Effects of the extraction and the addition of hemicelluloses combined with mechanical and ultrasonic refining in the quality of the pulps and recycled papers

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Abstract

The objective of this work was to study the recovery of the quality of recycled paper pulp through ultrasonification of the pulp combined with the addition of hemicelluloses, as an alternative method for producing pulps with different characteristics, in order to expand their marketing opportunities. The equipments that were used were the ultrasound, 475 Virsonic model, working with a nominal power of 190 Watts and wave frequency of 20 kHz and PFI type laboratory mill refining. The pulps used in this study were extracted from the trimming of post-consumer corrugated cardboard. The hemicelluloses that were added in the pulps were extracted from the own reference pulp through the CCE (Cold Caustic Extraction) process. Essentially, this study was conducted in three stages. Initially, we assessed the effects of increasing doses of hemicelluloses (0, 1, 2.5, 5 and 10%) on the paper properties and subsequently evaluated the influences of refining in PFI mills in varying the intensities of these treatments at 400, 800 and 1200 revolutions and ultrasonification 10, 20 and 30 minutes respectively and then the addition of the hemicelluloses in fixed dosage of 10% based on dry pulp was made, and finally we evaluated the quality of pulps extracted from hemicelluloses, refined in PFI mills (0, 400 , 800 and 1200 revolutions) and ultrassonificated (0, 10, 20 and 30 minutes). The ultrasonic treatment followed by the addition of hemicelluloses proved to be more efficient in the development of the mechanical strength properties of the paper, promoting the development of the properties, however, in a less pronounced form than the observed one when the pulp was refined in PFI followed by the addition of hemicelluloses. The drainage resistance and the properties directly influenced by interfiber links, such as the tensile index, corrugated medium test and tear resistance increased with the increasing content of hemicelluloses in whatever was the number of revolutions and ultrasonification time. The increase of the hemicelluloses content in the pulp produced papers with lower bulk and consequently more dense. The extraction and addition of hemicelluloses, compared to the reference allowed to obtain pulps with different behaviors: the pulp extracted from hemicelluloses showed lower mechanical strength compared to the reference, suggesting its application only for the production of crumb paper (differentiated Fluting). The pulp with addition of hemicelluloses showed higher resistance properties compared to the reference and requiring less energy during the refining process and can be recommended for the production of covers of corrugated cardboard (differentiated Testliner).

Keywords: Paper properties, recycling, refining, ultrasound, hemicelluloses

Introduction

The increased use of recycled fibers and the increasing demand for paper has stimulated the development of processes to improve the quality of secondary fibers. Although recycling is a promising activity, there are technical challenges with the product at the end of the process, requiring intensive studies for the development of workable solutions. These facts are related to the loss of quality in the final properties of recycled paper compared to the original product.

The main changes of the characteristics of the secondary fibers in comparison to primary pulps are: decrease in the freeness, reduction in mean fiber length, reduction in strength properties of paper, increase in the opacity of paper, less ability to form inter-fiber bonds, lower hydration capacity of the fiber, less fiber flexibility, lower water-holding capacity, the presence of internal delamination in the fiber, and reduction of fibrillation [1].

The use of ultrasonic waves can be considered as an alternative to redeem the necessary characteristics in the lost fibers in successive processes of recycling for the production of paper with higher strength properties. Morphological and structural changes caused by ultrasonic waves can contribute to a better formability, flexibility, and consolidation of the fibers during paper formation [2].

Another technology that can be applied in an attempt to recover the quality of recycled paper is the addition of hemicelluloses, since it is widely known that these carbohydrates significantly influence the properties of the paper. When they are present in the internal structure of the cell wall, they help in hydration of the fibers, facilitating their collapse. When they are present on the surface of the fibers they have an important role in the formation of interfiber links. The hemicelluloses decrease the intensity of refining required to reach a fixed value of a dry-strength property. The extraction of hemicelluloses from the recycled pulp itself is a unique option considered in the present study; in practice it represents one more potential use of post-consumption recycled paper. Such an approach does not require that factories purchase of these carbohydrates from other supplier sources.

In this study the aim was to evaluate the potential of two alternative technologies, ultrasonic treatment and the addition of hemicelluloses, in the development of the properties of recycled papers.

Experimental

Preparation of the Pulp

Secondary fibers were used for the study; they were obtained from post-consumption cardboard scrap (OCC - Old Corrugated Container). The scraps were hydrated for a period of 12 hours in distilled water. Then the material was taken to a laboratory disintegrator, centrifuged, and stored in plastic bags under adequate refrigeration for further processing and formation of papers.

Refining in PFI Mill

The refining was done with PFI laboratory equipment, following the TAPPI 248 sp-00 standard. This study was conducted in three stages. Initially the effects of increasing doses of hemicelluloses (0, 1, 2.5, 5 and 10%) on the paper properties were assessed, maintaining the extent of refining fixed (800 revolutions). Subsequently the influence of the intensity of refining on the retention of the hemicelluloses and on the properties of the paper was evaluated. For this step the dosage of hemicelluloses was fixed at 10% of dry pulp, varying the extent of refining (0, 400, 800, and 1200 revolutions). Finally, the properties of papers produced with pulp extracted of hemicelluloses were analyzed, varying the intensity of refining (0, 400, 800, and 1200 revolutions).

