Development of recycled paper properties by ultrasonic treatment and xylans addition

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Abstract

This study evaluates the potential of ultrasonic treatment and xylans addition to develop mechanical properties of recycled papers. Initially a study was conducted aiming to determine the better condition to performing the ultrasonic treatment. Were evaluated the effect of pH, pulp consistency and treatment time. Pulp consistency didn't affect the results. On the other hands, increasing pH and treatment time greater is the development of paper properties. After the optimization of ultrasonic treatment was performing a study to compare the effects of ultrasonification and the effects of PFI refine. The ultrasonic treatment was efficient to develop the mechanical strength of the paper. The properties were developed as a similar manner to that observed when pulp was refined in PFI, although less pronounced. The ultrasonic treatment acted mainly causing fiber external defibrillation. To the same bulk, the ultrasonification developed more the mechanical strength of the paper compared to PFI refine. Also was performed a study where aimed increase the recycled paper quality by addition of xylans to the pulp. The results showed that increasing the content of xylans the paper strength is enhanced as a more intense manner than observed by the PFI refine or ultrasonification of the pulp. Low charges of xylans were enough to increase significantly the paper strength. The development of properties due to xylans addition was enhanced by previously refine in PFI, reaching a maximum value of the properties with low levels of refine. The fact showed that xylans addition decreased the need of refine. The previously ultrasonification of the pulp didn't affect the results of xylans addition.

Keywords: eucalyptus; wood quality; kraft pulping; pulp utilization.

Introduction

At the last 10 years the recycled paper consumption in Brazil increased 60% [1]. The industries have working hard to develop new process and techniques to increase the recycled paper quality reaching a larger participation in the paper market. The creation of new technologies is an important way to reach a better process and paper quality.

Normally the recycled paper had less mechanical strength and optical quality than paper made by virgin fiber. Along the paper production process the fibers undergo structural modification that decreases the fiber ability to form a strong paper. The structural modification results in a reduction of intrinsic fiber strength and less fiber swelling and less external defibrillation [2]. The fiber swelling contributes to increase the contact area between the fibers. A larger contact area between fibers surfaces, even as the external defibrillation, favors the formation of the fibers bond, increasing the paper strength.

To recover the fibers ability for paper formation normally is used the refine operation. How ever, secondary fibers normally already were refined in a last production process that turns the fibers more susceptive to the negative effects of the refine. Even when conducted in low intensity, the refine of secondary fibers can cause damages in fibers structures and excessive fines production. To avoid this lost in fiber quality is necessary to develop a new technology able to further the fiber swelling and external defibrillation from a way that resulting in less fiber damage.

Some studies already proved the efficiency of ultrasonic vibration to develop paper [3-8]. Some of then showed that action of ultrasonic is similar to the mechanical refine but resulting in less damage in fibers structures [3-5, 8]. The ultrasonic treatment furthers the external defibrillation [3-6] and the internal defibrillation [4-6] of the fibers. These actions results in more fiber swelling and the formation of more bonds fiber to fiber. Comparing to the refine the ultrasonic treatment affects less the bulk to a same rise in a mechanical properties of the paper [3-5, 7]. This fact suggests that ultrasonic waves acts mainly further the external defibrillation than the collapses of the fibers wall. The ultrasonic technology is also attractive because permit control the fibers modifications by handle the frequency and power of the waves [8]. Another attractive is that the ultrasound can be applied in differs points in the process like tubes, tanks and towers.

The ultrasonification can be applied in line with refine (prefer ultrasound before refine) or as a substitute to the mechanical refine. The replacement of refine for ultrasonic treatment results in the largest change in paper properties than if the ultrasonic treatment is used together the refine (refine and ultrasonic treatment in the same line).

Other technology that can help to improve the recycled paper quality is the addition of xylans. The xylans have an important role in paper strength [9-19]. When in the fibers surface the xylans became an important structure to connect fiber to fiber [13, 18, 19]. When inside the fiber wall aid the fiber swelling. The fiber swelling further the collapse of the fiber wall and become the fiber more susceptive to the act of the refine and of the ultrasonification, reducing the energy consumption of these operation to reach the paper strength desired [10, 13, 19].

