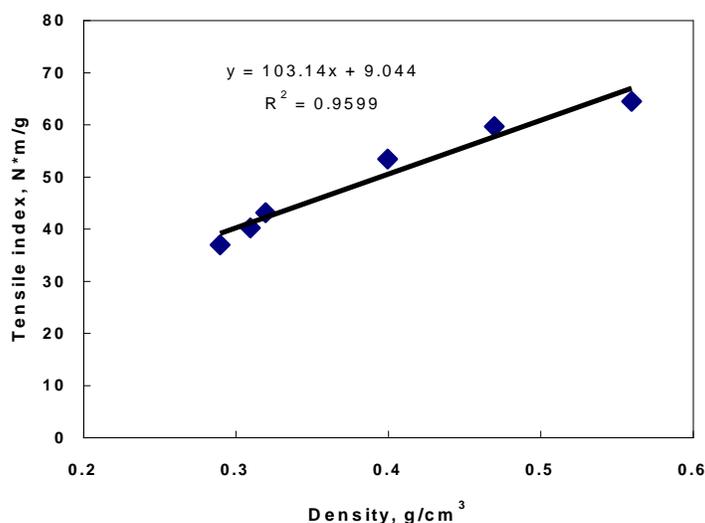

Fig. 4. Relationship between paper density and tensile strength for oxidized TMP long fibers

The effects of the carboxyl content on the TMP long fiber zero-span tensile and tear strengths are shown in Fig. 5. Zero-span tensile strength reflects the intrinsic fiber strength. As shown in Fig. 5, the zero-span tensile index decreased with an increasing number of carboxylic groups, which reflects the degradation of carbohydrates during TEMPO-mediated oxidation. The side reactions, such as β-elimination, could be responsible for the decrease in zero-span tensile strength (Shibata and Isogai 2003).
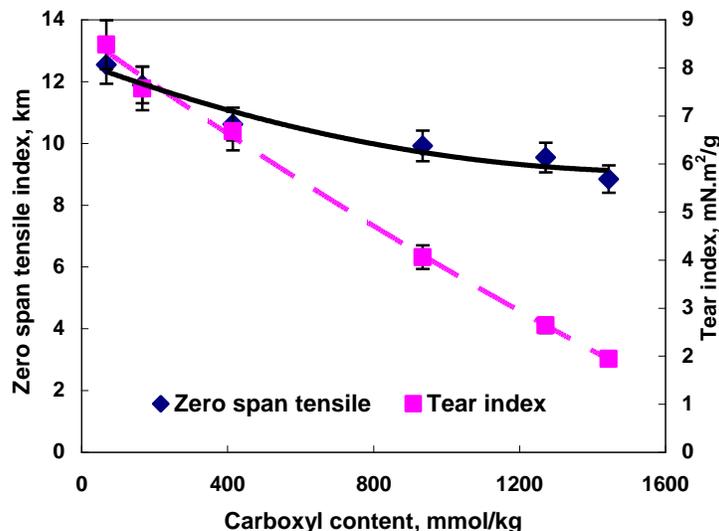
Fig. 5. Effect of carboxyl content on zero-span tensile strength and tear strength

In contrast to the tensile index, the tear index is directly related to the intrinsic fiber strength. Increasing carboxyl content resulted in a remarkable reduction of the paper tear index. Tear failure is primarily derived from the energy released when fibers fail, rather than when they are pulled out or when the bonds are broken, and a 10% loss in fiber strength can lead to a 25% to 30% loss in tear strength (Page 1994), which means that the drop in intrinsic fiber strength with increasing carboxyl content could lead to a significant decline in tear strength. In Fig. 5, the paper tear index was only 1.94 kPa*m^2/g when the carboxyl content of the oxidized TMP long fibers was 1444 mmol/kg; thus, the tear strength in the case of oxidation was only 22.9% of the value obtained for the control (8.48 kPa*m^2/g).

CONCLUSIONS

1. A large number of carboxylic groups were introduced onto oxidized TMP long fibers, facilitating the fibers' flexibility. Meanwhile, a rougher oxidized fiber surface was observed. The generation of carboxylic groups effectively enhanced the inter-fiber bonding capacity and resulted in a significant increase of the tensile and burst paper strength.

2. A portion of lignin in the TMP long fibers was degraded and dissolved during TEMPO-mediated oxidation, and more lignin was degraded as higher dosages of NaClO were applied. Both the uncondensed lignin and β-O-4 lignin contents declined with increased oxidation.

3. The selective TEMPO-mediated oxidation of TMP long fibers was an effective way to enhance paper strength. Both the paper tensile and burst strengths of oxidized fibers increased remarkably as carboxylic groups were introduced. However, the fiber intrinsic strength declined during TEMPO-mediated oxidation, resulting in a lower tear strength for oxidized TMP.

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