Ultrasonic Treatment

The ultrasonic treatment was performed using the Virsonic 475 ultrasonic equipment, working with the power of 190 Watts and wave frequencies of 20kHz. Initially the effects of increasing doses of hemicelluloses (0, 1, 2.5, 5 and 10%) on the properties of paper were assessed, holding constant the time ultrasonification (30 minutes). Subsequently, to evaluate the influence of the time of ultrasonification in the retention of the hemicelluloses and in the properties of paper, the dosage of hemicelluloses was fixed at 10% (basis dry pulp) and the time of ultrasonification was varied (0, 10, 20 and 30 minutes). Finally, the properties of paper produced with pulp extracted of hemicelluloses were analyzed, varying the time of ultrassonification at 0, 10, 20, and 30 minutes.

Extraction and Addition of Hemicelluloses

The extraction of the hemicelluloses was performed using the CCE process (Cold Caustic Extraction), in which 300 g of the reference pulp, at a consistency of 10%, and 240 g of sodium hydroxide were combined at a temperature of 25 °C. After 30 minutes the collection of liquor rich in hemicelluloses was made.

The liquor had its hemicelluloses content quantified indirectly (7.80 g per liter of liquor) through differences in the carbohydrate content in the initial and final pulp (after the extraction of the hemicelluloses) by spectroscopic analysis performed in an HPLC device (High Performance Liquid Chromatography), according to Wallis et al [3] The liquor was stored at low temperature without pH correction, which was 13.5.

The addition of hemicelluloses was always performed after refining or after the ultrasonic treatment. The addition of hemicelluloses in the pulp was made by mixing the liquor from the CCE to a fibrous suspension contained in a beaker, under conditions that favor the adsorption of these carbohydrates to fibers. Based on information from the literature [4,5], a temperature of 60 °C, pH of 7.5, and 60 minutes of treatment were adopted. A consistency of 3% was employed, and continuous gentle agitation was maintained. The dosages of the tested hemicelluloses were 1%, 2.5%, 5%, and 10% (basis dry pulp).

Physical and Mechanical Tests

To conduct the tests under tensile or compression modes an Instron model 4204 device was used. An Elmendorf device was used to determine the tearing index. All tests were performed according to TAPPI Technical Standards [6].

Statistical Analysis

The adjusted equations were compared by F test, using the models identity test and adopting a significance level of up to 5% probability, according to the methodology for linear models [15].

The equations were compared in order to verify the equivalence between them. If found equal between them, the equations were reduced to a single equation (common model). If a significant difference between the equations were found, was not tested them equations were that differed.The tested hypotheses were: H0: all equations are equal and they may be represented by a common reduced equation, and H1: the equations are different statistically and they can't be reduced to a common equation.

Results and Discussion

The Effect of Hemicelluloses Dosages

Retention

The retention of the hemicelluloses occurred in all cases, though to a greater or lower extent, as can be seen in Figure 1.

The retention, expressed here as the difference between amounts of hemicelluloses in the pulps after treatment and in the initial pulp (without the addition of hemicelluloses), showed that the pulps refined in PFI (800 revolutions) and ultrasonificated (30 minutes) retained more hemicelluloses than the reference pulp. This fact can be explained because when subjected to ultrasonification or refining in the PFI mill, the fibers undergo changes in their external surfaces, increasing the fibrillation and, consequently, their surface areas, which increases the reaction sites of the fibers (Manfredi and Oliveira 2010).

As in all situations it was observed that the retention of hemicelluloses was increased as the dosages were increasing, and therefore it cannot be concluded that it reached a point of saturation, since if this had occurred, the retention would thereafter remain constant.

Still considering Figure 1, it can be inferred that the treatment in the PFI mill provided the best conditions for the retention of the hemicelluloses, and for better retention it is necessary submit the slurry to a previous treatment (refining in mill PFI or ultrasonification).

