

INFLUENCE OF OXIDATION ON INTRINSIC FIBER STRENGTH

PU MA, KWEI-NAM LAW* and CLAUDE DANEALU*

*Jiangsu Provincial Key Laboratory of Pulp and Paper Science and Technology, Nanjing Forestry University, Nanjing 210037, China***Centre Intégré en Pâtes et Papiers, Université du Québec à Trois-Rivières, G9A 5H7, Canada*

Received August 6, 2009

The creation of carboxylic acid groups on fibers to improve the inter-fiber bonding potential by means of 4-acetamido TEMPO-mediated oxidation could influence intrinsic fiber strength. The effect of the conditions of such an oxidative process on the fiber strength of mechanical pulp fibers was examined. It was found out that the alkalinity and dose of NaBr had a particularly significant influence on intrinsic fiber strength, as measured by the zero-span tensile strength of the dry handsheets.

Keywords: TEMPO-mediated oxidation, thermo-mechanical pulp, intrinsic fiber strength, zero-span tensile strength

INTRODUCTION

The tensile strength of handsheets made from thermomechanical pulp (TMP) fibers can be greatly enhanced by creating carboxylic acid groups on the fiber surface through an oxidative process mediated by a free radical, 2,2,6,6-tetramethyl-1-piperidinyloxy (4-acetamidoTEMPO).¹⁻⁴ Further investigations raised concern over the influence of this oxidative treatment on the TMP fiber strength.⁵⁻⁶ To clarify this, the possible degradation of intrinsic fiber strength by TEMPO-mediated oxidation was examined and the results obtained were discussed.

EXPERIMENTAL**Material**

A low-freeness (~55 mL) TMP of a mixture of softwoods (mainly spruce and balsam fir), obtained from a local mill in Trois-Rivières, Québec, was divided into long- 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), and about 10 g (o.d. basis) of it 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. Washing, performed in batches, was continued until little fibers passed through the strainer. Such a process permitted the recovery of all fines with little effort, compared to that carried out with a Bauer McNett classifier. The long fibers (LF) retained on the strainer represented ~70%, while the short fibers (SF) passing through the strainer – ~30%.

Methods**Oxidation**

The oxidation conditions are given in Table 1 and the detailed procedures are similar to those described elsewhere.² Briefly, the experiment was conducted in a 2 L glass reactor at the required temperature (22 °C in trial A, C, D and 30 °C in trial B). The long fibers of 30 g (o.d. basis) were first diluted to 1.5% consistency in deionized water, to which predetermined amounts of 4-acetamido TEMPO, sodium bromide, sodium hypochlorite were then gradually added. The pH of the system was maintained at a stable level (pH 8 in trial A and B, 10.5 in trial C and D) using NaOH or HCl solutions, as depending on the situation. The pulp suspension was continuously shaken with an electric stirrer. At the end of the predetermined reaction time (50 min), the fibers were drained, washed and filtered, after which the pH of the fiber suspension was adjusted to 5.0. The pulp was again drained, washed and filtered for at least

four more times prior to the measurement of the carboxylic acid content.

Measurement of carboxylic acid content

The carboxylic acid content of all pulp samples was determined by a conductometric titration technique described elsewhere,⁷ on a Metrohm (Brinkmann) titrator and a conductivity meter (Thermo Orion, model 150). Briefly, the technique involved the use of a 3 g pulp sample (o.d. basis) which was first treated with 200 mL 0.1 M HCl for 45 min and thoroughly washed and filtered four times with 100 mL of deionized water. The washed specimen was again treated with 0.1 M HCl for 45 min and washed as described above. For titration, the filtered sample was suspended in 450 mL 0.001 M NaCl. The measurements of the carboxyl content, repeated twice, were computer-processed.

Measurement of total organic carbon

After oxidation, the treatment spent liquor was analyzed for the total organic carbon (TOC), on a Rosemount DC-190 TOC analyzer (Folio Instruments Inc.).

Measurement of Klason lignin content

The oxidized long TMP fibers were first extracted with dichloromethane, according to TAPPI method T204cm-97, and the Klason lignin content was determined following TAPPI method T222 om-02.

Measurement of handsheet properties

Standard handsheets of 60 g/m² were prepared and characterized in accordance with the PAPTAC (Pulp and Paper Technical Association of Canada) standard methods.

