TEMPO Mediated Oxidation Optimization on Thermomechanical Pulp for Paper Reinforcement and Nanomaterial Film Production

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The 4-acetamido-TEMPO mediated oxidation system is well known on pure cellulose, but further investigation on more complex cellulose sources, such as thermomechanical pulp that is also composed of hemicelluloses and lignin, is needed. The reaction on wood pulp allows improvement in paper strength and nanofibril material production. However, the effects of the reaction parameters are not known enough to scale up the oxidation. With the help of two experimental designs, the chemical amounts, reaction temperature and time, sodium hypochlorite injection time, and nanofibril dispersion time were all studied. During the experiments, it was possible to observe pulp bleaching or delignification. Increasing the 4-acetamido-TEMPO amount promoted the pulp oxidation. In contrast, a large excess of sodium bromide and sodium hypochlorite was advantageous for pulp bleaching and delignification. High temperature favored the oxidation but delignification was induced by the oxidation. For the paper reinforcement, chemical amounts were optimized according to the end user needs. For nanomaterial production, both oxidation and delignification were needed. The reaction had to generate a significant delignification and increase pulp carboxyl content higher than 1600 mmol/kg to be able to produce nanofibril material. The results showed new leads on the various times required for future industrial implementation.

Keywords: 4-Acetamido-TEMPO; Conditions optimization; Paper strength; Nanofibril material

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INTRODUCTION

2,2,6,6-Tetramethylpyperidine-1-oxyl (TEMPO) or 4-acetamido-2,2,6,6-tetra-methylpyperidine-1-oxyl (aTEMPO) mediated oxidation has been long studied on polysaccharides (de Nooy *et al.* 1995; Bragd *et al.* 2001). The TEMPO or aTEMPO, sodium bromide (NaBr), and sodium hypochlorite (NaOCl) oxidation systems have about the same oxidative effect and are well known for oxidizing primary alcohols into aldehydes and ultimately to carboxyl groups (Okita *et al.* 2010; Isogai *et al.* 2011), thus introducing carboxylic groups on cellulose fibers. This oxidation is easily controllable to achieve low carboxyl content and best used as paper reinforcement (Ma *et al.* 2009, 2011), or a high carboxyl content, suitable for nanocellulose production (Saito *et al.* 2007; Fujisawa *et al.* 2011; Fukuzumi *et al.* 2013). Saito and Isogai (2004) started by studying the influence of reaction time and sodium hypochlorite amount on carboxyl content and cellulose polymerization degree. Saito *et al.* (2006) proposed a reaction scheme of the TEMPO-mediated oxidation on cellulose, and Iwamoto *et al.* (2010) even studied other TEMPO derivatives for the cellulose oxidation. However, most such studies have been mainly

focused on native cellulose. Only a few researchers have investigated the TEMPO-mediated oxidation effect on other cellulose sources such as thermomechanical pulp (TMP).

In addition to cellulose, TMP also contains various amounts of hemicelluloses and lignin. Okita *et al.* (2009) analyzed the composition of the softwood TMP before and after the TEMPO-mediated oxidation. Their results showed that pulp weight decrease is directly related to the dissolution of hemicelluloses and lignin in the reaction medium (water). Sodium hypochlorite is a well-known TMP bleaching agent that removes surface lignin. However, their results have shown a higher pulp weight decrease with the TEMPO oxidation than with a simple sodium hypochlorite bleaching. This observation was confirmed by Ma *et al.* (2012), who focused on the aTEMPO oxidation effect on lignin. The aTEMPO oxidation on TMP was found to be effective for paper reinforcement by increasing the tensile strength (Ma *et al.* 2011; Myja *et al.* 2016). Yet, the oxidation also brings about a decrease in the fiber intrinsic strength (Ma *et al.* 2009; Ma and Zhai 2013), which means that an optimization is needed to obtain the strongest paper possible. TEMPO-oxidized nanofibril production has also been investigated on mechanical pulp (Kuramae *et al.* 2014) and were a bit longer than cellulose nanofibrils.

In this paper, the authors have continued this effort to further understand the reaction on TMP with many aTEMPO oxidation conditions. First, an optimization for low oxidation conditions was made to increase conventional paper strength. A second optimization for high oxidation conditions was realized to observe nanofibril film properties. Both optimizations were undertaken as preliminary work in anticipation of a future scale-up, from laboratory to pilot plant scale, of TMP aTEMPO oxidation.

EXPERIMENTAL

Materials

The TEMPO-mediated oxidation was made on a secondary unbleached softwood thermomechanical pulp. The pulp was from Kruger S.E.C. (Trois-Rivières, Canada) and was refined to a Canadian Standard Freeness (CSF) of approximately 150 mL in the authors' research center pilot refining unit (Valmet CD300 refining system; Valmet, Espoo, Finland). The chemical, which were used as received, included sodium hypochlorite from Sigma-Aldrich (Oakville, Canada), aTEMPO for the reaction from Chemos (Regenstauf, Germany), sodium bromide from Thermo Fisher Scientific Chemicals Inc. (Ward Hill, USA), and hydrogen peroxide from Thermo Fisher Scientific Chemicals Inc. (Fair Lawn, USA).

Methods

TEMPO-mediated oxidation

As shown in Fig. 1, aTEMPO reactions were carried out in a 5-L glass reactor disposed in a thermostated bath. A conventional stirrer was used during the reaction at 260 rpm. A pH controlling system was also used with sodium hydroxide and hydrochloric acid buffer solutions at 0.1 M to maintain the pH at 10 at all times. Finally, a metering pump was used for sodium hypochlorite addition to the reactor.

For every oxidation, 30 g of dry pulp was used. The pulp was first disintegrated in deionized water at a consistency of 1.5%. At the same time, the needed mass of aTEMPO and sodium bromide were dissolved in a small amount of deionized water before their

addition. Pulp and chemicals were then introduced into the reactor, and deionized water was added to get the consistency of 1% in a 3-L final volume. The temperature and pH of the pulp were then adjusted. As sodium hypochlorite was mandatory for the aTEMPO system, the reaction time only started when the first drop was added. To stop the reaction after the required time, 100 mL of hydrogen peroxide of 3% concentration was poured into the reactor to neutralize the sodium hypochlorite excess. The oxidized pulp was then filtered, and all the recovered pulp was weighed. A small amount of the pulp was used to determine the pulp dryness to calculate the oxidation yield. Finally, the pulp was stored at 6 °C until further use.