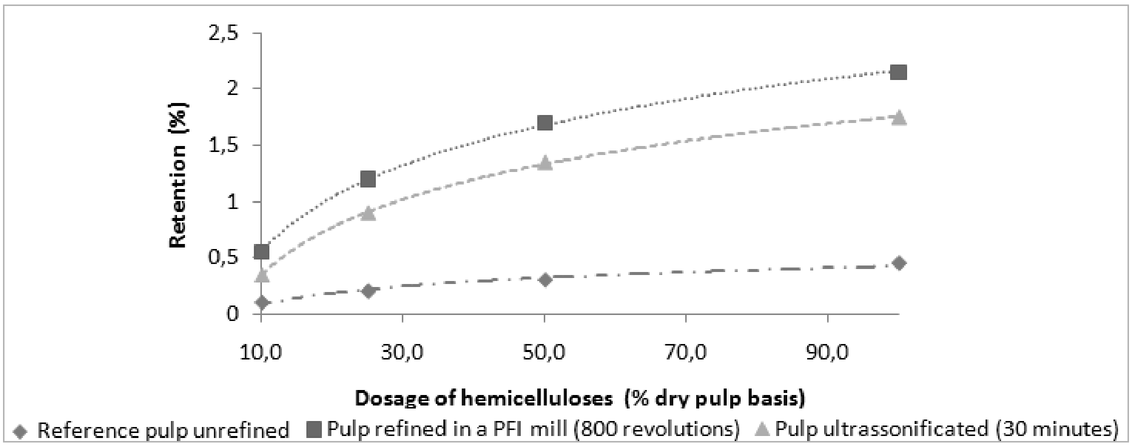

Figure 1. Retention of hemicelluloses versus the dosage for the unrefined reference pulps, refined in a PFI mill (800 revolutions) and ultrasonificated (30 minutes).

Retention efficiency of hemicelluloses by the pulp

The retention efficiency (Figure 2) was indicated in this study by the percentage of hemicelluloses retained in the final pulp compared to the amount added to the initial pulp.

Despite the increased retention observed in Figure 1, Figure 2 shows that the efficiency of retention was decreasing as the dosage of hemicelluloses was increasing.

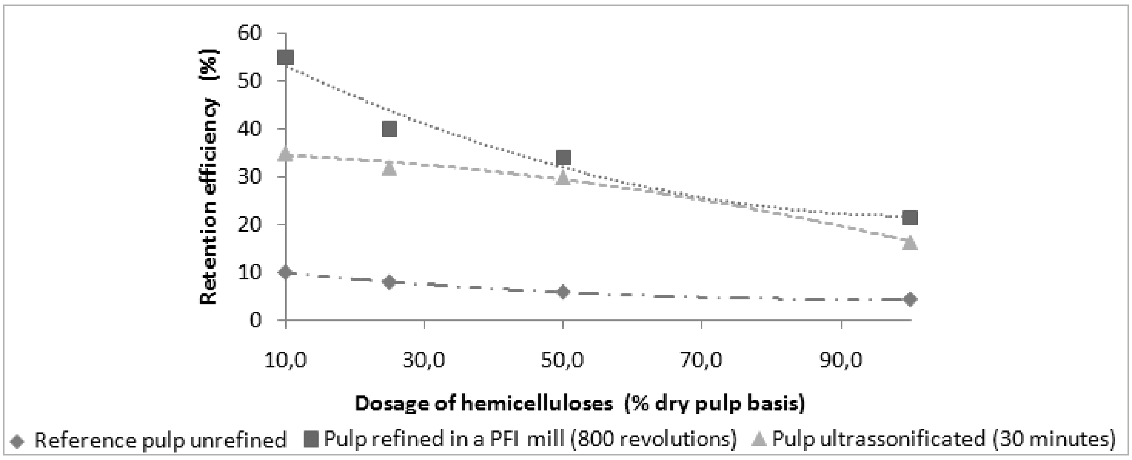

Figure 2. Retention efficiency as a function of the dosage of hemicelluloses for the unrefined reference pulps, refined in a PFI mill (800 revolutions), and ultrasonificated (30 minutes).

Physical and Mechanical Properties of the Paper

Tensile strength

The effect of added hemicelluloses on the tensile strength is widely reported in the literature [4,5,7-13]. As can be seen (Figure 3), to the extent that these carbohydrates were increased, the tensile strength was increased.

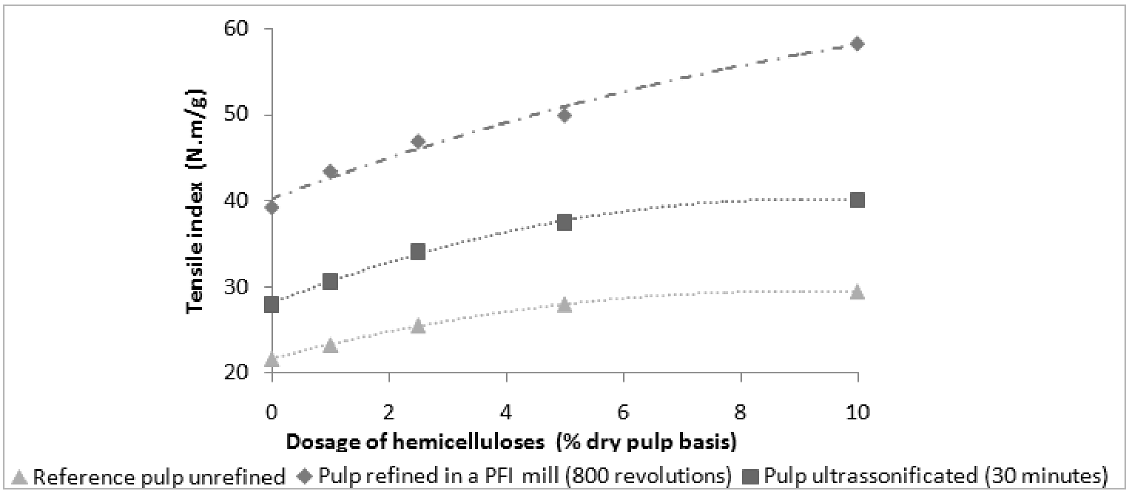

Figure 3. Tensile index as a function of dosage of hemicelluloses for the unrefined reference pulps, refined in PFI mill (800 revolutions), and ultrasonificated (30 minutes).

