Treatment Levels of 4-Acetamido-TEMPO Oxidized Thermomechanical Pulp to Improve Paper Properties and Clay Retention

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TEMPO-oxidized thermomechanical pulp (TMP) prepared at low-oxidized and highly oxidized levels was compared with untreated TMP to observe the advantage of each pulp on paper properties. While the low oxidized pulp and non-oxidized pulp gave similar properties, highly oxidized TMP significantly increased tensile strength and decreased tear strength. Brightness was negatively affected by oxidation. In order to improve the paper optical properties, the use of a conventional mineral filler retention system was studied, using clay as filler. The high charge induced by the oxidized pulp significantly modified the pulp retention behavior. Moreover, paper made from pulp containing oxidized pulp and clay presented considerably better tensile strength with a loss in tear resistance for the same brightness target, which could be interesting for some paper applications.

Keywords: 4-Acetamido-TEMPO oxidation; Thermomechanical pulp; Paper properties; Mineral filler retention

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INTRODUCTION

2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) mediated oxidation was applied on thermomechanical pulp (TMP) for two main objectives. The first one was to improve TMP paper properties. After Kitaoka *et al.* (1999) had observed significant paper properties improvement with a carboxylic group content around 400 mmol/kg, Law *et al.* (2007, 2008) used TEMPO oxidation on TMP long fibers, which resulted in an increase in paper strength but a decrease in brightness. The second objective of TEMPO oxidation of thermomechanical pulp was to produce nanofibers. Okita *et al.* (2009) had obtained nanofibers from TMP, such as in the case of more conventional kraft oxidized pulp, but a higher amount of sodium hypochlorite was needed for the reaction to be efficient. More precisely, in a previous work (Myja *et al.* 2018) the authors found that a significant amount of lignin (at least 30%) must be removed to produce nanofibers. Le Roux *et al.* (2006) decided to combine these two objectives by blending highly oxidized TMP (carboxylic group content of 1500 mmol/kg) with non-oxidized pulp to produce paper. They found that an optimum amount of oxidized pulp could significantly increase paper strength. However, this cited study did not use low-oxidized TMP, which could additionally improve the paper properties. To further investigate the use of TEMPO oxidized pulps used as paper reinforcement, the present work considered various blends of non-oxidized TMP, low oxidized TMP (carboxylic group content around 280 mmol/kg), and highly oxidized TMP (around 2750 mmol/kg). Moreover, Saito and Isogai (2007), and Xhanari *et al.* (2011) have shown interesting effects of the surface carboxylic group, introduced by the TEMPO oxidation, with cationic polymers. In order to determine the true potential of oxidized pulp for high-value paper, mineral filler retention experiments were included in the present work to access the retention properties of theses pulps. Research has been done with different retention systems (Gess 1998), but one of the highest efficiency systems with thermomechanical pulp was shown to be a system with cationic coagulant and cationic flocculent (Hubbe *et al.* 2009). Therefore, this kind of system was used for the retention analysis of clay, one of the most used fillers in papermaking.

EXPERIMENTAL

Material

The thermomechanical pulp used in this study was a secondary unbleached softwood thermomechanical pulp purchased from Kruger S. E. C. (Trois-Rivières, Canada). Before any experiment, the pulp was further refined in a pilot refiner (Valmet CD300 refining system, Valmet, Espoo, Finland) to reduce the Canadian Standard Freeness (CSF) from 370 mL to 150 mL. The TEMPO oxidation was made with 4-acetamido-TEMPO purchased from Chemos (Regenstauf, Germany), sodium hypochlorite from Sigma-Aldrich (Oakville, Canada), and sodium bromide and hydrogen peroxide from Thermo Fisher Scientific Chemicals Inc. (Waltham, MA). The retention analysis was made using Alcofix 110 (polyDADMAC) as coagulant and Percol 292 (cationic polyacrylamide, C-PAM) as flocculent purchased from BASF (Suffolk, USA). Finally, the mineral filler used was kaolin clay acquired from Kruger S.E.C. (Trois-Rivières, Canada).

Methods

4-Acetamido-TEMPO oxidation

The TEMPO-mediated oxidation was performed in a 5 L glass reactor at 25 °C. The reaction was made on 30 g of dry pulp disintegrated in deionized water. The 4-acetamido-TEMPO and sodium bromide were first dissolved in water and then added to the pulp suspension. The total volume was adjusted to 3 L in order to have a consistency of 1%. The pH was then increased and controlled during the reaction to a fixed value of 10. The reaction began when the sodium hypochlorite was first added to the suspension. The sodium hypochlorite was poured with a constant flow for 45 min. After 60 min, the reaction was stopped by the addition of 100 mL of hydrogen peroxide at 1%. Chemical amounts were required to change from low to high oxidation and determined according to the authors previous research (Myja *et al.* 2018). Exact values are reported in Table 1.

