CELLULOSE CHEMISTRY AND TECHNOLOGY

INFLUENCE OF OXIDATION AND CATIONIZATION ON PROPERTIES OF TMP FIBERS

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The study evaluates the influence of the interaction of oxidized, cationized and untreated fiber components upon paper properties. The oxidative treatment has been noted to improve fiber bonding, while degrading fiber strength. Comparatively, cationization has relatively reduced undesirable effects on the physical properties of fibers. Blending of untreated with treated fibers caused a general drop in sheet properties, depending on the degree of oxidation and cationization.

Keywords: TEMPO-mediated oxidation, cationization, thermo-mechanical pulp

INTRODUCTION

The fines of mechanical pulps play an important role in determining the physical and optical sheet properties,[1-5] as well as the quality of white water.[6,7] Due to their low sizes, significant portions could be lost through the paper machine wire, because of the high stock turbulence, which influences paper characteristics and whitewater quality. When mills run with a closed whitewater circuit, any material not retained in the first pass will be circulated back to the paper forming process, and most of it will be retained in the sheet. However, whitewater could be gradually enriched with fines and cause problems with deposits in a closed whitewater system.

Since the fibrous elements, fillers and most additives used in papermaking are negatively charged, cationic polymers are usually used to retain these materials in the sheet. Besides, papermaking specialists anticipate the development of more economical alternatives to silica and bentonite micro-particle retention aids, and of wet-end chemicals based on renewable resources. Recent studies indicate that long fibers of thermomechanical pulp (TMP) could be cationized and used for fines retention.[8,9] However, cationization has destroyed some of the carboxyl groups present on fibers, which is beneficial for fiber bonding,[10-15] reducing the inter-fiber bonding capacity. As known, this shortcoming can be mitigated by TEMPO-mediated oxidation, which converts the primary alcohol groups on cellulose into carboxylic acid groups.[16-21] It is also known that long TMP fibers have poor inter-fiber bonding capacity,[5,22] and their bonding potential could be significantly enhanced by oxidation.[16] The possible cationization of a portion of the long fiber as a retention agent was investigated, as well as the oxidation of another portion as a reinforcement component. The main objective was to eliminate or minimize the use of foreign agents in papermaking, involving the use of mechanical pulp.

Recent studies of ours[23,24] have confirmed the above-mentioned hypothesis. In this particular study, only one level of oxidation and cationization was performed. It is therefore of interest to increase the degree of oxidation and cationization, for better understanding the way in which modifications of fiber surface functionality affect the characteristics of whitewater and fibers. The effects on whitewater have been recently reported,[24,25] while those affecting the fiber properties are discussed here.

EXPERIMENTAL

Materials

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 fractionated into long and short fiber fractions, by a special 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 were 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 got through the strainer. Such a process permitted to easily recover all fines, as compared to that carried out with a Bauer McNett classifier. The long fiber fractions (LF) retained on the strainer represented ~66%, while the short fiber fractions (SF) passing through the strainer represented ~34%.

Oxidation

The oxidation conditions are given in Table 1; the detailed procedures are similar to those described elsewhere.[22] Briefly, the experiment was conducted in a 2 L glass reactor at 21 °C. The 30 g (o.d. basis) long fibers were first diluted, at 1.5% consistency, in deionized water, to which predetermined amounts of 4-acetamido TEMPO, sodium bromide and sodium hypochlorite were gradually added. The pH of the system was maintained at 10.5 using a NaOH or HCl solution, depending on the situation. The pulp suspension was continuously agitated with an electric stirrer. When the predetermined reaction time (50 min) was over, the fibers were drained, washed and filtered and the pH of the fiber suspension was adjusted to 5.0. The pulp was again drained, washed and filtered for at least 4 more times prior to measuring the carboxylic acid content, by the technique described by Katz.[26]