In this study, the maximum development of the tensile index was achieved with the dosage of 10% of base dry pulp in all situations. There was an increase of 49.98%, with the same dosage, for the pulp subjected to refining in PFI. There was also an increase of 43.14% for the pulp subjected to ultrasonification, and 35.45% for the unrefined reference pulp. These results showed the influence of retention percentage of the hemicelluloses in the increase of the tensile index and in the strengthening of the inter-fiber links. All the curves were statistically different according to the identity models test at the 5% level of probability.

Corrugated Medium Test (CMT)

The corrugated medium test was enhanced by the addition of hemicelluloses (Figure4). The refined pulp in PFI was the one that most developed this property, exhibiting an increase of 35.56%. The ultrasonificated pulp and the unrefined reference pulp showed maximum increases of 35.92% and 47.89%, respectively. All the curves were statistically different according to the identity models test at the 5% level of probability.

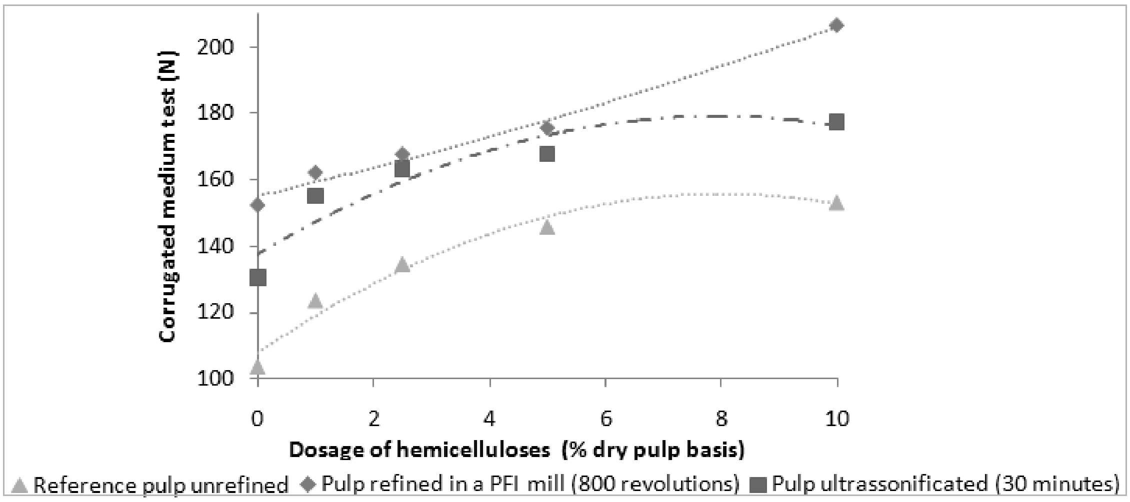

Figure 4. Corrugated medium test (CMT) as a function of hemicellulose dosages for the unrefined reference pulps, refined in a PFI mill (800 revolutions) and ultrasonificated (30 minutes).

Tear strength

Figure 5 presents curves for the tear index for the papers produced according to the changes in the dosage of hemicelluloses. The highest tear index values were found for the papers that had received a higher dose of hemicelluloses.

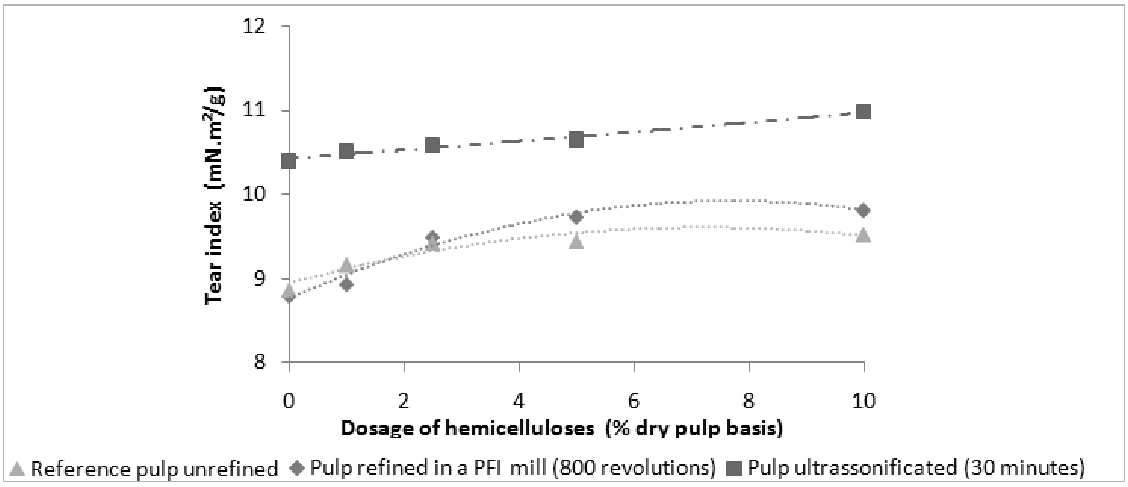

Figure 5. Tear index as a function of dosage of hemicelluloses for the unrefined reference pulps, refined in PFI mills (800 revolutions) and ultrasonificated (30 minutes).