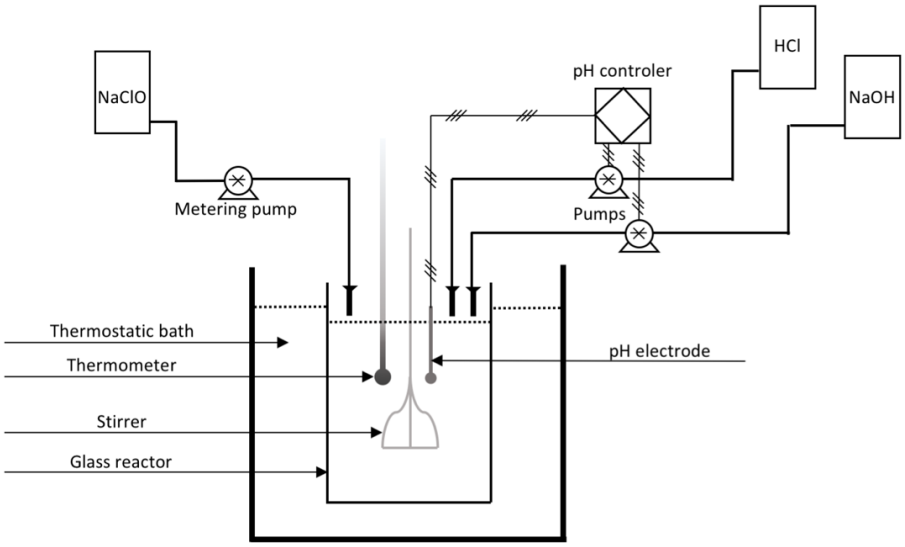

Fig. 1. aTEMPO mediated oxidation experimental setup

Handsheet preparation and testing

Pulp obtained after low oxidation was used to make handsheets according to the TAPPI T205 sp-02 (2006) standard. The ISO brightness was measured according to the TAPPI T571 om-03 (2006) standard, and the tensile and tear tests were made according to the TAPPI T220 sp-01 (2001) standard.

Carboxylic groups measurement

The carboxylic groups in the pulp after the oxidation were measured by conductimetric titration following Beatson's (1992) method. The pulp was first protonated twice with hydrochloric acid at 0.1 M during 40 min. After filtration and pulp washing with 1 L of deionized water, the pulp was added to 450 mL of salted water (10^{-3} M) prepared with sodium chloride. Then 10 mL of hydrochloric acid at 0.1 M was added before the titration with sodium hydroxide (0.1 M). The pulp carboxylic groups content could then be determined according to the titration curve.

Nanomaterial film preparation and testing

Pulp obtained after the high oxidation was used to make nanomaterial film. A mass of oxidized pulp corresponding to 1.5 g of dry pulp was dispersed in deionized water at 0.5% consistency with a household blender. Each film was made from 50 mL of the dispersion poured into a 10-cm diameter aluminum dish. The dishes were then placed in a

forced air enclosure for 48 h at room temperature. After this time, films can be recovered from the dishes without any apparent defects.

Films were then cut in 1.5-cm-wide strips for tensile testing with an Instron 4201 (Instron, Norwood, MA, USA) device at 10 mm/min. Those tests allowed the authors to measure the films' Young's modulus, tensile stress, and tensile strain at the breaking point. However, only the Young's modulus and the tensile strain results will be analyzed because of the strong correlation between Young's modulus and tensile stress. The light transmission through each film was measured with a Tint Meter Inspector (TM200; Laser Labs Inc., Scituate, MA, USA) that measured the light transmitted from a source to a receiver. This apparatus is normally used by police to evaluate tinted windows on cars.

Experimental design software and conditions

Both experimental designs were made and analyzed with JMP Pro 13 software (SAS Institute Inc., Cary, NC, USA). For each optimization, five factors were studied to observe potential interactions with a manageable number of tests. Both optimizations were made with a response surface design and, more precisely, a central composite design with uniform precision.

For the first optimization, chemical amounts (per g of dry pulp), reaction temperature, and reaction time were studied. For the second optimization, the chemical amounts were still studied for a high amount of sodium hypochlorite and low amount of aTEMPO and sodium bromide. The sodium bromide and sodium hypochlorite amounts were calculated with a ratio of aTEMPO. The second design allowed those ratios to be optimized. In addition, the sodium hypochlorite injection time and the dispersion time for nanomaterial film production were both studied. Such experimental testing will enable the authors to reduce secondary phenomenon at high sodium hypochlorite content, namely pulp bleaching, on TMP. The conditions and factor levels for both designs are given in Table 1.

Table 1. Oxidation Optimization Conditions and Factor Levels

First Optimization: Low Oxidation Fixed conditions: pH = 10; NaOCl injection time = 30 min					
	-1.608	-1	0	+1	+1.608
aTEMPO (mmol/g)	0.031	0.038	0.050	0.062	0.069
NaBr (mmol/g)	0.200	0.238	0.300	0.362	0.400
NaOCl (mmol/g)	2.000	2.378	3.000	3.622	4.000
Temperature (°C)	30.1	37.6	50.0	62.4	69.9
Reaction time (min)	60.0	71.3	90.0	108.7	120.0
Second Optimization: High Oxidation Fixed conditions: pH = 10; temperature = 25 °C; total reaction time = 60 min					
	-1.820	-1	0	+1	+1.820
aTEMPO (mmol/g)	0.027	0.150	0.300	0.450	0.573
NaBr ratio (× n_{aT})	1.4	3.0	5.0	7.0	8.6
NaOCl ratio (× n_{aT})	25.9	30.0	35.0	40.0	44.1
NaOCl injection time (min)	2.7	15.0	30.0	45.0	57.3
Dispersion time (min)	1.8	10.0	20.0	30.0	38.2

RESULTS AND DISCUSSION

Low Oxidation: Paper Reinforcement

Table 2 shows all of the conditions tested for the low oxidation optimization with the yield, handsheet tensile index, tear index, and ISO brightness obtained. The minimum and maximum of each response were also reported at the bottom of the table. The difference between each minimum and maximum was wide enough to consider that the modifications of aTEMPO oxidation conditions had a significant effect on final results.

Table 2. Tests and Results for the Low Oxidation Optimization

Trial	aTEMPO (mmol/g)	NaBr (mmol/g)	NaOCl (mmol/g)	Temp. (°C)	Time (min)	Yield (%)	Tensile Index (N•m/g)	Tear Index ($mN•m^2/g$)	ISO Bright. (%)
18	0.031	0.300	3.000	50.0	90.0	95	41.3	9.1	57.2
12	0.038	0.238	2.378	37.6	71.3	94	37.3	9.2	54.9
3	0.038	0.238	2.378	62.4	108.7	97	39.7	8.7	51.6
27	0.038	0.238	3.622	37.6	108.7	98	40.7	8.4	60.4
9	0.038	0.238	3.622	62.4	71.3	93	47.8	8.1	59.3
22	0.038	0.362	2.378	37.6	108.7	98	37.2	9.1	50.8
2	0.038	0.362	2.378	62.4	71.3	95	38.7	9.0	49.6
10	0.038	0.362	3.622	37.6	71.3	87	39.2	8.2	56.7
11	0.038	0.362	3.622	62.4	108.7	94	41.1	7.3	50.2
29	0.050	0.200	3.000	50.0	90.0	93	39.3	8.9	61.1
17	0.050	0.300	2.000	50.0	90.0	96	37.1	8.5	49.3
20	0.050	0.300	3.000	30.1	90.0	99	45.4	9.7	55.0
23	0.050	0.300	3.000	50.0	60.0	94	38.3	8.6	58.0
14	0.050	0.300	3.000	50.0	90.0	98	39.2	8.5	52.2
16	0.050	0.300	3.000	50.0	90.0	96	38.0	8.5	55.4
25	0.050	0.300	3.000	50.0	90.0	94	37.1	8.4	55.9
26	0.050	0.300	3.000	50.0	90.0	98	38.0	8.0	53.6
28	0.050	0.300	3.000	50.0	90.0	96	38.5	8.5	55.1
30	0.050	0.300	3.000	50.0	90.0	98	37.6	8.2	53.4
21	0.050	0.300	3.000	50.0	120.0	94	39.1	7.6	54.4
19	0.050	0.300	3.000	69.9	90.0	95	43.1	8.2	45.5
31	0.050	0.300	4.000	50.0	90.0	96	41.4	7.0	61.1
32	0.050	0.400	3.000	50.0	90.0	92	38.5	8.3	50.4
8	0.062	0.238	2.378	37.6	108.7	94	37.7	9.2	56.7
4	0.062	0.238	2.378	62.4	71.3	94	39.3	9.6	53.7
15	0.062	0.238	3.622	37.6	71.3	100	38.3	8.3	59.2
5	0.062	0.238	3.622	62.4	108.7	90	46.9	8.5	53.7
1	0.062	0.362	2.378	37.6	71.3	100	38.6	9.1	49.0
6	0.062	0.362	2.378	62.4	108.7	92	41.7	8.6	39.7
24	0.062	0.362	3.622	37.6	108.7	97	37.1	8.3	57.1
7	0.062	0.362	3.622	62.4	71.3	92	40.6	7.3	52.4
13	0.069	0.300	3.000	50.0	90.0	96	37.2	7.9	54.3
Min	0.031	0.200	2.000	30.1	60.0	87	37.1	7.0	39.7
Max	0.068	0.400	4.000	69.9	120.0	100	47.8	9.7	61.1