A lot of research was conducted aiming add xylans to the pulp [19-24]. These studies showed that xylans adsorption is favor for the use of high temperature, pH and treatment time. How ever, is possible to add xylans in the pulp using the condition typically used for the paper factores.

The goal of this study is develop the mechanical properties of recycled paper by ultrasonic treatment of the fibers and by xylans addition. Therewith, help the recycled paper industry to reach a larger participation on paper market.

Experimental

Material

The OCC (Old Corrugated Container) was choose as fiber source because this material is the main kind of paper recycled in Brazil. The Table 1 shows the morphological features of the OCC used.

Table 1. Morphological features of the fibers

Material (layers)	Average length (mm)	Average width (µm)	Coarseness (mg/100m)	Fines (%)
Internal linerboard	1,46	31,04	15,76	18,63
External linerboard	0,91	32,37	10,66	11,24
Corrugated	0,97	32,39	12,71	22,43
Complete OCC	1,09	32,01	12,96	19,21

Pulp preparation and sheetmaking

The OCC was left in distilled water for 12 hours. After that, it was disaggregated, dried (around 70% of moisture) and saved in plastic bag in the refrigerator. Handsheet with 120 g/m² were made to compression tests and with 60g/m² to another tests according to TAPPI 205 sp-95. The handsheets were kept in environmental controlled room with 23 ± 1 °C and humidity arond 50 ± 2 %.

Ultrasonic treatment

The equipment used to ultrasonification was the Virsonic 475 working at 190 Watts and wave frequency of 20kHz. At each operation was treated 1 liter of pulp at different consistency inside the beaker. The beaker was used on a magnetic stirrer to propitiate a homogenous treatment of the fibers. The probe tip was inserted into the diluted pulp at a temperature of 30°C. Along the treatment the temperature increases.

A preliminary test was conducted to determine the best treatment conditions. The effect of pulp consistency (0,5%, 1%, 2% e 4%), pH (7 and 10) and treatment time (5, 10 and 20 minutes) were evaluates. To the study of xylans addition the condition of ultrasonic treatment used was 3% of pulp consistency, pH 8 and 20 minutes.

PFI refine

The pulp was disaggregated as the same way used to prepare the pulp to ultrasonification. The refine was performed in PFI according TAPPI 248 sp-00. The numbers of revolution were choose aiming to reach similar value of tensile index of the the ultrasonificated pulp.

Xylan experiment

The xylans were obtained from an eucalyptus kraft pulp by a CCE (Cold Caustic Extraction). The equivalent of 300g of pulp completely dried was treated with 240g of sodium hydroxide at 25°C and 10% of consistency during 30 minutes. After that the pulp was centrifuged and the liquor rich in xylans was collected. The quantity of xylans in the liquor was measured by spectroscopy. The result showed around 15g of xylans per liter of liquor. The liquor was kept at low temperature at pH 13,7.

The xylans was added after the refine in PFI or the ultrasonic treatment. To add the xylans the right volume of liquor was add to the pulp at 3% consistency, 60°C of temperature, pH 8 and the mass was mixed for 1 hour. The quantity of xylans added were 1%, 2,5%, 5% an 10% base pulp weight. The pulps used in this study were the original pulp (unrefined and not ultrasonificated), refined pulp in PFI for 200 revolutions and an ultrasonificated pulp for 20 minutes.

In a second part of the xylans study were used pulp refined for 200, 400 and 600 revolution in PFI and pulp ultrasonificated for 5, 10 and 20 minutes. A quantity of 10% base pulp weight of xylans was added to these pulps aim to evaluated the effect of pretreatment of the pulp in xylans adsorption.

Physical and mechanical tests

To the tension tests was used the equipment Instron 4204 and the proceedings TAPPI T494 om-96. The same equipment was used to compressing tests. To determination of tear index, burst index and air permeance were used respectively the equipments Elmendorf, Mullen e porosity meter “Gurley”. The tests were performed according to Tappi Standarts showed in the Table 2. To statistic analyses was used the method of identity of regression model at 95% of significance.