The maximum development was achieved with the dose of 10% of base dry pulp in all situations. There was an increase of 11.60%, with the same dosage, for the pulp subjected to refining in PFI. There was also an increase of 5.58% for the pulp subjected to ultrasonification and 7.44% for the unrefined pulp reference. All the curves were statistically different according to the identity models test at a 5% level of probability.

Bulk

Figure 6 shows curves for the bulk (reciprocal of apparent density) for the papers produced as a function of the changes in the hemicellulose dosages. The highest values of bulk were obtained in the papers with the lower content of hemicelluloses.

It was observed that after refining in the PFI mill the addition of hemicelluloses provided a reduction of up to 9.04% in the bulk, while in ultrasonificated pulps the maximum reduction was 10.71% and in the reference pulp there was a reduction up to 12.63%. The lower percentage of reduction observed for the pulps refined in the PFI mill can be related to the limit of fiber collapse, since the refining operation already tends to collapse the fibers.

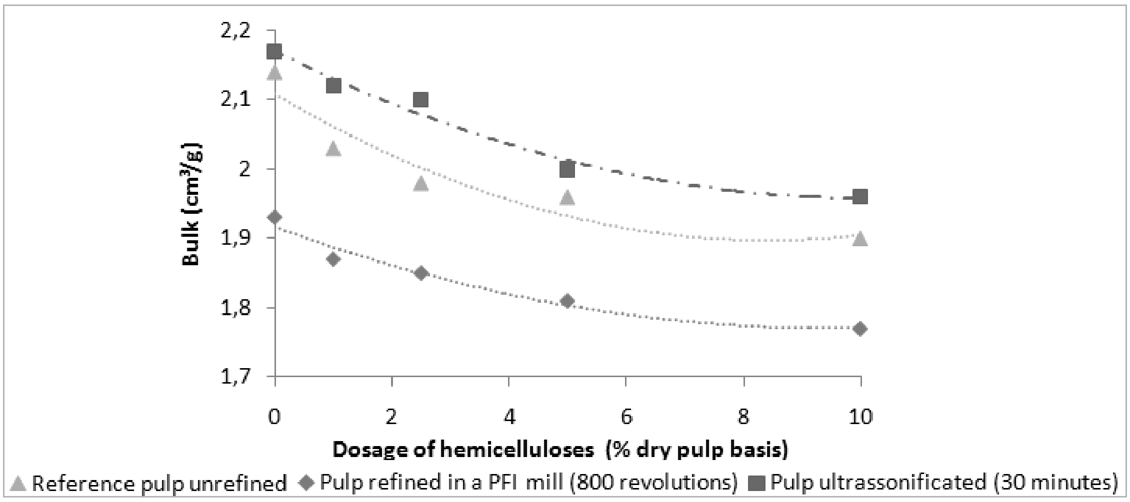

Figure 6. Bulk as a function of hemicellulose dosage for unrefined reference pulps, refined in a PFI mill (800 revolutions) and ultrassonificated (30 minutes)

The reduction of the bulk of the ultrasonificated pulps, despite the higher retention of hemicellulose when compared to the reference, occurred to a lesser extent than this. It could be explained by the effect of the diameter increase of the fibers when subjected to ultrasonic waves. All the curves were statistically different according to the identity models test at a 5% level of probability.

Influence of Refining in PFI and Ultrasonification

Drainage resistance

As might be expected, the drainage resistance as a function of the energy consumed in refining in a PFI mill and ultrasound increased with increasing extent of mechanical treatment in the pulps where the addition of hemicelluloses was performed as shown in Figure 7. It is observed that the pulps with lower levels of hemicelluloses refined more slowly than those that contained higher content of hemicelluloses.

The pulps, even when not refined or ultrasonificated, possessed high Schopper Riegler degree, showing that the drainability is complicated with the addition of hemicellulose. As can be seen, with the addition of hemicellulose alone there was an increase of 21.74% in the pulp drainage resistance when compared with the initial reference pulp.