To analyze all of those results, models were calculated by the step-by-step method with a p-value of 0.05. The estimated coefficient and a summary of some statistics are reported in Table 3 for each response model.

Table 3. Estimated Coefficient and Adjustment Information for a Model with a Significant Probability at 95% for the Low Oxidation Optimization

Term	Initial Tensile Index (N•m/g)	Yield (%)	Tensile Index (N•m/g)	Tear Index ($mN•m^2/g$)	ISO Brightness (%)
Constant	38.4	96.1	38.8	8.3	55.2
aTEMPO	-	0.2*	-0.4*	-	-0.8
NaBr	-0.7*	-0.3*	-0.7	-0.2	-2.9
NaOCl	1.3	-0.6*	1.3	-0.5	2.9
Temperature	1.2	-1.3	1.7	-0.2	-2.4
Reaction time	-	0.2*	0.2*	-	-1.0
aTEMPO × NaOCl	-	-	-0,6	-	-
aTEMPO × Temperature	-	-1.6	-	-	-0.7
aTEMPO × Reaction time	-	-1.9	0.7	-	-
NaBr × NaOCl	-1.1	-1.1	-1.1	-	0.7
NaBr × Temperature	-	-	-0.6	-	-
NaOCl × Temperature	-	-	0.8	-	-
Temperature × Reaction time	-	-	-	-	-1.6
$NaBr^2$	-	-1.4	-	-	-
$Temperature^2$	1.9	-	1.1	0.3	- 1.8
R^2	0.67	0.76	0.90	0.68	0.94
Adjusted R^2	0.60	0.67	0.84	0.63	0.92
SS_{model}	158.35	194.31	183.8	8.29	612.65
$SS_{pure\ error}$	24.90	13.33	2.6	2.18	10.11
$SS_{lack\ of\ fit}$	54.39°	46.57	17.9	1.79	26.46

* Not significant at 95%, but term included in interactions; ° Significant lack of fit

An initial model was calculated for the tensile index with all the experiments, but an important lack of fit was observed for this model. The authors' investigation has identified the tensile index value obtained from trial number 20 as responsible for this lack of fit. That test condition had an extreme level of temperature that was not repeated elsewhere in the experimental design. To achieve a valid model, other calculations were made only for the tensile index by excluding trial 20. The estimated coefficients of both tensile index models were nearly the same, but the statistics of the second model were far better. The corrected tensile index model was used for the results analysis reported here.

According to the calculated models, temperature was an important condition in aTEMPO oxidation for paper reinforcement. It had a significant effect on each studied response, a significant interaction with all other conditions for at least one response, and a quadratic effect on all paper properties. As explained previously, the aTEMPO oxidation on TMP is in competition with pulp bleaching, and both phenomena are influenced by the temperature (Sain *et al.* 1997; Sun *et al.* 2005). For the same reason, the sodium hypochlorite amount had significant effects and interactions on all responses, but more so on paper properties. The aTEMPO and sodium bromide amounts have naturally significant effects on the responses because they are directly linked to the aTEMPO oxidation kinetic (Sain *et al.* 1997). Finally, the reaction time did not have an important impact on responses in comparison to the other conditions. Ma *et al.* (2012) showed that increasing the reaction time should increase the fiber delignification. However, the time variation in the

experimental design did not allow the authors to observe such a delignification effect. This was mainly related to the long time period used.

To optimize the TEMPO oxidation conditions, the condition effects on each response are represented in Fig. 2. The reaction time had a rather small impact on paper properties, so it will be kept to the lower value studied. This decision was made with industrial implementation in mind, where a low reaction time can be more beneficial. At this point, other conditions cannot be fixed because of their important impact and interactions between them. However, a few observations can be made with respect to Fig. 2. Increasing the aTEMPO amount at fixed sodium bromide and sodium hypochlorite increased the oxidation yield, but it also reduced the tensile index and ISO brightness, which was expected because a high aTEMPO content helped the sodium hypochlorite be used more for the aTEMPO oxidation rather than for fiber delignification. The same observation was made for sodium bromide, but a large excess led to an excess of sodium hypobromite.

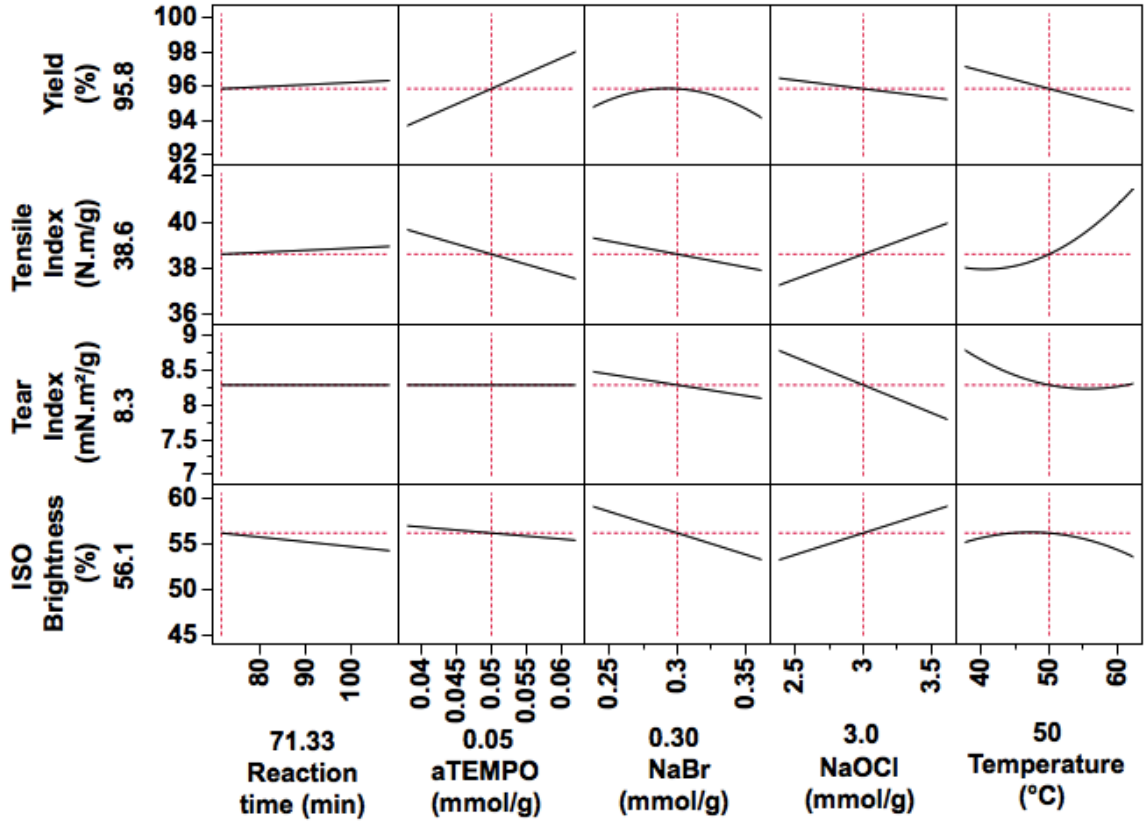

Fig. 2. Representation of condition effects on each response for the low oxidation optimization