Table 1. TEMPO-mediated Reaction Conditions for Low and High Oxidation

	Low Oxidation	High Oxidation
Mass of pulp (g)	30	
pH	10	
4-Acetamido-TEMPO (mmol/g)	0.055	0.45
Sodium bromide (mmol/g)	0.238	3.158
Sodium hypochlorite (mmol/g)	3.0	18.0

After the reaction, the pulp was filtered and washed a first time. Considering the large quantity of oxidized pulps needed in this study, TEMPO oxidation was performed many times. In order to have homogenous pulps along the study, all low oxidized pulps were mixed together and then washed and filtered a second time. The same procedure was done with highly oxidized pulp.

First experimental design: Paper composition optimization

The first experimental plan in this work was performed to access the effect of non-oxidized (NO), low oxidized (LO), and highly oxidized (HO) pulps on three paper properties: the tensile index, the tear index, and the ISO brightness. However, limits were fixed to define a study field. First, in order to conserve a significant amount of non-oxidized pulp, the lower limit was chosen at 30%. In addition, according to Le Roux *et al.* (2006), a decrease in paper strength was observed when 50% of highly oxidized pulp was introduced in paper. Thus, the high limit of highly oxidized pulp was fixed to 50%. The final mixture design was determined with the JMP Pro 14 software (SAS Institute Inc., Cary, NC, USA). The design finally contained 24 experiments dispersed in the studied field with 4 central points (Fig. 1).

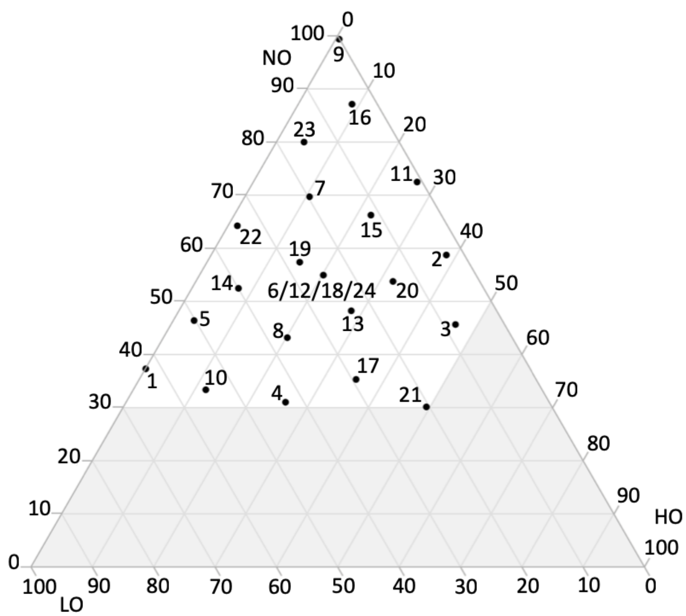

Fig. 1. Representation of the mixture design in a ternary diagram

Experimentally, pulps were mixed together during the pulp disintegration required by the TAPPI T205 sp-02 (2006) formation standard. Then, the TAPPI T571 om-03 (2006) and TAPPI T220 sp-01 (2001) methods were used to determine tensile and tear index and the ISO brightness.

Second experimental design: Pulp retention analysis

From the first experimental design and the analyzed results, several pulp mixtures were studied to observe the effect of each pulp on filler retention. Mixtures resulted in tensile and tear index values above 40 N·m/g and 9.5 mN·m^2/g, respectively, which are the usual strength values for newspaper. In addition, the choice was made to increase non-oxidized pulp for economic reasons. The retention analysis was performed in a Dynamic Drainage Jar (DDJ) or Britt Jar system with a 60-mesh screen at the bottom. First, the pulp was added to the Britt Jar at 0.5% consistency. Then, the stirrer was started at 1000 rpm, and the mineral filler poured. Twenty seconds later, the coagulant was introduced, followed by the flocculent after another 20 s. Finally, after 20 more seconds, the stirring was stopped, and the suspension started to recover. The first 50 mL were discarded, and the next 100 mL were filtered on ashless filter paper (Whatman grade 42). This method reduces polymer relaxation at fiber surface and better represents filler retention in real sheet formation (Chabot *et al*. 2004; Oulanti *et al*. 2009). The filter was initially put in a 100 °C oven overnight to determine the total first pass retention, then in a 900 °C furnace to determine the ash content according to the TAPPI T413 om-93 (1993) standard. From the suspension composition, ash content was considered as clay content.