Cationization

Cationization of LF with 2,3-epoxy-propyl-tri-methyl ammonium chloride (EPTMAC) was conducted in polyethylene bags. The experimental conditions are given in Table 2. Each bag contained 30 g (o.d. basis) of LF, at 11% consistency. A predetermined amount of NaOH (20% o.d. weight of pulp) was used to activate the cellulose and hemicellulose in the fiber, for making them react with the epoxy groups of EPTMAC to form an ether. The alkali-treated fiber mixture was kneaded manually and let to stand for 20 min, after which a required quantity of EPTMAC solution was introduced into the bag, which was then sealed. The mixture was well-mixed before being submerged in a water bath at 45 °C for 90 min. Intermittent kneading of the mixture was performed throughout the reaction. The reaction was stopped by adding acetic acid (4% by weight of pulp) to the system, which was then well kneaded. The acidified pulp was then filtered and thoroughly washed with de-ionized water. Cationic charge density on the grafted fibers was determined[9,14] by the back titration method, using Mutek PCD03. In fact, it was measured by colloidal titration with poly-vinyl sulfonic acid potassium salt (PVSK) and poly-diallyl-dimethyl ammonium chloride (polyDADMAC). At first, the sample was diluted to ~0.5% consistency and its pH was adjusted to 2.5 to eliminate the anionic charge of the carboxylic acid, which begins to dissociate at pH 2.9. An excess of PVSK was added to the pulp slurry and the unreacted portion of PVSK was back-titrated using polyDADMAC. The amount of PVSK reacted with the fibers represents the cationic charge.

Pulp blending

Four different scenarios were considered for the blending trials:

(A) short fraction (SF) mixed with cationized long fibers (CLF),

(B) SF mixed with oxidized long fibers (OLF),

(C) SF mixed with equal proportions of untreated long fibers (ULF), OLF and CLF,

(D) SF mixed with equal proportions of CLF and OLF.

The long fiber fractions (ULF, CLF and OLF) were recombined with the SF ones, following the ratios indicated in Table 3. Note that the OLF and CLF fibers were oxidized and, respectively, cationized to various levels of carboxylic acid content and cationic charge density, as shown in the last columns of Tables 1 and 2.

Table 1

Oxidation conditions and carboxylic acid content

Exp. no.	Long fibers, g (o.d.)	TEMPO, g	NaBr, g	NaOCl (705 mmol/L), mL	Temperature, °C	Time, min	Carboxylic acid, mmol/kg
1	30	0.05	19	30	21	50	146
2	30	0.05	19	80	21	50	262
3	30	0.05	19	165	21	50	515
4	30	0.05	19	250	21	50	744
5	30	0.05	19	335	21	50	912

Table 2
Cationization conditions and cationic charge density

No.	Long fibers, g	NaOH, g	EPTMAC, g	Temperature, °C	Time, min	Cationic charge density, mmol/kg
1	30	6	15	45	50	229.07
2	30	6	30	45	50	362.87
3	30	6	50	45	50	452.92
4	30	6	75	45	50	655.81
5	30	6	90	45	50	733.66

Table 3
Fiber composition of pulp blending (%)

BLEND	ULF	CLF	OLF	SF
A	0	66	0	34
B	0	0	66	34
C	22	22	22	34
D	0	33	33	34

RESULTS AND DISCUSSION

Characteristics of oxidized long fibers

As shown in Table 1, TEMPO-mediated oxidation is effective in generating carboxylic acid groups on mechanical fibers, having a remarkable effect on fiber properties (Table 4). For example, pulp freeness dropped from 300 to 175 mL (an about 42% decrease), when the TMP long fibers were oxidized to yield 911 mmol/kg of carboxylic acid. Oxidation increased fiber flexibility, improving the sheet density by nearly 50%. The increases in carboxylic acid content and fiber flexibility led to significant improvement in inter-fiber bonding, as a result of improved fiber conformability. Consequently, the tensile index of the handsheet was considerably enhanced. The burst index was also improved.

However, the oxidative treatment also brought about some undesirable effects. Particularly, it degraded the intrinsic fiber strength, as shown by the noticeable decreases in zero-span tensile breaking length of the dry handsheets. Additionally, the tearing resistance of paper suffered severe losses, which could reach almost 70% when the fibers were oxidized to a high carboxylic acid content, *e.g.*, 911 mmol/kg. When sheet density and inter-fiber bonding are greatly increased, tearing strength greatly depends on intrinsic fiber strength which, in this case, was indeed greatly reduced, as mentioned earlier. As to the optical properties, decreases in brightness, opacity and light scattering coefficient were generally recorded, which are believed to be related to the physical and chemical changes brought about to fibers by the oxidative reactions. For instance, the increase in sheet density would usually reduce opacity and light scattering power. Chemical modification of the chromorphoric groups on fibers could induce changes in brightness, so that further studies are necessary to better understand the exact mechanism involved.