RESULTS AND DISCUSSION

As already stated, the main purpose of the present investigation was to study the influence of the oxidation conditions on intrinsic fiber strength. Usually, the measurement of viscosity is used to indicate fiber degradation during TEMPO-mediated oxidation. However, the viscosity of the TMP fiber is rather difficult to determine, due to the fiber high lignin content, compared to that of kraft pulp. In this situation, the zero-span tensile strength of dry TMP handsheets was applied as an indicator of fiber degradation brought about by the oxidative treatment. This property was plotted as a function of the chemical changes produced on the fiber, which were evaluated in terms of the carboxylic acid group content,

Klason lignin content and total organic carbon (TOC) of the spent liquor after oxidation. Since the intrinsic fiber strength affects the tensile and tear strength values of the handsheet, its relation with the latter was also graphically expressed. The molecular masses of the cellulose fractions and the hemicellulose contents of the oxidized fiber were also changed during oxidation. Unfortunately, the influence of the sugar fractions and of their contents on the properties of handsheets and on intrinsic fiber strength were not available at this moment, because of equipment failure.

The detailed oxidation plan was shown in Table 1; based on previous experiments, trial A was established as a reference, trial B represented the effect of temperature (30 vs. 22 °C for the reference), while trial C showed the influence of pH (10.5 vs. 8 for the reference). Trial D indicated the impact of the NaBr charge variation at high pH (10.5). The effects of these variations on the properties of both fiber and spent liquor are shown in Table 2.

Zero-span tensile – Carboxylic acid group content relation

The experimental results of this study and of previous works^{1-4,8,9} showed that the tensile index of the handsheets is positively and closely related to the carboxylic acid content of the treated fibers. In contrast, the zero-span tensile decreased with an increasing amount of carboxylic acid groups, as shown in Figure 1. Figure 1 also illustrates that the increase in temperature from 22 to 30 °C had an insignificant effect on the formation of the carboxylic acid group and on the zero-span tensile strength (trial A vs. trial B). On the other hand, an increase in pH from 8 to 10.5 brought about an additional substantial drop in the zero-span tensile, at a given carboxylic acid group content. This means that the alkalinity of the treatment liquor played a remarkable role in degrading the cell wall components and lowered to some extent the intrinsic fiber strength. It was observed that such degradation at high pH could be minimized by reducing the NaBr charge (trial D in Table 2), an improvement in the zero-span tensile thus resulting (*e.g.* trial D vs. trial C).

Zero-span tensile – Lignin content relation

It has been reported that, by TEMPO-oxidation, the lignin and hemicellulose components in the TMP can be removed as water-soluble fractions, which could affect the fiber properties.¹⁰ In the present study,

when the oxidative treatment was conducted at 22 °C and pH 8 (trial A), the oxidation at 30 °C and pH 8 (trial B) had little impact on lignin dissolution and, hence, showed no influence on the zero-span tensile, as evidenced in Figure 2.

Table 1
Conditions of TEMPO-mediated oxidation

Trial no.	Long fibers, g (o.d.)	TEMPO, g/30 g fiber (o.d.)	NaBr, mmol/g fiber (o.d.)	NaClO added, mmol/g fiber	Temperature, °C	Reaction time, min	pH
A	30	0.05	6	0.71; 1.88; 3.88; 5.88;	22	50	8
B	30	0.05	6	0.71; 1.88; 3.88; 5.88;	30	50	8
C	30	0.05	6	0.71; 1.88; 3.88; 5.88;	22	50	10.5
D	30	0.05	0; 3; 6	1.88	22	50	10.5