The second experimental design was determined with the JMP Pro 14 software to observe mineral filler, coagulant, and flocculent amounts effect on total first pass retention and filler first pass retention. The conditions of testing are reported in Table 2. The experimental design was a uniform precision central composite design leading to 20 experiments with 6 central points.

Table 2. Secondary Experimental Design Factors Level

	a	-	0	+	A
Filler (%)	2.1	10.0	25.0	40.0	47.9
Coagulant (%)	0.02	0.05	0.10	0.15	0.18
Flocculent (%)	0.02	0.05	0.10	0.15	0.18

Paper properties with the mineral filler

To complete the mineral filler retention analysis, tensile index, tear index, and ISO brightness were measured for paper containing around 6.5% and 16% of mineral filler. Mineral filler, coagulant, and flocculent were added to pulp suspension before making handsheets according to the same procedure as for the previous retention analysis. For these tests, coagulant and flocculent amounts were fixed to 0.10% to keep the same conditions for all mixtures. This value is also in the typical range of use of retention aids (Hubbe *et al.* 2009). Mineral filler amount added to the suspension was adjusted to achieve the targeted amount of filler in paper handsheets. The paper analysis was made to the TAPPI standard previously given, and the mineral filler content in the paper was verified according to the previously given standard.

RESULTS AND DISCUSSION

Pulp Composition Effect on Paper Properties

Results and models obtained with the first experimental plan design are reported in Table 3. Models had a good R^2 without significant lack of fit, which means that experiments led to well defined models.

According to these models, non-oxidized and low oxidized pulp had similar effects on the paper. However, low oxidized pulp was slightly better for mechanical properties, while non-oxidized pulp was better for the paper brightness. These observations could be explained by the small morphological effect of low oxidation on pulp, while introduced carboxylic groups increased potential hydrogen bonding as observed by Lianshan *et al.* (2008). The more aggressive oxidation produced high carboxylic group content on the fibers but also decreased their intrinsic strength (Ma *et al.* 2009). These phenomena resulted in an increase in the tensile index, but a tear index decrease. The highly oxidized pulp was also harmful for the brightness. Le Roux *et al.* (2006) had seen the same effect while introducing the highly oxidized pulp in paper. In addition, the combination of low oxidized and highly oxidized pulp had the most beneficial effects on tensile strength. Comparing the tensile strength of non-oxidized/highly oxidized pulp mixtures to low oxidized/highly oxidized pulp mixtures, it was possible to affirm that highly oxidized pulp became better bonded to low oxidized pulp than non-oxidized pulp, probably due to carboxylic groups content and an increase of potential hydrogen bonding.

Table 3. Paper Properties Obtained for the First Experimental Design Tests and Resulting Models

Experimental design results				**Models parameters**			
Test	Tensile index (N·m/g)	Tear index (mN·m^2/g)	ISO brightness (%)	Term	Tensile index (N·m/g)	Tear index (mN·m^2/g)	ISO brightness (%)
1	33.5	11.6	47.2	(NO-30%)/70%	30.3	10.8	49.7
2	42.9	8.3	45.1	LO/70%	31.6	11.2	47.4
3	45.7	6.9	43.4	HO/70%	42.9	3.8	38.4
4	46.2	8.9	46.0	NO*LO	9.8	-0.8	0.5
5	35.6	10.5	48.0	NO*HO	26.3	6.0	3.1
6	42.5	10.2	47.1	LO*HO	43.7	4.0	9.8
7	38.1	10.7	48.0	R^2	0.97	0.89	0.92
8	42.1	9.6	47.4	Adjusted R^2	0.96	0.86	0.89
9	30.6	10.3	49.8	SS_{model}	566.0	27.9	63.6
10	39.0	10.5	48.0	$SS_{pure\ error}$	2.7	0.7	1.0
11	42.3	9.5	45.3	$SS_{lack\ of\ fit}$	15.3	2.7	4.5
12	41.2	9.3	46.4				
13	45.9	9.4	45.7				
14	37.2	10.6	48.0				
15	42.8	10.0	46.0				
16	34.8	10.9	49.1				
17	49.3	8.8	45.3				
18	43.6	10.2	47.6				
19	41.9	10.4	47.0				
20	46.6	8.9	46.0				
21	48.5	7.2	42.6				
22	34.5	10.1	48.9				
23	35.3	11.4	48.5				
24	42.5	9.5	47.6				

To find an optimum composition, a tensile index at 40 N·m/g and a tear index at 9.5 mN·m^2/g were targeted. These are usual mechanical strength values for newspaper. These two limits are represented in the mixture ternary diagram in Fig. 2. Several brightness values were added to see its evolution. According to the diagram, paper with tensile and tear strength higher than fixed limits could be obtained in a range mainly limited by highly oxidized pulp content from 11.5% to 27.5%. For further analysis, an optimum composition with non-oxidized, low oxidized, and highly oxidized pulp content respectively of 65%, 15%, and 20% (M1 on Fig. 2) was chosen. This proportion was selected because it maximizes non-oxidized pulp (easier to produce than oxidized pulps), and other mixtures around this point (M2 to M4) could be obtained for the mineral filler retention analysis. All these mixtures were compared to a pulp composed with only non-oxidized TMP (M0). Exact mixtures compositions are regrouped in the Table 4.