Table 2 – Tests methods

Test	Method
Thickeness	TAPPI 551 om-06
Gramage	TAPPI 410 om-08
Burst Index	TAPPI 403 om-02
Tear Index (Elmendorf)	TAPPI 414 om-04
Air permeance (Gurley)	TAPPI 536 om-07
Tensile Index	TAPPI 494 om-06
Elongation	TAPPI 494 om-06
Tensile Energy Absorption (TEA)	TAPPI 494 om-06
Tensile Stiffeness	TAPPI 494 om-06
Ring Crush Test (RCT)	TAPPI 822 om-93
Corrugated Medium Test (CMT)	TAPPI 809 om-93
Specific density	TAPPI 220 sp-06
Bulk	TAPPI 220 sp-06
z-direction tensile adapted	TAPPI 541 om-05

Chemical analyzes

The carbohydrates analyses were performed at equipment High Performance Liquid Chromatography (HPLC) according to standard from Pulp and Paper Laboratory at Viçosa. The proceeding basically consist to perform at acid hydrolyze to convert polymers to quantifiable monomers.

Fibrous material analyzes

Were determinate the fines rate and coarseness of the pulp and average length and average width of the fibers. Fines were considered every material with length smaller than 0,07mm. To determinate the fibers dimensions the software considered only material between 0,07mm and 3mm of length. The analyses were performed in equipment Galai CIS-100 and software Wshape. For that, the pulps were diluted to 0,001% of consistence. These pulps were left for at least 8 hours in rest before each analyze.

Results and Discussion

Ultrasonic treatment

The Figure 1 shows that the ultrasonic treatment increased the paper resistance to compression forces (evaluated by the Ring Crush Test). Comparing the effects when the treatment was performed in pH 7 (Figure 1a) and in pH 10 (Figure 1b) notice a similar behavior, but more intense in alkaline condition. The pH effect is evident when the pulps not ultrassofinicated (time zero) are compared. In alkaline conditions the fibers wall are more hydrated and easily can be collapsed. According to the statistic analyze there is no difference in the results found to different pulp consistency. Therefore, every pulp consistency evaluated are represented for only one line in the graphics.

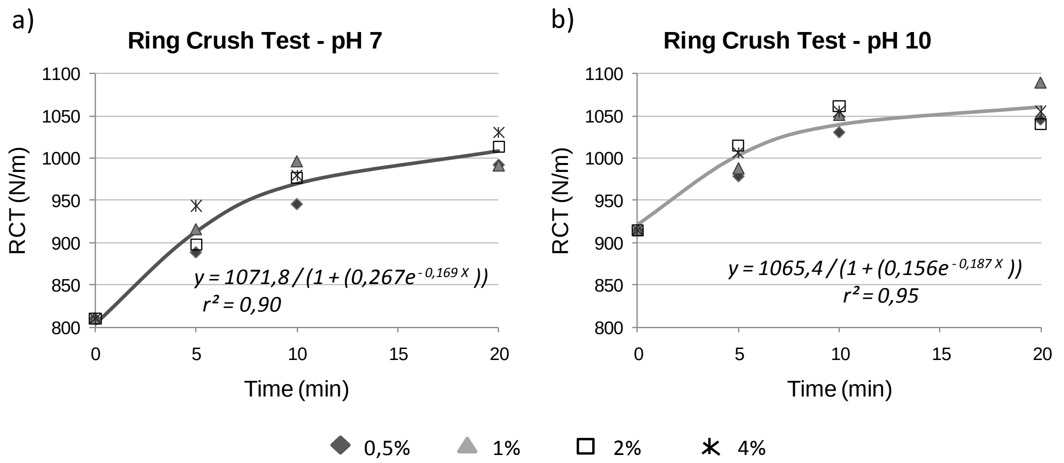

Figure 1. Effect of the ultrasonic treatment in the pulp resistance to compression (RCT) when the treatments were performed in pH 7 (a) and pH 10 (b)

The Figure 2 shows that the ultrasonification increased the tensile index of the pulp. According to the statistics analyze the pulp consistency didn't affected the results. In the other hand, the pulp pH hardily affected the development of paper strength. When the treatment is conduced in alkaline condition, the effect is observed even in the firsts minutes (Figure 2b). The fact suggest that the pH not influences the tensile index just by the effect of swelling the fiber wall, but it even becomes the fiber wall more susceptive to the action of the ultrasonic waves. Therewith, alkaline conditions enables to use lower treatment times.