Table 2
Experimental results of TEMPO-mediated oxidation

Trial A, 22 °C, pH = 8					
NaClO added, mmol/g (o.d. fiber)	0.71	1.88	3.88	5.88	7.88
Carboxylic acid group content (mmol/kg)	115.2	253.0	566.3	814.6	897.3
TOC (ppm)	77.4	134.9	255.1	450.2	647.4
Klason lignin content (%)	26.2	25.9	22.6	18.1	13.9
Tensile index (N·m/g)	36.07	37.24	44.17	57.16	67.67
Tear index (kPa·m ² /g)	7.36	6.86	6.86	5.42	5.06
Zero-span tensile (km)	12.25	11.87	11.33	11.24	10.90
Trial B, 30 °C, pH = 8					
NaClO added, mmol/g (o.d. fiber)	0.71	1.88	3.88	5.88	7.88
Carboxylic acid group content (mmol/kg)	124.0	264.1	518.9	709.6	837.7
TOC (ppm)	71.2	150.5	301.3	459.2	587.6
Klason lignin content (%)	25.6	25.6	23.2	18.7	14.2
Tensile index (N·m/g)	39.15	41.33	45.62	59.45	65.23
Tear index (kPa·m ² /g)	7.08	6.66	6.45	5.42	4.67
Zero-span tensile (km)	12.12	11.57	11.25	11.30	10.90
Trial C, 22 °C, pH = 10.5					
NaClO added, mmol/g (o.d. fiber)	0.71	1.88	3.88	5.88	7.88
Carboxylic acid group content (mmol/kg)	166.9	415.0	935.2	1271.7	1444.2
TOC (ppm)	99.2	227	465	680.8	944.6
Klason lignin content (%)	24.9	24.1	20.5	15.4	11.2
Tensile index (N·m/g)	39.99	42.93	53.23	59.44	60.31
Tear index (kPa·m ² /g)	7.57	6.68	4.06	2.64	1.94

Zero-span tensile (km)	11.89	10.62	9.91	9.54	8.84
Trial D, 22 °C, pH = 10.5, NaClO charge = 1.88 mmol/g fiber (o.d.)					
NaBr dose, mmol/g (o.d. fiber)	0	3	6		
Carboxylic acid group content (mmol/kg)	197	404.7	415		
TOC (ppm)	140.2	202.4	227		
Klason lignin content (%)	24.4	24	24.1		
Tensile index (N·m/g)	41.05	41.40	42.93		
Tear index (kPa·m ² /g)	7.12	6.33	6.68		
Zero-span tensile (km)	12.64	11.34	10.62		

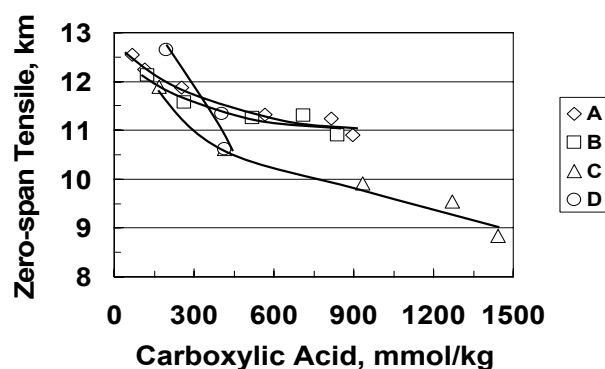


Figure 1: Zero-span tensile strength as a function of the carboxylic acid group content (trials A, B, C and D)

However, when the pH was raised to 10.5 (trial C), the degradation of lignin and of the cellulosic components were considerably accelerated, resulting in an additional substantial reduction in fiber strength at a given lignin content. The significant drop in zero-span tensile at pH 10.5, for a given lignin content, may signify that the cellulosic backbone in the cell wall was particularly affected. This means that high pH in TEMPO-mediated oxidation had an adverse effect on intrinsic fiber strength, although the carboxylic acid group content of the oxidized fibers increased with increasing pH.

Besides the creation of carboxylic acid groups on fibers, aldehyde groups were also introduced to the fibers.¹¹⁻¹³ Side reactions, especially β -elimination, which occurred on the aldehyde groups, could lead to the drop in the cellulose DPw, thus possibly weakening the fiber structure.¹⁴⁻¹⁵ Interestingly, the NaBr charge affects intrinsic fiber strength, as indicated in Figure 2 (trial D), which has not been reported before. It is known that a decrease in the NaBr charge might decrease the oxidation

rate and the formation of carboxylic acid and aldehyde groups.¹⁶⁻¹⁸ At a given reaction time, more aldehyde groups were produced when a higher NaBr charge was used. Meanwhile, more numerous β -elimination reactions occurred on the aldehyde groups when the oxidation reaction was ended within 50 min, a higher cellulose degradation and decreased intrinsic fiber strength thus resulting.

Zero-span tensile – TOC relation

TOC measurements reflect the dissolution of the cell wall components. As illustrated in Figure 3, the rise in temperature from 22 to 30 °C had little influence on both TOC and zero-span tensile. However, it was observed again that an increase in the alkalinity of the treatment liquor further degraded the wood components, weakening the fiber strength at a given TOC level. It is believed that most of the cellulose was not totally degraded to monosaccharide compounds, it still remained as a polysaccharide compound when the oxidation reaction was over, as it was not readily leachable under the experimental conditions employed.