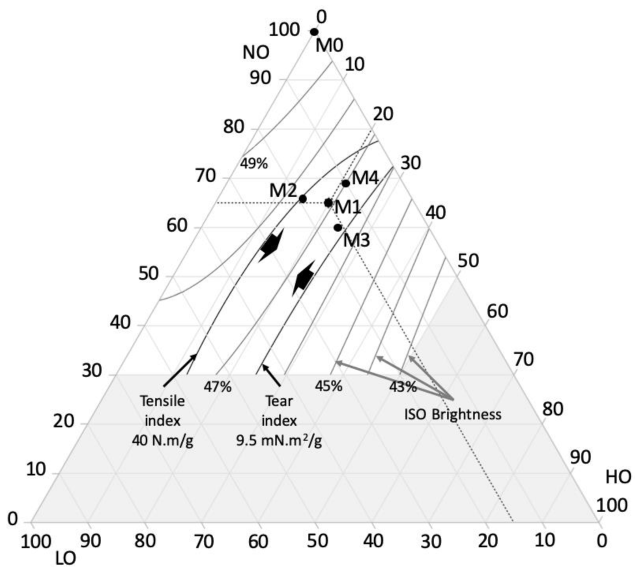

Fig. 2. Paper properties evolution with the paper composition to find an optimum mixture

Table 4. Pulp Compositions for the Mineral Retention Analysis

Pulp	NO (%)	LO (%)	HO (%)
M0	100	0	0
M1	65	15	20
M2	66	19	15
M3	60	16	24
M4	69	10	21

Effect of pulp composition on mineral filler retention

Total first pass retention and mineral filler first pass retention measured for each experiment of the experimental design for all pulps are reported in Table 5. With the experimental setup used, pulp composed with only non-oxidized pulp seemed to retain most of the clay. On the contrary, other pulps first pass retentions changed from one experiment to the other. Charges introduced by oxidized pulp had significantly affected the retention system. The main hypothesis that could be made to explain these results was a negative influence on the flocculation process.

To further understand the retention process, models obtained with a step-by-step method with a p-value of 0.05 are reported in Table 6. First, the total first pass retention model for M0 had a low R^2 due to the very small differences between results in the experimental design. In addition, total and mineral filler first pass retention for M0 were independent of mineral filler added. Thus, no matter the amount of mineral filler, the fiber flocculation was fast and retained the clay completely. On the contrary, retentions for mixtures containing oxidized pulp were significantly affected by the amount of clay introduced. However, the mineral filler content had lower impact on retentions when the pulp mixes contained a higher amount of non-oxidized pulp (M4).

Table 5. Total and Mineral Filler First Pass Retention Obtained for Each Design Experiments for All Pulps

	Total first pass retention (%)					Mineral filler first pass retention (%)				
Configuration	M0	M1	M2	M3	M4	M0	M1	M2	M3	M4
−−−	98	97	93	96	89	94	91	73	91	57
a00	100	88	98	97	97	100	72	77	91	82
−−+	100	95	97	97	95	100	84	85	88	78
000	97	88	90	92	88	97	72	73	80	70
0a0	96	92	90	87	89	92	75	72	68	72
++−	100	70	66	80	80	100	47	41	65	61
A00	100	62	57	62	59	100	45	33	43	38
0A0	99	87	94	92	89	100	67	77	80	69
00A	100	88	86	90	90	100	76	64	81	74
000	100	90	89	90	89	100	73	76	81	71
000	97	80	90	90	92	100	58	75	81	73
−++	98	96	95	96	97	100	87	83	89	83
000	99	84	86	87	91	100	65	66	73	73
−+−	100	88	95	96	96	100	63	80	84	79
+−+	100	69	72	82	79	99	47	52	70	62
+−−	94	50	71	64	80	93	22	48	38	60
+++	100	74	80	85	82	99	54	66	71	66
000	98	82	89	88	88	100	60	73	72	72
00a	100	77	87	87	88	99	47	70	68	69
000	100	80	91	83	88	100	54	75	62	70

Table 6. Models Obtained for Total and Mineral Filler First Pass Retention for All Mixtures