Characteristics of cationized fibers

Cationization had also significant impact on fiber characteristics, as revealed in Table 5. Depending on fiber properties, these effects were, however, different and more complex, in comparison with those caused by oxidation. Complexity is manifested particularly by sheet density, tensile and burst indices. As seen in Table 5, these properties increased with increasing the cationic charge density, after which it fell off noticeably at about 450 mmol/kg cationic charge, possibly because of the highly cationized fiber.

Other fiber properties, such as freeness, tear index and optical characteristics, suffered, generally, gradual losses with increasing the catioinc charge. These decreases occurred, however, to a relatively lower extent, when compared to those caused by oxidation. Evidently, this phenomenon is associated with differences in the nature of the chemical treatment, further investigations being still necessary to elucidate the possible associated mechanisms. For example, the effect of a relatively high dosage of NaOH (20% on o.d. fiber) used in cationization deserves extended study.

Strength properties of paper made of mixed furnish

Zero-span tensile strength

When the cationized (CLF) or oxidized (OLF) long fibers were blended (the long fiber/short fiber ratio was the same as that of the initial whole pulp) with the untreated short fibers (SF), the zero-span tensile strength of the handsheets dropped relatively sharply as a function of the cationic charge or carboxylic acid content (Fig. 1). Unexpectedly, the decrease rate of the CLF/SF blend was greater than that of the OLF/SF mixture. As seen earlier, the loss in fiber strength was greater for OLF (Table 4) than for CLF (Table 5). This observation suggests that factors other than intrinsic fiber strength also play a role in determining the zero-span tensile strength of the dry handsheet, such as the evenness of the paper sheet.

When the long fiber ratios were equally shared by the three types of long fibers (22% ULF + 22% CLF + 22% OLF) and mixed with SF (34%), the zero-span tensile strength of the handsheets also showed relatively sharp decreases (Fig. 2), which were directly associated with both carboxylic acid content and cationic charge density. The loss in zero-span tensile strength of paper due to cationization is particularly intriguing.

Table 4
Properties of oxidized long fibers

-COOH, mmol/kg	85*	146	262	525	744	911
Freeness, mL	300	265	255	215	190	175
Sheet density, g/cm^3	0.33	0.32	0.32	0.36	0.42	0.49
Zero-span tensile, km	12.6	12.3	11.5	10.3	9.8	9.1
Tensile index, N*m/g	36.8	37.9	41.8	45.1	50.3	54
Burst index, kPa*m^2/g	2.21	2.28	2.39	2.58	2.55	2.61
Tear index, mN*m^2/g	8.5	9.4	8.4	6.4	4.4	2.7
Brightness, % ISO	52	39.8	44.5	50.0	48.9	46.8
Opacity, %	94.8	97.3	94.3	89.7	87.3	83.6
Light scat. coef., m^2/kg	47.1	45.0	43.0	38.1	33.3	28.7
Light abs. coef., m^2/kg	4.2	7.1	4.3	2.5	2.3	2.2

* untreated

Table 5
Properties of cationized long fibers

Cationic charge density, mmol/kg	0*	230	363	453	656	733
Freeness, mL	300	255	220	215	210	220
Sheet density, g/cm^3	0.33	0.38	0.38	0.39	0.31	0.28
Zero-span tensile, km	12.6	12	11.1	11	10.2	10
Tensile index, N*m/g	36.8	46.7	48.4	44.7	32.7	30.9
Burst index, kPa*m^2/g	2.21	2.93	3.24	3.21	2.48	2.34
Tear index, mN*m^2/g	8.5	8.3	6.9	6.6	6.3	5.9
Brightness, % ISO	52.3	33.9	31.2	30.1	30.0	29.9
Opacity, %	94.8	95.5	93.2	92.2	92.4	90.7
Light scat. coef., m^2/kg	47.1	39.4	33.7	30.4	31.4	30.4
Light abs. coef., m^2/kg	4.2	5.1	4.6	4.1	3.9	3.8

* untreated

Similar trends in zero-span tensile strength reduction, related to oxidation and cationization of the long fibers, were also observed in mixed furnish without ULF, as shown in Figure 3.

Handsheet density

As revealed in Table 4, oxidation increased handsheet density. As a result, when OLF was blended with SF, sheet density augmented with increasing the carboxylic acid content (Fig. 4). In contrast, mixing of CLF with SF had a negative impact on sheet density, particularly when CLF carried a high cationic charge.