Zero-span tensile – tensile index relation

Figure 4 shows that the tensile index is not directly correlated with the zero-span tensile strength, suggesting that the former is mainly associated with the availability of functional groups such as the carboxylic acid group.¹⁹ However, quite interestingly, the relationship between the tensile index and the carboxylic acid group content depends on the treatment conditions. For example, the fibers from trial B (Table 2, 30 °C, pH 8) had a lower carboxylic acid group content, yet showing a higher tensile index when compared to those of trial C (Table 2, 22 °C, pH 10.5). Again, this shows the adverse effect of using high alkalinity in oxidation, despite the lower temperature applied. The tensile strength of paper is related both to fiber strength and to inter-fiber bonding;²⁰⁻²¹ to attain a high tensile strength, high carboxylic acid groups should be obtained on the fiber surface, while minimizing the adverse effect of oxidation on intrinsic fiber strength. For a given tensile index, the zero-span tensile of the fiber is dependent on the

degradation degree of the cell wall components, particularly cellulose, which is the main structural backbone.

Zero-span tensile – tear index relation

In contrast to the tensile index, the tear index is directly related to intrinsic fiber strength, as shown in Figure 5, as the energy of tear failure is primary derived from the energy released when fibers fail rather than when they are pulled out or when the bonds are broken.²² The tear strength at a given tensile strength is proportional to the fiber strength with a ratio of 2.5/3.0, which means that a 10% loss in fiber strength can lead to a 25-30% loss in tear strength,²³ meaning that the zero-span tensile of the fiber has a significant effect on the tear index of paper made from oxidized fibers. However, for a given tear index, the zero-span tensile is dependent on the treatment conditions; low pH (*e.g.* 8) and low NaBr charge (*e.g.* < 6 mmol/g fiber) could better contribute to preserving fiber strength in 4-acetamido TEMPO-mediated oxidation.

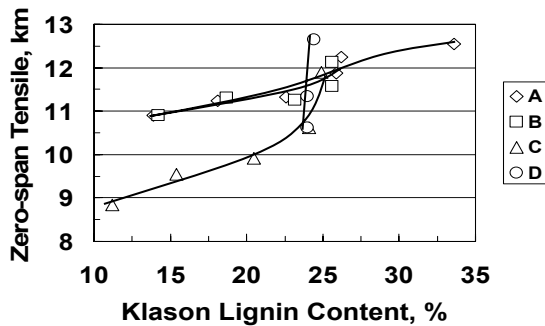


Figure 2: Zero-span tensile strength as a function of Klason lignin content (trials A, B, C and D)

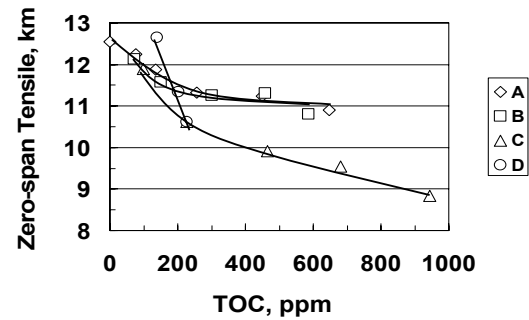


Figure 3: Zero-span tensile strength as a function of TOC (trials A, B, C and D)

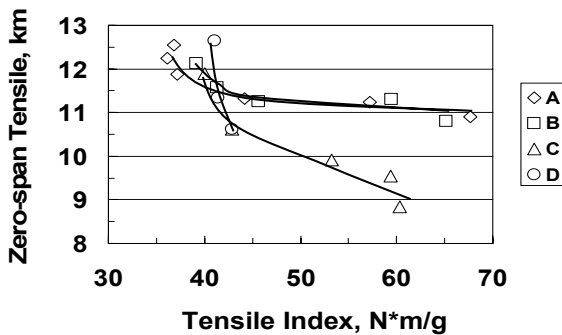


Figure 4: Zero-span tensile strength as a function of tensile index (trials A, B, C and D)