	Total first pass retention (%)					Mineral filler first pass retention (%)				
Term	M0	M1	M2	M3	M4	M0	M1	M2	M3	M4
Constant	98.8	84.6	89.1	89.1	89.9	99.6	63.0	72.4	73.8	71.7
Mineral Filler (MF)		-12.1	-12.1	-10.1	-9.0		-15.5	-14.3	-14.3	-9.1
Coagulant (Co)	0.8			2.0		2.0				
Flocculent (Fl)	0.5	3.6		2.3		1.0	7.4		4.7	
MF x Co				2.5						
MF x Fl				2.8						
Co x Fl	-1.3					-1.6				
MF^2		-4.4	-5.2	-3.3	-4.0			-7.0		-4.4
Co^2						-1.5				
R^2	0.44	0.80	0.92	0,92	0.87	0.87	0.70	0.84	0.74	0.65
Adjusted R^2	0.33	0.77	0.92	0.88	0.85	0.84	0.66	0.82	0.71	0.61
SS_{model}	0.24	22.18	21.53	16.26	12.02	1.09	37.29	31.24	28.78	12.53
$SS_{pure\ error}$	0.23	3.99	1.62	0.49	0.61	0.09	11.44	5.80	7.42	4.60
$SS_{lack\ of\ fit}$	0.08	1.44	0.14	0.94	1.21	0.06	4.92	0.64	2.81	2.22

Carboxylic group content, which induced negatives charges at the fibers surface, seemed to reduce the fiber flocculation process, leading to a lower mineral filler retention. Furthermore, the coagulant amount used had almost no significant effect for both total and mineral filler first pass retention in mixtures containing oxidized pulps. The coagulant could have two effects in the retention process. The coagulant could complex with anionic trash (as TMP fines) to improve their retention, or it could act as a site-blocker to improve the flocculent effect (Hubbe *et al.* 2009). The fact that no significant effect of coagulant was observed for most pulps could be explained by a very low content of anionic trash in the pulp and/or the high negative charges at fibers surface. The chosen addition level of coagulant seems to be not enough to saturate the fiber surface negative charges. The flocculent had mainly significant effects for mixtures containing high content of highly oxidized pulp. Another hypothesis could also explain this observation. The high content of anionic charges at the fiber surface due to the highly oxidized pulp content induced repulsion between fibers and reduced their abilities to flocculate. Adding a cationic flocculent allowed creation of bonds between fibers, improving fibers aggregations and then directly increased pulp retention behavior. This hypothesis was schematized in Fig. 3.

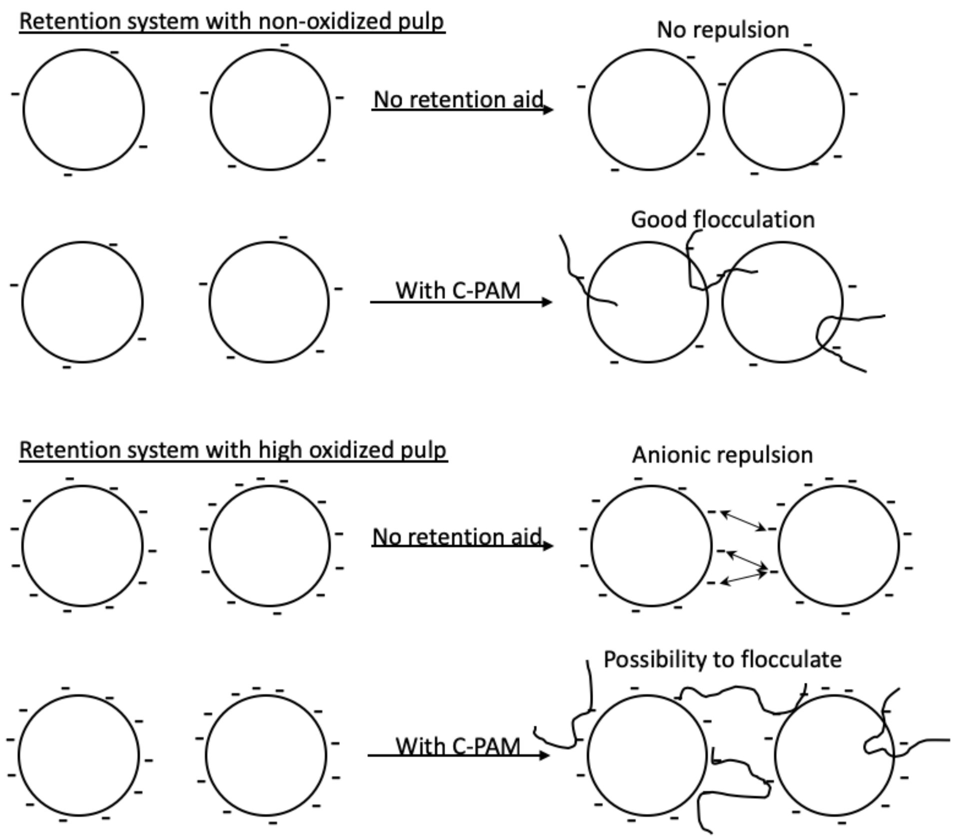

Fig. 3. Representation of the possible retention system for non-oxidized and highly oxidized pulp with and without cationic flocculent (C-PAM)