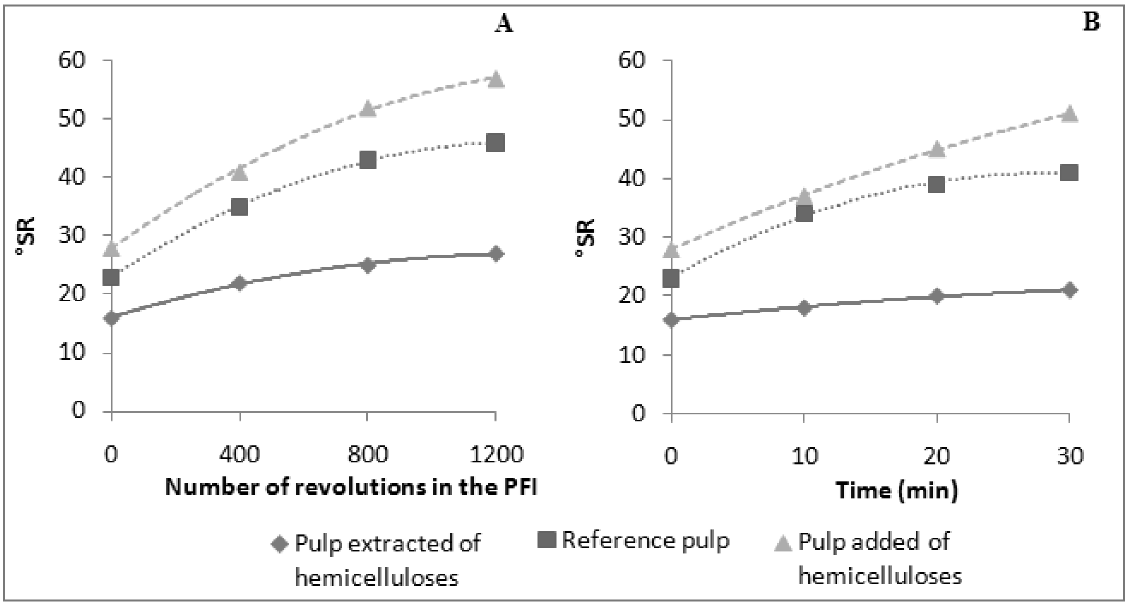

Figure 7. Evolution of the drainage resistance (°SR) as a function of the pulp refining (A) and ultrassonification (B).

An increase in drainage resistance was observed when the pulps were first refined in the PFI mill or ultrasonificated. The pulps refined in the PFI mill responded more quickly to the drainage resistance than those that were ultrasonificated, and this is justified by the mode of action of each technology.

For the same increment in the number of revolutions, the pulps refined in a PFI mill and which received hemicelluloses presented a maximum increase of 103.57% in the drainage resistance, consuming 15Wh of energy, while the reference pulp showed a 100% increase in drainage resistance, consuming the same amount of energy. The pulp extracted of hemicelluloses showed a 68.75% increase in drainage resistance, consuming 51Wh of energy.

Ultrasonificated pulps that had received hemicelluloses showed an increase of 82.14% in the drainage resistance of the pulp, while the reference pulp showed an increase of 78.26% and the pulp extracted of hemicelluloses showed an increase of 31.25% for the same time of ultrassonification and required energy. All the curves were statistically different according to the identity models test at a 5% level of probability.

Tensile index

Figure 8 presents the effect of the number of revolutions and ultrassonification time respectively of the reference pulps, of added hemicelluloses and of samples extracted of hemicellulose. The results showed that when performing the addition of hemicellulose, the need for refining and ultrasonification to obtain better results for the tensile index becomes smaller.

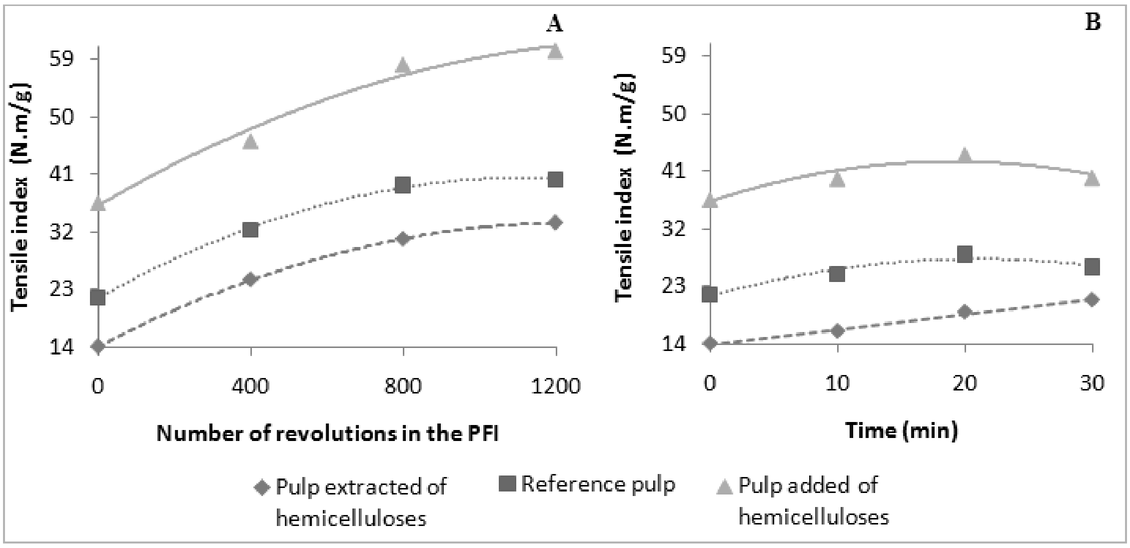

Figure 8. Evolution of the tensile index in function of pulp refining (A) and ultrassonification (B)