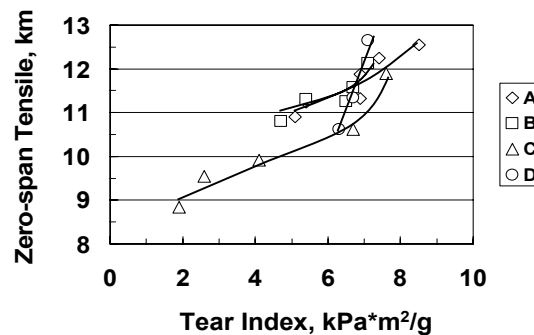


Figure 5: Zero-span tensile strength as a function of tear index (trials A, B, C and D)

CONCLUSIONS

Intrinsic fiber strength, expressed in terms of zero-span tensile strength of dry standard handsheets, is considerably affected by the conditions of oxidation, mediated by 4-acetamido TEMPO, particularly the alkalinity of the treatment liquor and the NaBr charge. Mild alkalinity and practically low NaBr dosage reduce the risk of severe degradation of cellulose and better preserve intrinsic fiber strength.

The tensile index of handsheets appears to be much more dependent on the carboxylic acid content rather than on intrinsic fiber strength, in contrast to the tear index which relies closely on intrinsic fiber strength.

ACKNOWLEDGEMENTS: The authors thank the Natural Science and Engineering Research Council of Canada for its financial support.

REFERENCES

- ¹ K. N. Law, C. Daneault and G. Guimond, *Cellulose Chem. Technol.*, **42**, 31 (2008).
- ² K. N. Law, L. S. Mao, F. Brouillette and C. Daneault, *Appita J.*, **62**, 119 (2009).
- ³ L. S. Mao, K. N. Law, C. Daneault and F. Brouillette, *Ind. Eng. Chem. Res.*, **47**, 3809 (2008).
- ⁴ Y. Han, K. N. Law, C. Daneault and R. Lanouette, *Tappi J.*, **7**, 13 (2008).
- ⁵ P. Ma, K. N. Law and C. Daneault, in *Procs. 95th Ann. Meeting*, Montreal, February, 2009, pp. 321-326.

- ⁶ P. Ma, K. N. Law and C. Daneault, (submitted for publication in *TAPPI J.*, March, 2009).
- ⁷ S. Katz, R. P. Beatson and A. M. Scallan, *Svensk Papperst.*, **87**, 48 (1984).
- ⁸ J. Le Roux, C. Daneault and B. Chabot, *Pulp Pap.-Canada*, **107**, 39 (2006).
- ⁹ Z. Dang, J. G. Zhang and A. J. Ragauskas, *Carbohydrate*, **70**, 310 (2007).
- ¹⁰ Y. Okita, T. Saito and A. Isogai, *Holzforschung*, **63**, 529 (2009).
- ¹¹ T. Saito and A. Isogai, *Colloid Surface A*, **289**, 219 (2006).
- ¹² T. Satio and A. Isogai, *Ind. Eng. Chem. Res.*, **46**, 773 (2007).
- ¹³ T. Saito, I. Shibata, A. Isogai, N. Suguri and N. Sumikawa, *Carbohyd. Polym.*, **61**, 414 (2005).
- ¹⁴ I. Shibata and A. Isogai, *Cellulose*, **10**, 151 (2003).
- ¹⁵ A. Potthast, A. Kostic, S. Schiehser, F. Liebner and T. Rosenau, in *Procs. 14th ISWFPC*, Durban, South Africa, July, 2007, pp. 82-87.
- ¹⁶ P. L. Bragd, A. C. Besemer and H. V. Bekkum, *Carbohyd. Res.*, **328**, 355 (2000).
- ¹⁷ B. Sun, C. J. Gu., J. H. Ma and B. R. Liang, *Cellulose*, **12**, 59 (2005).
- ¹⁸ L. S. Mao, K. N. Law, C. Daneault and F. Brouillette, *J. Pulp Pap. Sci.*, **34**, 198 (2008).
- ¹⁹ D. Barzyk, D. H. Page and A. Ragauskas, *Fundamentals of Papermaking Materials*, **2**, 893 (1997).
- ²⁰ D. H. Page and R. S. Seth, *Tappi J.*, **71**, 182 (1988).
- ²¹ D. H. Page, *Tappi J.*, **52**, 674 (1969).
- ²² D. H. Page, *Tappi J.*, **77**, 201 (1994).
- ²³ D. J. Page and J. M. MacLeod, *Tappi J.*, **75**, 172 (1992).