Paper properties with clay

In addition to the retention analysis, it was important to observe the properties of clay-containing papers. Tensile index, tear index, and ISO brightness of paper produced from pulps M0 to M4 containing around 6.5% and 16% of clay are reported in Fig. 4. In general, mixtures from oxidized pulp presented a better tensile resistance at the same ash content. Benefits of oxidized pulp remained during paper formation with the addition of clay. The tear resistance was lower for mixtures with oxidized pulp at low ash content. However, the tear resistance quickly decreased with the addition of clay for the non-oxidized pulp.

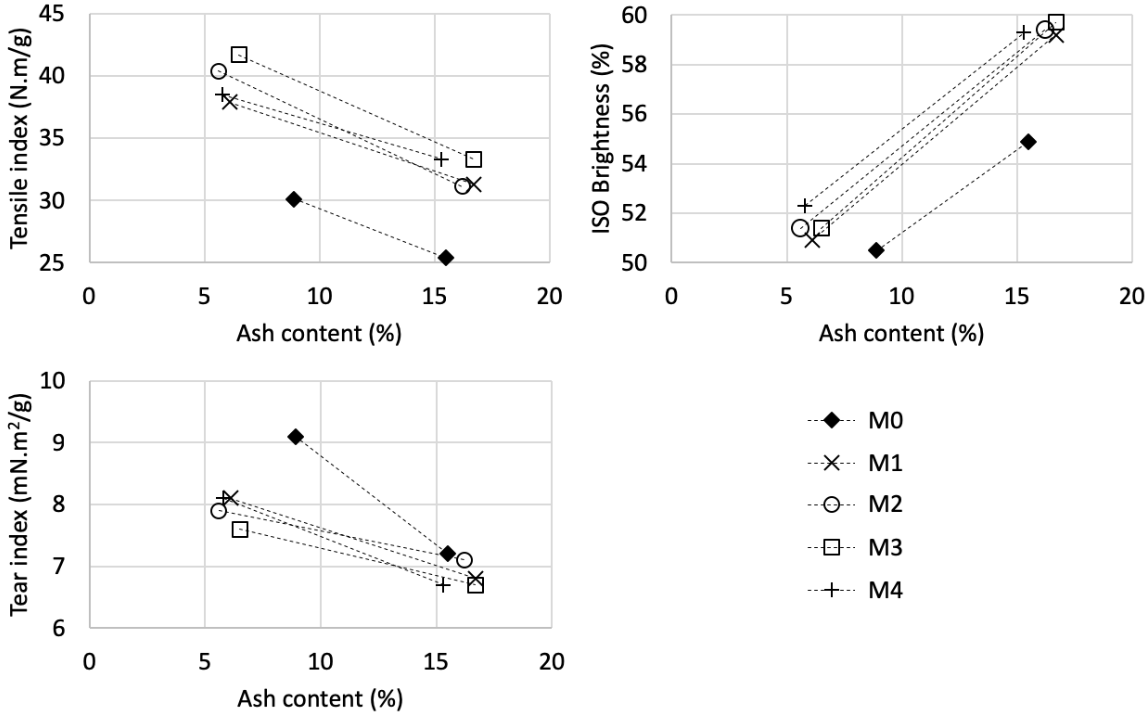

Fig. 4. Paper properties containing clay

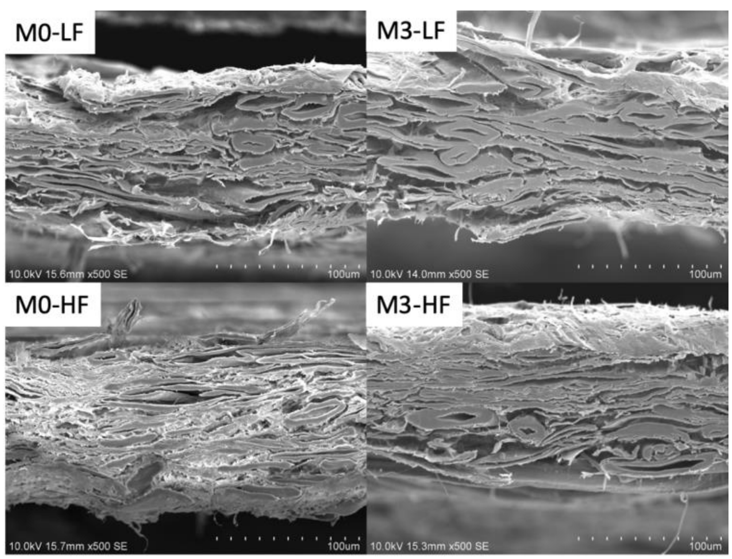

Fig. 5. SEM images of cross section sheets from mixes M0 and M3 at low filler content (LF) and high filler content (HF)