Usually, the sodium hypobromite activates the aTEMPO to oxidize the fibers selectively (Saito *et al.* 2006), but sodium hypobromite is an oxidant and could oxidize fibers directly, as observed from the decreasing yield at high sodium bromide amounts. As mentioned previously, an excess of sodium hypochlorite induced a higher bleaching effect, which promoted pulp delignification. Delignification has consequences, such as a drop in reaction yield, an increase in tensile strength from better fiber-to-fiber bonds, and a decrease in the fibers' intrinsic strength, which induce overall tear strength decrease.

Finally, the temperature presents an optimum value at approximately 47 °C for ISO brightness. This temperature is in the lower range of known values for pulp bleaching (Sain *et al.* 1997). However, the temperature had many interactions with other conditions, so it was the last condition optimized.

An important observation for the optimization was the interaction between sodium bromide and sodium hypochlorite. However, any optimum value could be fixed for the aTEMPO amount, which is why the interaction was studied for different aTEMPO amounts.

Figures 3, 4, and 5 present isoresponse profiles of tensile and tear index, yield, and ISO brightness according to sodium bromide and sodium hypochlorite at various aTEMPO quantities. As expected, the tensile strength and ISO brightness increased with a high sodium hypochlorite and a low sodium bromide content, because the sodium hypochlorite bleaching was responsible for this effect. In contrast, increasing the sodium bromide and decreasing sodium hypochlorite favored the oxidation over bleaching. This condition induced a yield increase, but it induced a drop in tensile and brightness as well. The tear index was negatively affected by both bleaching and oxidation because of the decrease in the fibers' intrinsic strength.

The highest tear strength was obtained at low chemical amounts. Moreover, the tear strength decrease was smaller due to increased sodium bromide rather than sodium hypochlorite. This meant that bleaching was more harmful to fiber intrinsic strength than aTEMPO oxidation. In the same way, increasing the aTEMPO amount resulted in a decrease of tensile index and brightness in favor of a yield with no impact on tear strength. However, for all aTEMPO levels, the same point could be chosen as an optimum of tensile and tear index with a good brightness value and without a huge decrease in yield. The chosen point was at 0.24 mmol/g of sodium bromide and 2.95 mmol/g for sodium hypochlorite. Depending on what is preferable for the end user, it was possible to adapt the aTEMPO amount to increase either the tensile strength and brightness or treatment yield.

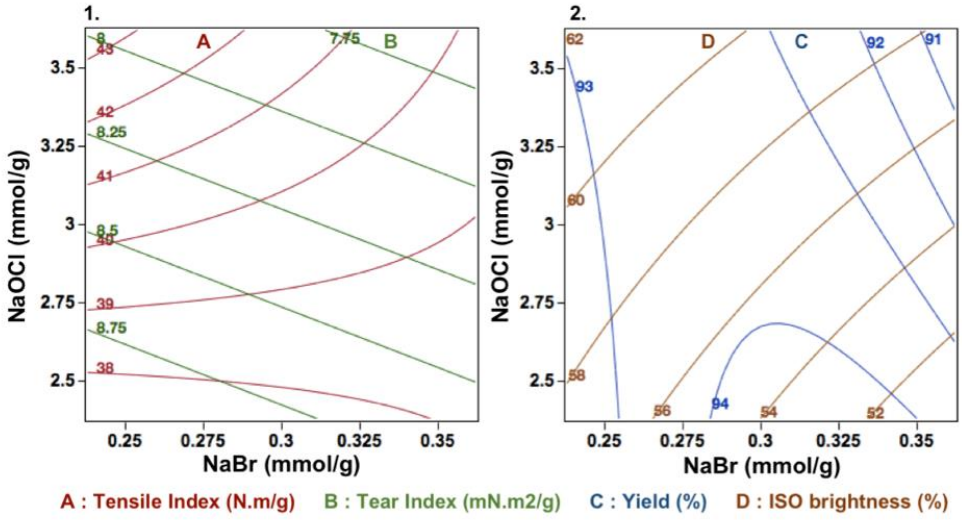

Fig. 3. Isoresponse profiles of (1) tensile and tear index and (2) yield and ISO brightness, with respect to sodium bromide and sodium hypochlorite at 0.038 mmol/g of aTEMPO

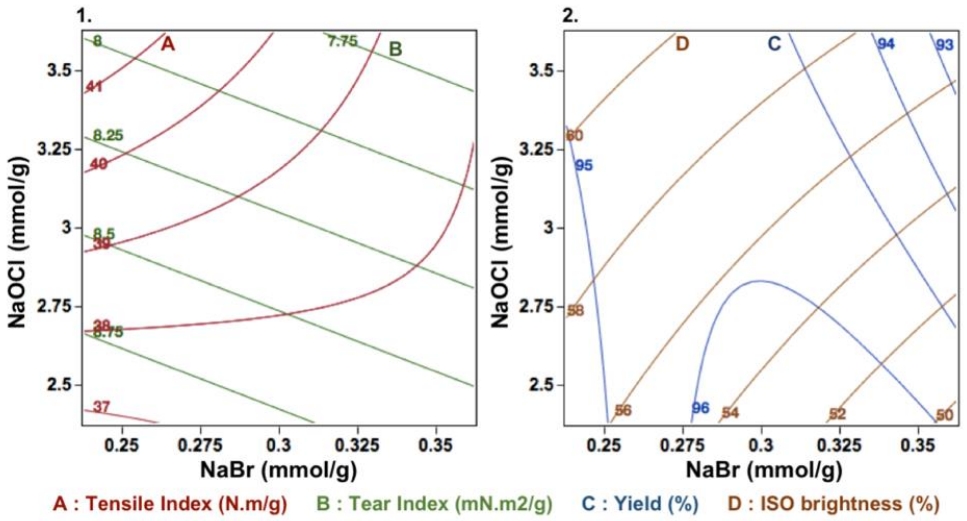

Fig. 4. Isoresponse profiles of (1) tensile and tear index and (2) yield and ISO brightness, with respect to sodium bromide and sodium hypochlorite at 0.050 mmol/g of aTEMPO