Note that the extraction of hemicelluloses resulted in a pulp with reduction of 54.59% of the tensile index when compared to the reference pulp and an increase of 68.78% in the same property for the pulp added with hemicelluloses. It was also observed that there is an influence of the content of hemicelluloses in the observed increments. The pulp from which the hemicelluloses had been extracted showed a maximum variation of 64.89%, the reference pulp showed 85.35%, and the pulp added of hemicelluloses showed an increase of 128.08% as a result of the refining in the PFI mill. The developments in the observed increments for the ultrassonificated pulps were less intense, but the influence of the hemicelluloses was also marked. The extracted pulp showed a maximum increase of 48.83%, the reference showed 28.91%, and the added with hemicelluloses presented 19.07% in the tensile index. All the curves were statistically different according to the identity models test at a 5% level of probability.

Corrugated Medium Test

Figure 9 represents the results for the corrugated medium test. The pulp from which the hemicelluloses had been extracted showed a corrugated medium test maximum of 108.08 N, while the pulp to which hemicelluloses head been added (100g/kg pulp) had a maximum compressive strength of 212.21 N, when refined at 1200 revolutions, showing a difference of 96.35% between them. As for the pulps previously ultrasonificated for 30 minutes, the pulp extracted from hemicelluloses showed a corrugated medium test maximum of 92.67 N, while the pulp to which hemicellulose had been added (10% based on dry pulp) had a maximum compressive strength of 177.42 N, representing a variation of 91.45% between them. All the curves were statistically different according to the identity models test at the 5% level of probability.

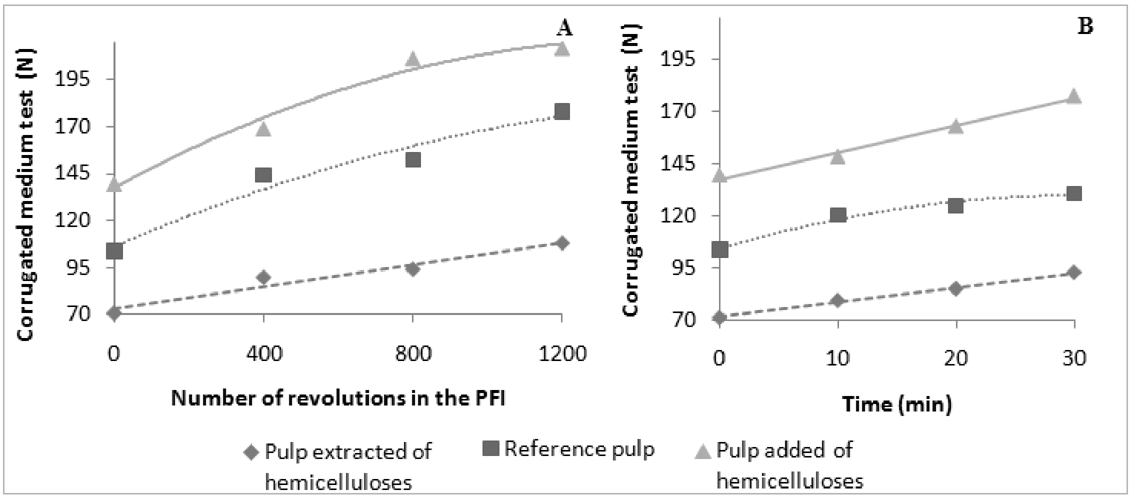

Figure 9. The Evolution of corrugated medium test (CMT) as a function of pulp refining (A) and ultrasonification (B)

Bulk

Figure 10 shows the obtained results for the bulk. As can be seen, the pulps to which hemicelluloses had been added showed lower values in the volumes when compared to pulp to which hemicellulose had not been added (reference) and the pulp from which these carbohydrates had been extracted.

Refining in the PFI mill resulted in reduction the bulk by 13.89% for sheets formed from the pulps extracted from hemicellulose, 14.95% for the reference, and 13.90% for sheets formed from the pulp added with hemicelluloses. On the other hand, the ultrasonification led to an increase of 3.70% for sheets formed from pulps extracted from hemicellulose and also an increase of 1.40% for the reference pulp. This increase is due to the form of action of the ultrasound waves on the fibers, which leads to an increase in the fibril diameter. The pulp added with hemicelluloses showed a decrease of 7.55% in the bulk, showing that this effect is directly related to the content of hemicelluloses in the pulp. All the curves were statistically different according to the identity models test at a 5% level of probability.