For a clay content higher than 15%, paper with oxidized pulps presented a same or better tear resistance. Finally, the addition of clay seemed to be a good way to counterbalance the harmful effect on brightness observed previously by the addition of oxidized pulp. Indeed, the ISO brightness values of papers were significantly higher for pulp with oxidized pulp compared to non-oxidized pulp. One hypothesis to explain these results could be in the sheet formation and related to floc formation. It was possible to consider that the high brightness was induced by a higher amount of clay at the paper surface. Therefore, it is supposed that oxidized pulp decreased the mineral filler retention, but that the clay was mainly at the paper surface. With non-oxidized pulp, the mineral was well retained but, due to fast flocculation, the clay was also in paper structure, which reduced the clay's overall beneficial effect on paper brightness. Further experiments are required to confirm this hypothesis. This hypothesis was confirmed with SEM images (Fig. 5) and EDX analysis (Fig. 6) on paper from mixes M0 and M3 at low and high filler content.

SEM images of sheets cross section made it possible to observe the clay distribution (bright white areas in images) inside the paper. For paper made only with non-oxidized pulp (M0), the filler was homogeneously distributed in the paper thickness. This phenomenon gives a lower impact on paper surface brightness, even at high filler content. On the contrary, mineral filler was mainly concentrated at the paper surface for sheets made with a mix of non-oxidized, low oxidized, and highly oxidized pulps. Therefore, for such pulps, a high brightness was found on the surface, while the inside fiber core was less affected by the fillers. These observations were also confirmed with EDX analysis by a silica and aluminum spectrum, which are two characteristic elements of clay. As aluminum and silica were observed in the whole thickness for mix M0. In paper from mix M3, these elements were also present in the whole paper but with a higher amount at the paper surface.

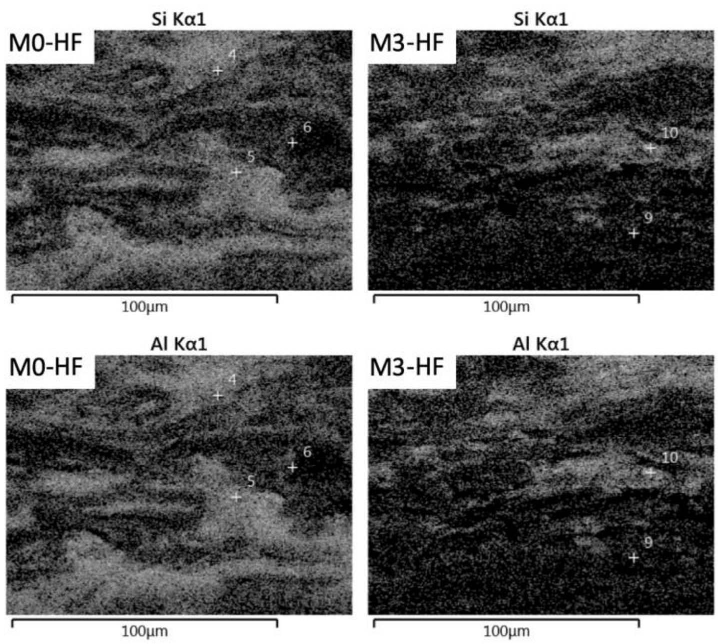

Fig. 6. Silica and aluminum mapping on cross section of sheets from mixes M0 and M3 at high filler content

To observe a beneficial effect of using oxidized pulp combined with a retention system of clay, it was possible to compare the mixture containing the highest content of oxidized pulp (M3) and low content of clay (6.5%) to the original thermomechanical pulp. Paper properties are reported in Table 7. The two compared pulps had closely the same brightness but the use of oxidized pulp with clay allowed a significant increase in the tensile index (+ 36%). However, the tear index was drastically decreased (-26%). This showed that depending on the final properties wanted from the final paper, the use of oxidized pulp could be interesting.