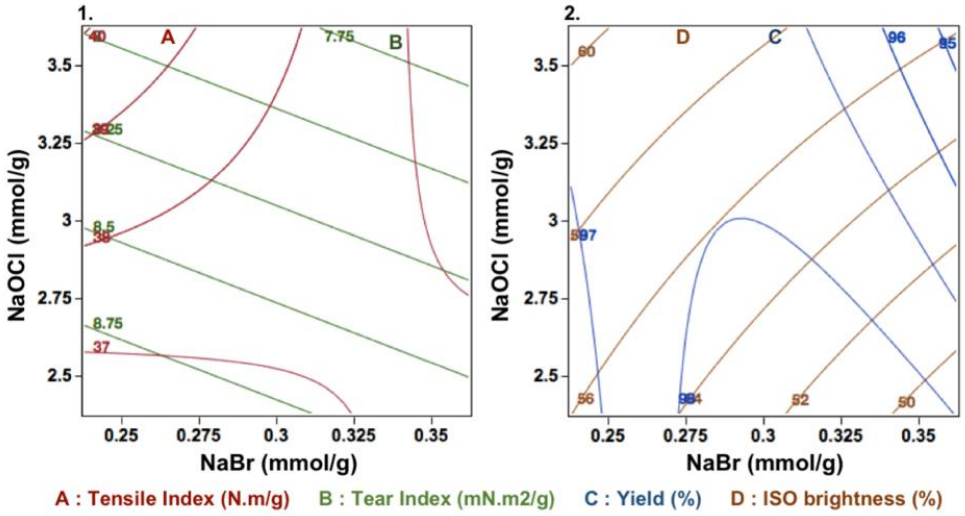

Fig. 5. Isoresponse profiles of (1) tensile and tear index and (2) yield and ISO brightness, with respect to sodium bromide and sodium hypochlorite at 0.062 mmol/g of aTEMPO

Finally, the last condition analyzed and optimized was the reaction temperature. In Fig. 6, the temperature effect is presented for three aTEMPO amounts at 0.24 mmol/g and 2.95 mmol/g of sodium bromide and sodium hypochlorite, respectively. It was possible to observe that, except for the yield, the temperature had the same effect on paper properties no matter what was the aTEMPO quantity. The only changes that occurred with aTEMPO level were the tensile index and ISO brightness value, but always with a peak value between 45 °C and 55 °C. The temperature effect on yield appeared to be controlled by competing mechanisms. When the aTEMPO oxidation was favored by the chemicals, increasing temperature increased the oxidation rate. In that way, when the temperature increased the oxidation was more effective and led to a drop of yield from fiber delignification and a tensile strength increase. However, at high temperature the tensile index increased, but at the same time the brightness decreased. The tensile strength improvement was was brought

about by the aTEMPO oxidation, but not by the pulp bleaching. At low aTEMPO quantity, the same observation can be made. However, because of the excess sodium hypochlorite, there was a higher bleaching effect, which made observations on yield harder to observe.

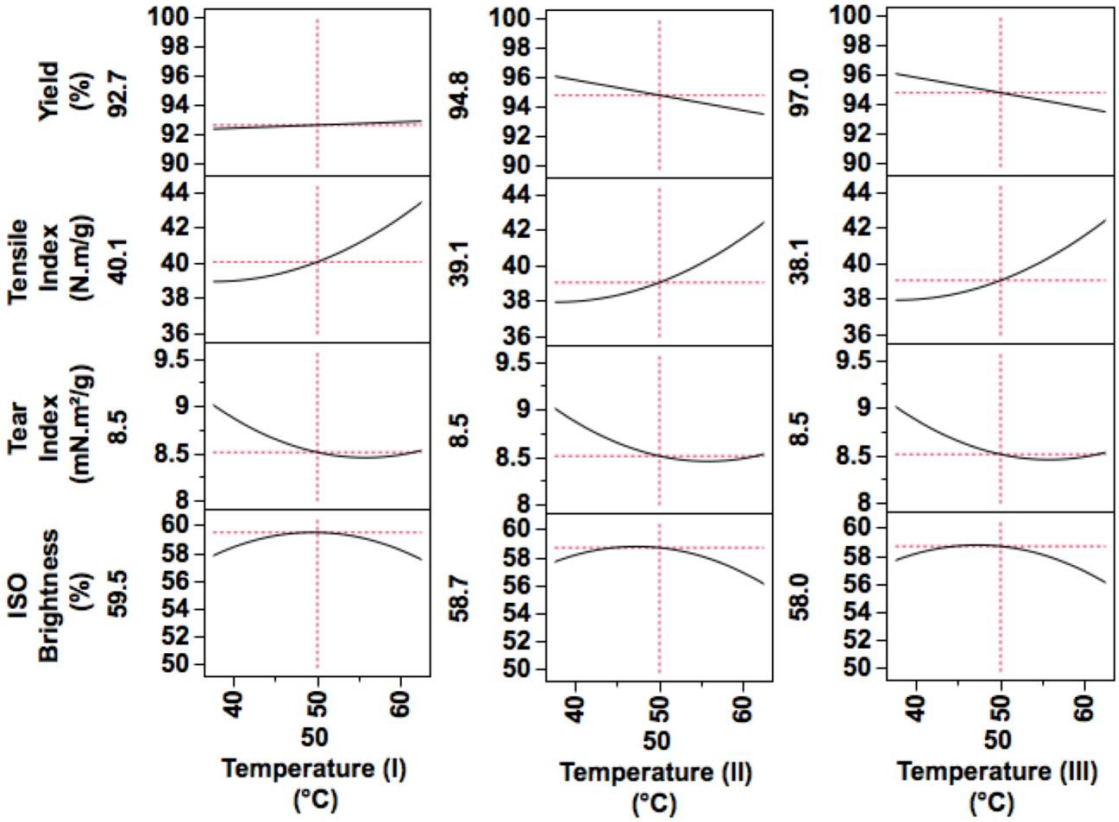

Fig. 6. Temperature effect on each response at 0.24 mmol/g of NaBr, 2.95 mmol/g of NaOCl, and different aTEMPO amounts (I: 0.038 mmol/g; II: 0.050 mmol/g; and III: 0.062 mmol/g)

To summarize the discussion related to the optimization in the case of low oxidation, the reaction time had only a slight effect on reaction yield or paper properties. In contrast, chemicals and temperature had an important impact on all responses and were linked together because of the competition between aTEMPO oxidation and pulp bleaching (delignification). Depending on the final application desired and the response to improve, the aTEMPO conditions can be completely different from one application to another.

High Oxidation: Nanomaterial Film Production

The second application to optimize was the nanomaterial film production. Table 4 contains all tests made with their conditions and results. As for the first experimental design, the minimum and maximum of each response were different enough to consider all effects to be significant. In addition, it is possible to observe that the maximum carboxyl content value was at 2233 mmol/kg, which is much higher than was observed by Isogai *et al.* (2011), who reported a maximum value of 1700 mmol/kg. The difference between the work of Isogai *et al.* and the present study is the nature of the pulp. Isogai *et al.* used kraft pulp. Hence there was relatively pure cellulose with only few residual other components, whereas thermomechanical pulp was used in this work.