Figure 5 shows that, when the blend contained equal amounts of each kind of long fiber (ULF, OLF and CLF), sheet density somewhat increased with increasing the carboxylic acid content, but it slightly dropped as the cationic charge of CLF augmented. It is speculated that attraction and, consequently, deposition of anionic trash and fines onto the CLF might interfere with sheet consolidation, affecting the cohesion between the long fibers. A similar phenomenon was observed on the sheets prepared from a mixture of 33% CLF + 33% OLF + 34% SF, as illustrated in Figure 6. In the latter case, the influence of various levels of cationic charge on paper density was not clear.

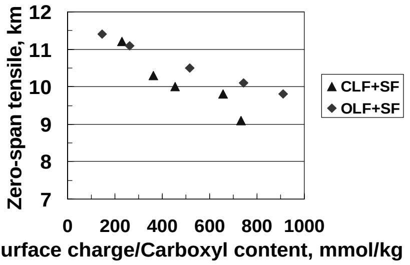

Figure 1: Zero-span tensile strength of handsheets prepared from cationized (CLF) or oxidized (OLF) long fibers mixed with untreated short fibers (SF)

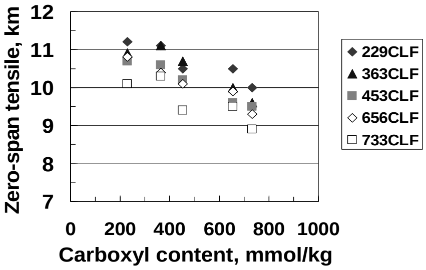

Figure 2: Zero-span tensile strength of handsheets prepared from a mixture of 22% ULF + 22% CLF + 22% OLF + 34% SF

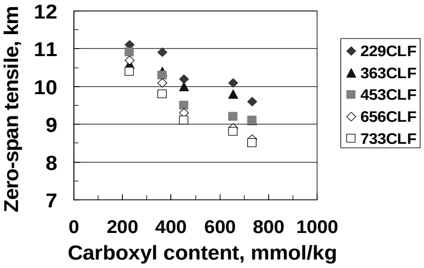

Figure 3: Zero-span tensile strength of handsheets prepared from a mixture of 33% CLF + 33% OLF + 34% SF

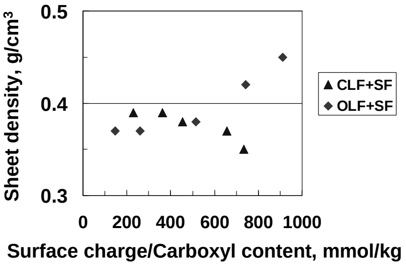

Figure 4: Density of handsheets prepared from cationized (CLF)/oxidized (OLF) long fibers mixed with untreated short fibers (SF)

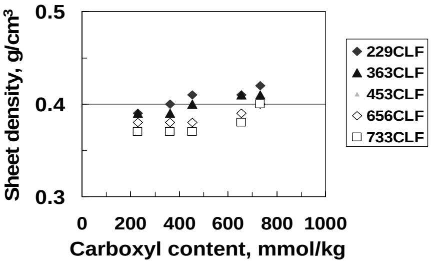

Figure 5: Density of handsheets prepared from a mixture of 22% ULF + 22% CLF + 22% OLF + 34% SF

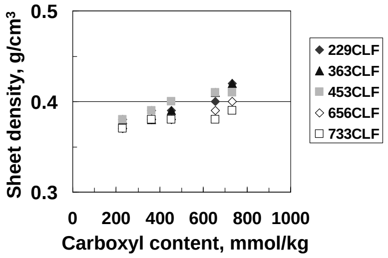

Figure 6: Density of handsheets prepared from a mixture of 33% CLF + 33% OLF + 34% SF

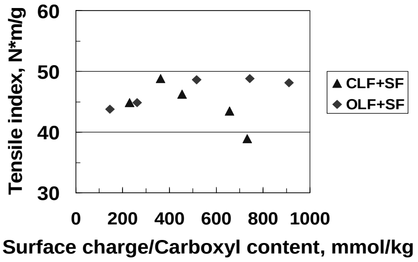

Figure 7: Tensile index of handsheets prepared from cationized (CLF)/oxidized (OLF) long fibers mixed with untreated short fibers (SF)

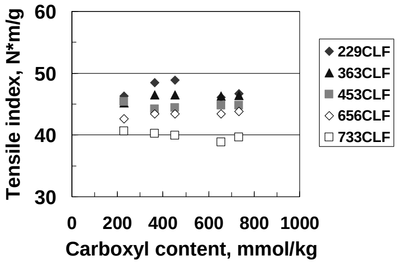

Figure 8: Tensile index of handsheets prepared from a mixture of 22% ULF + 22% CLF + 22% OLF + 34% SF