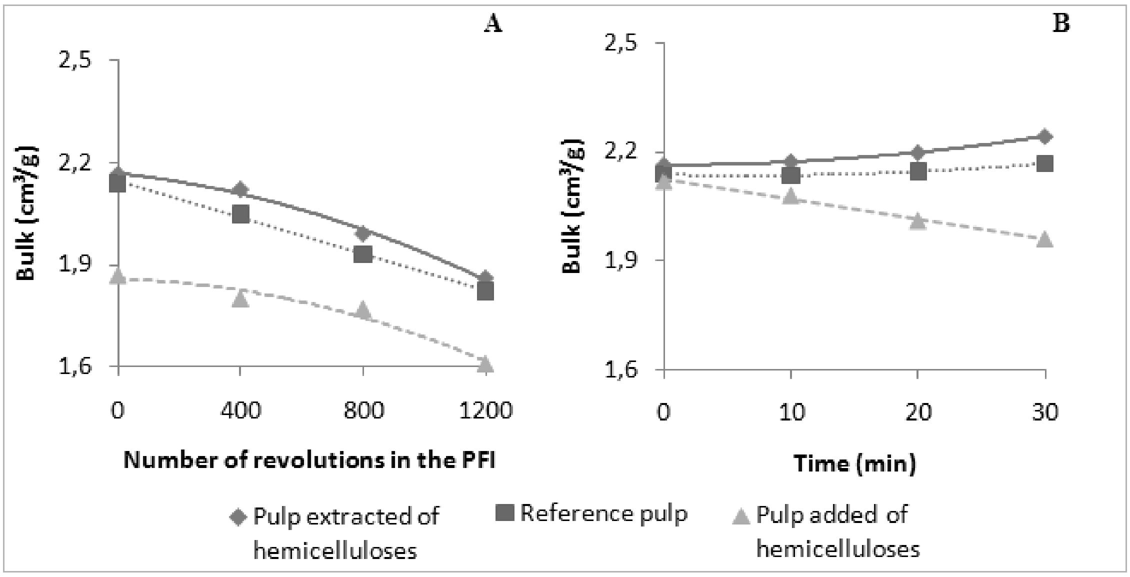

Figure 10. Evolution of the bulk of pulps as a function of refining (A) and ultrassonification (B)

In a general manner, physical and mechanical properties analyzed mainly influenced by the interfiber binding are more developed by refining in PFI mill than in ultrasound. It was also observed that the content of hemicelluloses in the pulp influenced in the paper properties so that the increase after the addition of these carbohydrates were the most significant in the pulps refined in PFI mills, since the ultrasonic treatment resulted in a lower retention of the hemicelluloses.

For some types of papers, the high levels of hemicelluloses may not be desired: tissue papers, decorative papers, filter papers, impregnated base papers, etc. [14], the removal of hemicelluloses could be a possible alternative to better match the characteristics of the pulp that such papers require. Therefore, the removal of hemicellulose from a pulp and the addition of these other offers in obtaining pulps with different characteristics that can be employed in manufacturing roles that require different features and applications.

The first showed physical and mechanical strength properties inferior to the reference pulp but it proved to be susceptible to the development of properties as with refining in PFI mill as well as the ones with ultrasound waves. This pulp produced paper with highest bulk and can be used purely or blended with other pulps for production, for example, paper crumb (differentiated Fluting). The second showed an increase in the strength properties of the paper, and demonstrated to require less energy during the refining process and it may be used, for example, for the preparation of the top ply of corrugated cardboard (differentiated Testliner).

Conclusions

Based on the previously exposed results it is possible to conclude that:

- Significant deposition of the hemicelluloses occurred in pulps, irrespective of mechanical treatment. Among samples submitted to refining in a PFI mill, with ultrasound, and without refining, the treatment in the PFI mill provided the best conditions for the retention of the dosed hemicelluloses.
- Both the combination of the refining in PFI mill and ultrasound, respectively, with the addition of hemicellulose were effective in the development of properties of recycled paper from post-consumer scrap paperboard.
- The drainage resistance, and the properties directly affected by interfiber bonding, such as tensile index, corrugated medium test, ring crush resistance, and tear resistance increased with increment of hemicellulose content, whatever the number of revolutions in the PFI and the considered time of ultrasonification.
- The pulp with lower content of hemicelluloses refined much more slowly than samples containing a higher content of hemicelluloses. The drainage resistance, density and tensile index increased with the increase in hemicellulose content, whatever is the number of revolutions in the PFI question.

- The increase of hemicellulose contents in the pulp generates papers with lower bulk, i.e. denser papers.
- The ultrasonification of the pulp achieved property gains of the paper similar to those observed when the paper was refined with the PFI mill, although it was in a less pronounced form.
- The gains from the addition of hemicellulose were less expressive in the ultrassonificated pulp, although the effects of addition of the hemicelluloses became more evident as the prior ultrassonification treatment of the pulp intensifies.
- The increases observed from the combination of refining in a PFI mill and of ultrasonic treatment, respectively, with the addition of hemicellulose made it possible to refine or ultrasonificate at a constant level (keeping the consumption of energy that was used), and to gain in terms of physical and mechanical strength of the paper or constant specifications of the papers properties, which leads to reduction of energy required for operations.
- The hemicelluloses extracted from own recycled pulp and measured in the pulp reference were able to develop the properties of physical and mechanical strength of the formed papers and represent more than one strategy to use recycled paper post-consumption.

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