Table 4. Tests and Results of the High Oxidation Optimization

Trial	aTEMPO (mmol/g)	NaBr (× n_{aT})	NaOCl (× n_{aT})	NaOCl Inj. Time (min)	Dis. Time (min)	Yield (%)	Carboxyl Content (mmol/kg)	Young's Modulus (MPa)	Tensile Strain at Breaking Point (%)	Light Trans. (%)
25	0.027	5,0	35.0	30.0	20.0	100	193	477	3.09	14
32	0.150	3.0	30.0	15.0	10.0	100	433	391	2.80	16
3	0.150	3.0	30.0	45,0	30.0	99	387	528	3.61	14
2	0.150	3.0	40.0	15.0	30.0	100	495	615	3.07	16
28	0.150	3.0	40.0	45.0	10.0	92	496	329	2.15	15
10	0.150	7.0	30.0	15.0	30.0	100	588	810	3.16	17
12	0.150	7.0	30.0	45.0	10.0	97	643	517	2.77	15
17	0.150	7.0	40.0	15.0	10.0	97	822	799	2.44	9
22	0.150	7.0	40.0	45.0	30.0	96	756	766	2.62	16
1	0.300	1.4	35.0	30.0	20.0	100	773	411	2.99	15
6	0.300	5.0	25.9	30.0	20.0	100	1164	929	2.73	22
4	0.300	5.0	35.0	2.7	20.0	100	1347	1123	2.85	28
29	0.300	5.0	35.0	30.0	1.8	98	1419	508	1.14	23
5	0.300	5.0	35.0	30.0	20.0	100	1211	1423	1.83	11
16	0.300	5.0	35.0	30.0	20.0	94	1436	1935	2.38	14
18	0.300	5.0	35.0	30.0	20.0	90	1379	1151	2.19	13
19	0.300	5.0	35.0	30.0	20.0	89	1377	2950	1.94	17
27	0.300	5.0	35.0	30.0	20.0	100	1302	2019	2.03	24
31	0.300	5.0	35.0	30.0	20.0	100	1279	1342	1.84	12
8	0.300	5.0	35.0	30.0	38.2	97	1361	1462	2.06	30
13	0.300	5.0	35.0	57.3	20.0	100	1818	1983	2.11	21
20	0.300	5.0	44.1	30.0	20.0	92	1533	1590	2.20	20
14	0.300	8.6	35.0	30.0	20.0	92	1678	1160	2.83	75
30	0.450	3.0	30.0	15.0	30.0	92	523	1528	2.23	17
9	0.450	3.0	30.0	45.0	10.0	97	1524	1349	2.34	32
23	0.450	3.0	40.0	15.0	10.0	88	1528	1774	3.03	74
26	0.450	3.0	40.0	45.0	30.0	92	1778	1558	2.23	78
7	0.450	7.0	30.0	15.0	10.0	90	1300	671	2.48	79
21	0.450	7.0	30.0	45.0	30.0	83	1990	2278	1.72	83
15	0.450	7.0	40.0	15.0	30.0	73	1520	2715	1.99	80
11	0.450	7.0	40.0	45.0	10.0	63	1614	1479	2.63	80
24	0.573	5.0	35.0	30.0	20.0	70	2233	1624	2.06	83
Min	0.027	1.4	25.9	2.7	1.8	63	193	329	1.14	9
Max	0.573	8.6	44.1	57.3	38.2	100	2233	2950	3.61	83

Models for each response, except for the light transmission (to be explained further in the analysis), were calculated according to the same method mentioned previously. Table 5 summarizes the estimated coefficient of each condition and the adjustment information of each model. First, it can be seen that the pulp carboxyl content, related to the oxidation progress, was related to the chemicals' quantity, but also related to the sodium hypochlorite injection time. Increasing the sodium hypochlorite injection time reduced its excess for the oxidation cycle and limited its consumption for pulp bleaching. The oxidation yield was also directly related to the chemicals. At high chemical amounts, the oxidation promoted delignification, which is why the sodium hypochlorite injection time had no significant effect. The delignification effect of pulp bleaching and aTEMPO oxidation was not different enough to observe a significant effect of the injection time. Finally, the mechanical properties of the obtained material were principally affected by

chemicals, more specifically aTEMPO, and dispersion time. Both were involved in material structural arrangement. However, the Young's modulus model had an important level of random error, which explained the low R^2 and the low number of significant terms. Still, the model could be used for analysis.

Table 5. Estimated Coefficient and Adjustment Information for a Model with a Significant Probability at 95% for the High Oxidation Optimization

Term	Carboxyl Content (mmol/kg)	Yield (%)	Young's Modulus (MPa)	Tensile Strain at Breaking Point (%)
Constant	1334	95.9	1542	2.04
aTEMPO	480	-7.0	472	-0.26
NaBr ratio	164	-3.3	147*	-0.09*
NaOCl ratio	101	-3.2	-	-0.08*
NaOCl injection time	125	-	-	-0.11
Dispersion time	-	-	231	0.07*
aTEMPO × NaBr ratio	-	-3.7	-	-
aTEMPO × NaOCl ratio	-	-2.2	-	0.20
aTEMPO × NaOCl injection time	131	-	-	-
aTEMPO × Dispersion time	-	-	-	-0.29
NaOCl ratio × NaOCl injection time	-89	-	-	-
aTEMPO^2	-108	-3.9	-	0.16
NaBr ratio^2	-104	-	-233	0.26
NaOCl ratio^2	-	-	-	0.13
NaOCl injection time^2	-	-	-	0.13
Dispersion time^2	-	-	-172	-0.13
R^2	0.87	0.83	0.59	0.88
Adjusted R^2	0.83	0.78	0.51	0.81
SS_{model}	7311202.7	2203.9	8582601	7.37
$SS_{pure\ error}$	40352.0	300.1	3773652	0.23
$SS_{lack\ of\ fit}$	1037596.8	162.2	2184737	0.73
* Not significant at 95% but term included in interactions				

For the light transmission, it was noticed that the results were separated into two groups: one group with a light transmission between 9% and 32%, and a second group with values between 74% and 83%. For all of the tests, the light transmission was determined on materials with a thickness of 0.010 ± 0.002 cm. Differences in light transmission are therefore not explained by the difference in thickness but by the nature of the material obtained. Materials in the first part were more like a paper sheet, but in the second part, the materials obtained were nanomaterial translucent films. Because of this discontinuity in the results, no models could be calculated for the light transmission. Nevertheless, interesting information was extracted from this response. A representation of the light transmission according to the carboxyl in pulp, in Fig. 7, shows that the discontinuity in material properties occurred at approximately 1500 mmol/kg in carboxyl content. This clearly indicated that the oxidation must be done at high carboxyl content in order to obtain nanomaterial films by means of the current method used. Negative charge (carboxyl groups) at fiber surfaces induced a repulsion between the fibers and between microfibers.

This repulsion facilitated micrometric and nanometric fibril production for an easier and better dispersion, thus resulting in an increase in light transmission.