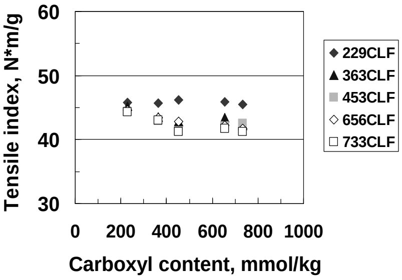

Figure 9: Tensile index of handsheets prepared from a mixture of 33% CLF + 33% OLF + 34% SF

Tensile index

As in the case of sheet density, the tensile index of the handsheets increased as the carboxylic acid content or the cationic charge augmented (Fig. 7). However, the increases dropped off after reaching a peak value at approximately 500 mmol/kg carboxylic acid content or cationic charge density. Increased degradation of the oxidized fibers and increased repulsive forces between the cationic components could be accountable in both situations.

As for the sheets containing equal amounts of three different types of long fibers (Fig. 8), the effect of the carboxylic acid content on tensile index was generally reduced, except when the cationic charge density was low, *e.g.* 229 mmol/kg. In this case, the initial increase in tensile index fell off at about 400 mmol/kg of cationic charge, as seen in Figure 8. Note that tensile strength dropped when the cationic charge of CLF increased.

When the ULF component was excluded from blending (Fig. 9), a gentle reduction in tensile strength occurred, as a function of the carboxylic acid content; an exception was noted for the sheet made with CLF with a low degree of cationization (229 mmol/kg). Again, a general decrease was observed in the tensile index with increasing cationic charge density.

Tear index

Figures 10-12 reveal that the tearing resistance of the handsheets fell sharply with increasing the carboxylic acid content, which is related to the degradation of intrinsic fiber strength.

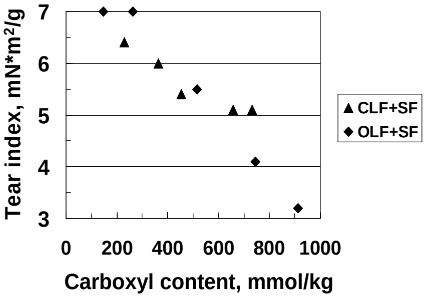

Figure 10: Tear index of handsheets prepared from cationized (CLF)/oxidized (OLF) long fibers mixed with untreated short fibers (SF)

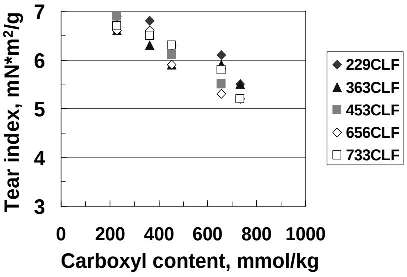

Figure 11: Tensile index of handsheets prepared from a mixture of 22% ULF + 22% CLF + 22% OLF + 34% SF

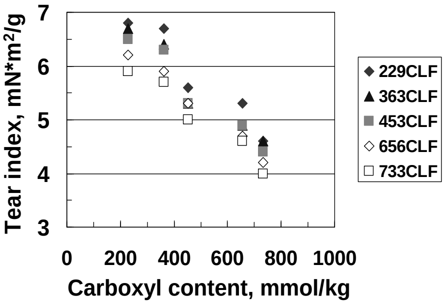

Figure 12: Tensile index of handsheets prepared from a mixture of 33% CLF + 33% OLF + 34% SF

As previously stated, the improvement in inter-fiber adhesion through oxidation was accompanied by server fiber degradation, resulting in a drastically reduced tear index. This would suggest that the oxidative treatment should be optimized to produce optimal fiber bonding capacity, while preserving good intrinsic fiber strength. On the other hand, the cationic charge density had similar but relatively small adverse influence on the tear index. Generally, a low cationic charge had less impact than the high levels.

CONCLUSIONS

1. TEMPO-mediated oxidation enhances the inter-fiber bonding potential of the mechanical fiber, while also degrading intrinsic fiber strength; the oxidative process should be optimized to yield the most beneficial attributes.
2. Comparatively, cationization has relatively little negative impacts on fiber properties, with the exception of the optical ones, particularly brightness, believed to be associated with the dosage of sodium hydroxide, which needs further optimization.

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