Table 7. Paper Properties Compared between Original TMP and a Mix Containing Oxidized Pulp (M3) and Clay

	Untreated TMP (Point 9 in Fig. 1)	M3 with 6.5% of clay
Tensile index (N·m/g)	30.6	41.7
Tear index (mN·m²/g)	10.3	7.6
ISO brightness (%)	49.8	51.4

CONCLUSIONS

1. The addition of 4-acetamido-TEMPO oxidized thermomechanical pulp to non-oxidized thermomechanical pulp for paper production was mainly beneficial for tensile strength. The low oxidized pulp had closely the same effect as the non-oxidized pulp, while the highly oxidized pulp significantly increased the tensile index but also induced a decrease of the tear index and ISO brightness.
2. The addition of clay to a pulp containing oxidized pulp made it possible, for a same brightness, to significantly increase paper tensile strength but decrease the energy consumed in tearing the paper.
3. The high charge surface content on the fiber of highly oxidized pulp decreased the global pulp capacity to flocculate and then, decrease the global pulp total first pass retention and mineral filler first pass retention. However, the mechanism of the retention system remained mostly unknown.

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REFERENCES CITED

Chabot, B., Daneault, C., Fournier, F., Morneau, D., and Arial, M. (2004). “A methodology to determine retention and drainage in laboratory,” *Paper and Timber* 86(6), 445-449.

Gess, J. M. (1998). *Retention of Fines and Fillers during Papermaking*, TAPPI Press, Atlanta, GA.

Hubbe, M. A., Nanko, H., and McNeal, M. R. (2009). "Retention aid polymer interactions with cellulosic surfaces and suspensions: A review," *BioResources* 4(2), 850-906. DOI: 10.15376/biores.4.2.850-906

Kitaoka, T., Isogai, A., and Onabe, F. (1999). "Chemical modification of pulp fibers by TEMPO-mediated oxidation," *Nordic Pulp and Paper Research Journal* 14(4), 279-284. DOI: 10.3183/npprj-1999-14-04-p279-284

Law, K., Daneault, C., and Guimond, R. (2007). "Enhancement of TMP long fibers," *Journal of Pulp and Paper Science* 33(3), 1-5.

Law, K.-N., Daneault, C., and Guimond, R. (2008). "TEMPO-mediated oxidation of

softwood thermomechanical pulp long fibers," *Cellulose Chemistry and Technology* 42(1), 31-36.
Le Roux, J., Daneault, C., and Chabot, B. (2006). "Acidic groups in TMP oxidized fibres by TEMPO to improve paper strength properties," *Pulp and Paper Canada* 107(4), 39-41.
Lianshan, M., Law, K.-N., Daneault, C., and Brouillette, F. (2008). "Effects of carbonyl content on the characteristics of TMP long fibers," *Industrial & Engineering Chemistry Research* 47(11), 3809-3812. DOI: 10.1021/ie071274z
Ma, P., Law, K.-N., and Daneault, C. (2009). "Influence of oxidation on intrinsic fiber strength," *Cellulose Chemistry and Technology* 43(9-10), 387-392.
Myja, D., Loranger, E., and Lanouette, R. (2018). "TEMPO mediated oxidation optimization on thermomechanical pulp for paper reinforcement and nanomaterial film production," *BioResources* 13(2), 4075-7092. DOI: 10.15376/biores.13.2.4075-7092
Okita, Y., Saito, T., and Isogai, A. (2009). "TEMPO-mediated oxidation of softwood thermomechanical pulp," *Holzforschung* 63(5), 529-535. DOI: 10.1515/HF.2009.096
Oulanti, O., Chabot, B., Brouillette, F., and Daneault, C. (2009). "Relaxation phenomenon effect of adsorbed polymer at fibre/water interfaces on the pulp fibre retention process," *Appita* 62(3), 201-207.
Saito, T., and Isogai, A. (2007). "Wet strength improvement of TEMPO-oxidized cellulose sheets prepared with cationic polymers," *Industrial and Engineering Chemistry Research* 46(3), 773-780. DOI: 10.1021/ie0611608
TAPPI T205 sp-02 (2006). "Forming handsheets for physical tests of pulp," TAPPI Press, Atlanta, GA.
TAPPI T220 sp-01 (2001). "Physical testing of pulp handsheets," TAPPI Press, Atlanta, GA.
TAPPIT413 om-93 (1993). "Ash in wood, pulp, paper and paperboard: combustion at 900 °C," TAPPI Press, Atlanta, GA.
TAPPI T571 om-03 (2006). "Diffuse brightness of paper and paperboard (d/0)," TAPPI Press, Atlanta, GA.
Xhanari, K., Syverud, K., Chinga-Carrasco, G., Paso, K., and Stenius, P. (2011). "Reduction of water wettability of nanofibrillated cellulose by adsorption of cationic surfactants," *Cellulose* 18(2), 257-270. DOI: 10.1007/s10570-010-9482-y

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