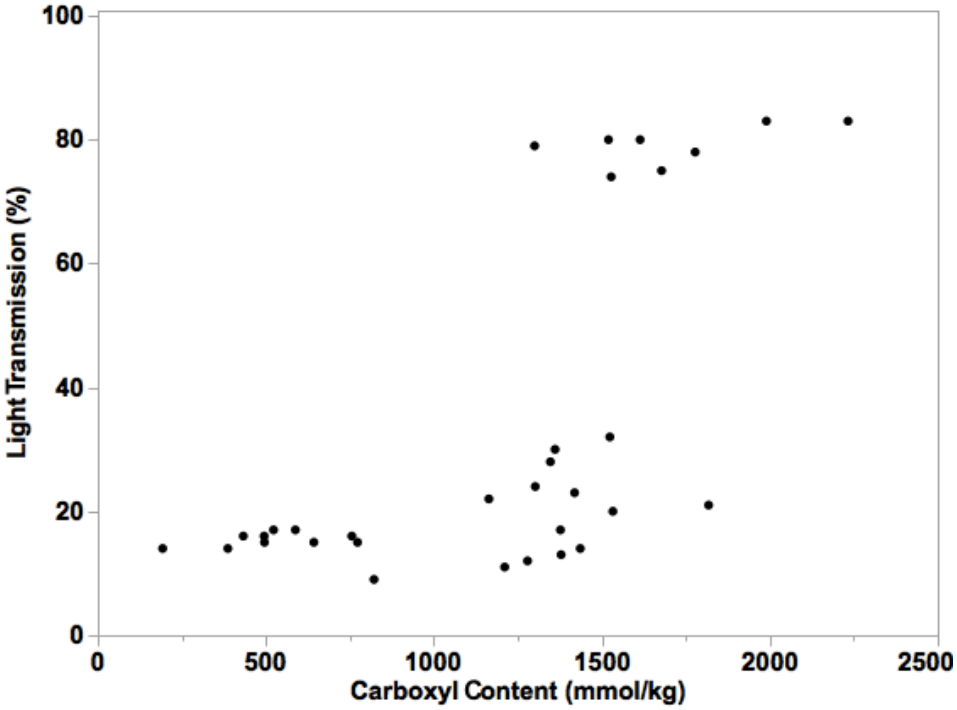

Fig. 7. Light transmission according to the carboxyl content of the pulps

According to the calculated model, carboxyl content was mostly correlated to the chemical amount. For each trial, exact chemical quantities, instead of ratio, were calculated according to the aTEMPO amount and both sodium bromide and sodium hypochlorite ratios. The light transmission according to each chemical quantity is shown in Fig. 8, which also displays the minimum value required of each chemical. Nanomaterial film was obtained when aTEMPO, sodium bromide, and sodium hypochlorite quantities were higher than 0.30 mmol/g, 1.35 mmol/g, and 10.5 mmol/g, respectively. In contrast, at least one, but often two, chemicals should be in a quantity higher than those limit values. For example, trial 13 presented a paper sheet-like material, but each quantity was equal to or greater than the limit values.

Actually, two conditions were possible for producing film. The first was to increase the aTEMPO and sodium hypochlorite at the same time to greater than 0.45 mmol/g and 18.0 mmol/g, respectively, with a sodium bromide equal to or greater than 1.35 mmol/g. This first condition was represented by trials 23 and 26. The second condition to obtain films, represented by trial 14, was to use a high sodium bromide quantity, up to 2.59 mmol/g, with aTEMPO and sodium hypochlorite equal to or greater than 0.30 mmol/g and 10.5 mmol/g, respectively. Those conditions not only led to a high carboxyl content, but also to a significant delignification. Both effects were needed to produce good quality films. For example, the pulp of trial 30 had a low carboxyl content (523 mmol/kg) but a significant delignification (yield drop to 92%), which did not make a film. In contrast, the pulp of trial 13 with a high carboxyl content (1818 mmol/kg) but no delignification (yield of 100%) did not make a film either.

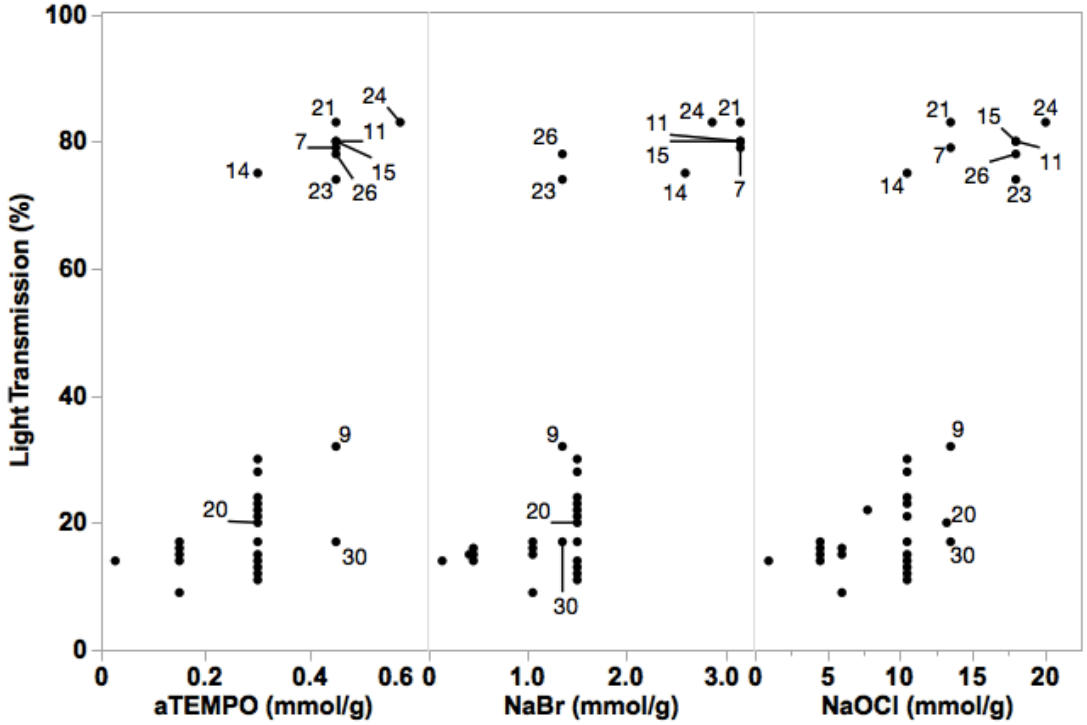

Fig. 8. Representation of light transmission for each trial according to chemical quantities

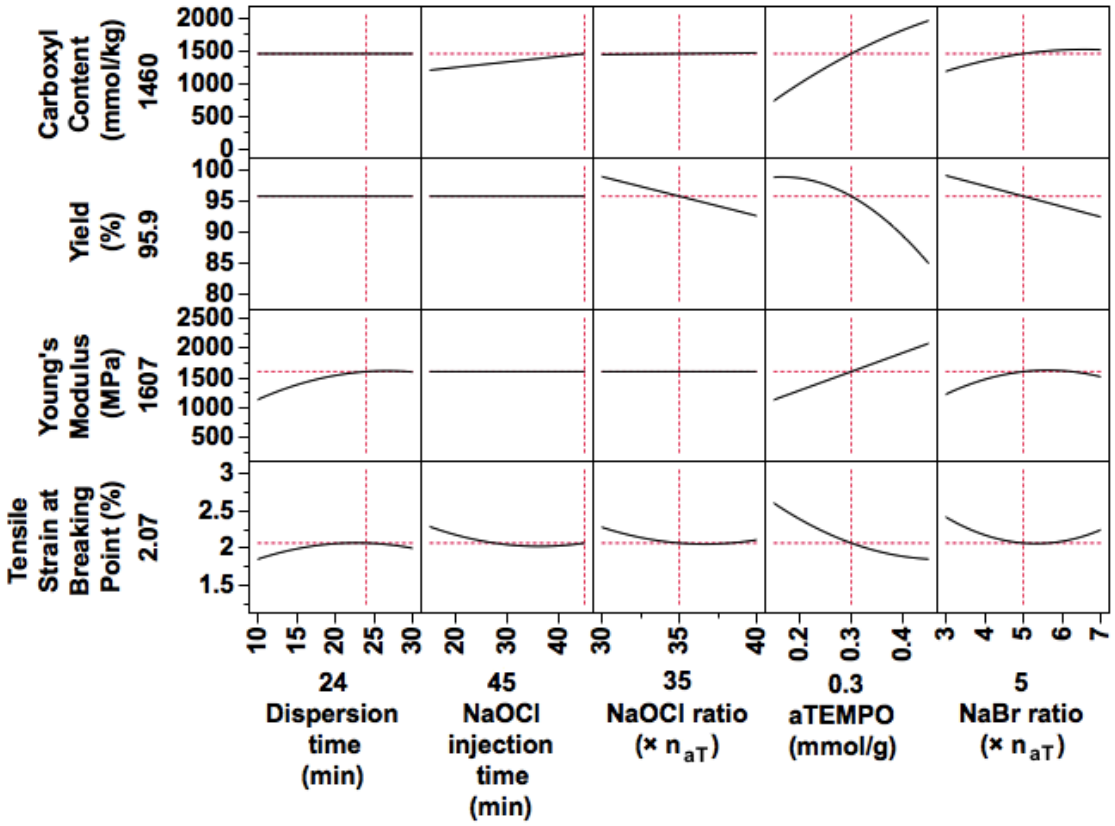

Fig. 9. Representation of condition effects on each response of the second experimental design

Concerning the optimization of aTEMPO oxidation and the material mechanical properties, the model representation in Fig. 9 allowed three parameters to be fixed. The first condition to be fixed was the dispersion time. The maximum Young's modulus and tensile strain was reached at 24 min. At this time, the whole pulp defibrillation was made, so no more time was needed for dispersion improvement. The sodium hypochlorite injection time was maximized to favor the high carboxyl content even if a slight drop of tensile strain was found. Increasing the injection time allowed the use of sodium hypochlorite to decrease in secondary reaction (pulp bleaching) to get higher carboxyl content. Finally, the sodium hypochlorite ratio was fixed in a way to reach its minimum quantity to get film at the minimum aTEMPO quantity needed. In that way, it was possible to reduce the sodium hypochlorite excess that had no important effect on the material's mechanical properties.

The aTEMPO quantity and the sodium bromide ratio effects on the responses are presented in Fig. 10. As expected, the oxidation yield and pulp carboxyl content were inversely proportional. As clarified previously, the aTEMPO oxidation involved fiber delignification at high carboxyl content, which further promoted yield drop. Regarding the material's mechanical properties, the Young's modulus and tensile strain had opposite behavior. However, both properties presented a peak value at a sodium bromide ratio of approximately 5.5. Therefore, it was possible to obtain a material with the same mechanical properties achieved with different chemical amounts for the oxidation. For example, points 1 and 2 both had a Young's modulus of 1800 MPa and a tensile strain of 2.0%, but the used quantities of aTEMPO, sodium bromide, and sodium hypochlorite were not the same. In fact, point 1 had a higher carboxyl content (1764 mmol/kg) and a lower oxidation yield (88.9%) than point 2 (1724 mmol/kg and 92.1%). This difference meant that a higher delignification occurred when sodium bromide was used in excess.

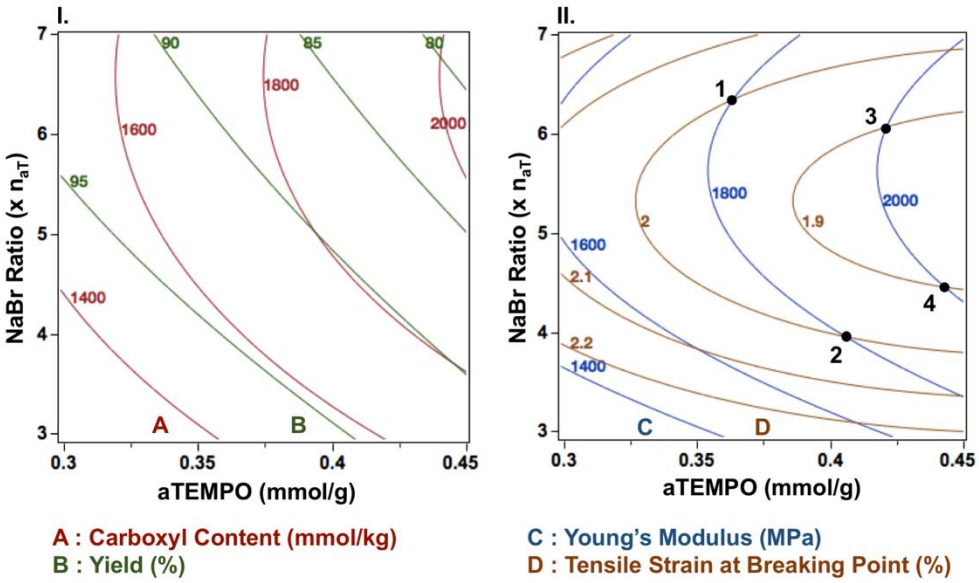

Fig. 10. Isoresponse profilers of aTEMPO oxidation yield and pulp carboxyl content (I) and material Young's modulus and tensile strain at breaking point (II) according to aTEMPO quantity and sodium bromide ratio

Points 3 and 4 showed this phenomenon with aTEMPO and sodium hypochlorite nearly the same (chemicals quantities were respectively, for points 3 and 4, 0.421 mmol/g

and 0.443 mmol/g for aTEMPO and 14.74 mmol/g and 15.51 mmol/g for sodium hypochlorite). The pulp at point 3 had a carboxyl content higher than point 4 by 48 mmol/kg, but with a 3.2% lower yield. However, according to previous observation on the light transmission, points 1 and 3 tended to be more advantageous, depending on the mechanical properties needed, because they had a better light transmission and a higher nanomaterial film behavior.

Finally, the high oxidation gave rise to two phenomena on the pulp as well: the aTEMPO oxidation and the pulp delignification. Both effects were needed to produce a good quality nanomaterial film. Mechanical properties of those films were optimized with chemical quantities, but a high sodium bromide ratio was needed to increase the material light transmission. In addition, the sodium hypochlorite injection time could be increased to favor the aTEMPO oxidation, which would give a slight increase of light transmission. Lastly, the dispersion time could be optimized according to the dispersion method. In the present work, the dispersion time was fixed at 24 min to maximize mechanical properties.

CONCLUSIONS

1. During the aTEMPO reaction on TMP, both oxidation and delignification occurred. Modification of chemical amounts easily promoted one or the other. Increase in aTEMPO and/or sodium bromide content favored the oxidation. In contrast, increasing sodium hypochlorite fostered the delignification.
2. Temperature was an important condition to consider for aTEMPO pulp oxidation and bleaching kinetic. At high temperatures, the oxidation was favored but induced a delignification, which caused a drop in the yield.
3. At a carboxyl content higher than 1500 mmol/kg and a slight delignification, nanofibril materials were obtained with high light transmission. Mechanical properties of those materials were optimum with a 24 min dispersion time, but they were easily modified by changes of chemical amounts. Identical mechanical properties were observed for different chemical amounts depending on oxidation and delignification balance, but the material nature can differ from nanomaterial to non-nanofibers film, thus showing different light transmission.
4. Reaction time and sodium hypochlorite injection time did not have a huge effect on the final properties. However, the sodium hypochlorite injection time could be increased to favor the oxidation instead of the sodium hypochlorite direct delignification.

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