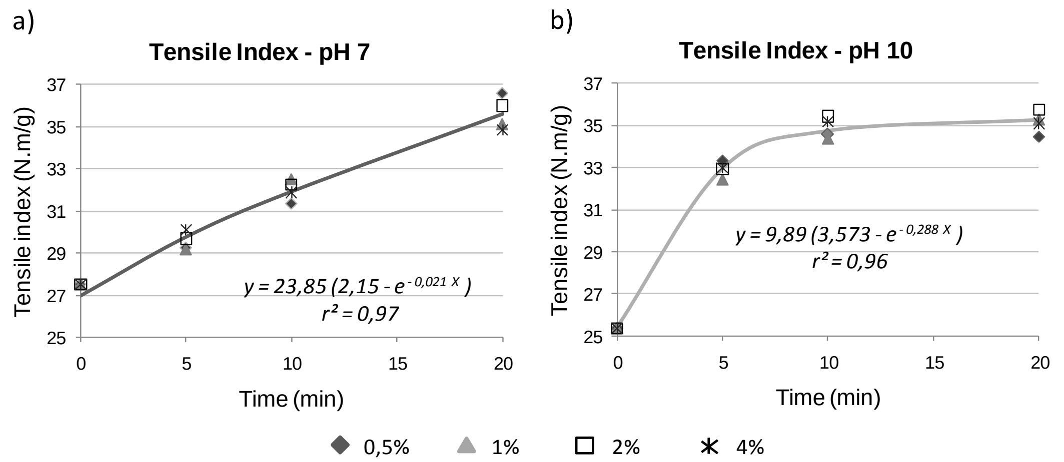

Figure 2. Effect of the ultrasonic treatment in the tensile index of the pulp in pH 7 (a) and pH 10 (b)

At the Figure 3 is possible to notice that the ultrasonic treatment increased very low the tear index of the pulp. This result must be associated to the best fiber network formation. Important is notice that the ultrasonification didn't decreased the tear index while increasing the treatment time suggesting that the treatment didn't hardly affected the intrinsic fiber strength.

The results of this experiment showed that the ultrasonic treatment can increase the pulp strength as reported in the literature [3-8]. How ever, this properties development is a little different from the observed when the conventional refine is used. The Figures 4, 5 e 6 compares these two technologies using the Schopper Riegler (°SR) as reference.

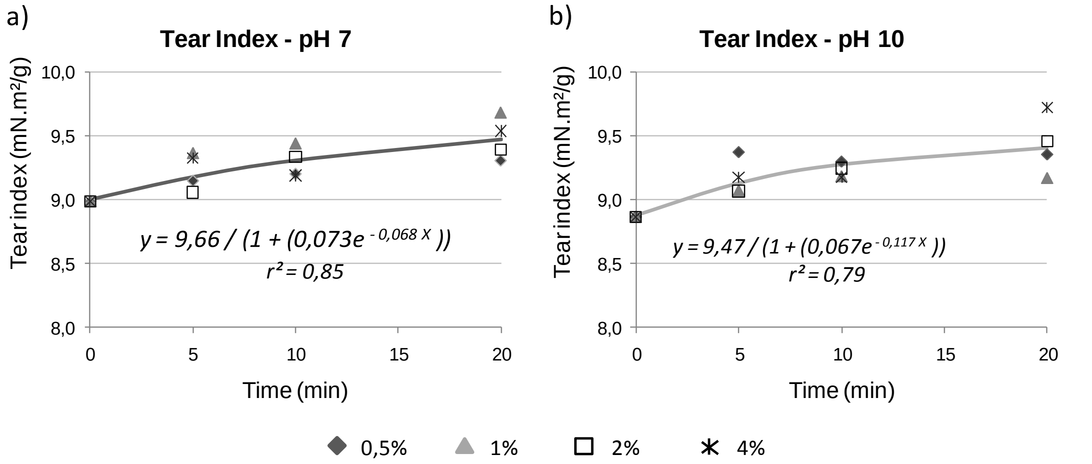

Figure 3. Effect of the ultrasonic treatment in the tear index of the pulp in pH 7 (a) and pH 10 (b)

The Figure 4 shows that the ultrasonic treatment is less efficient to increase the pulp resistance to the compression forces (RCT) than the PFI refine.

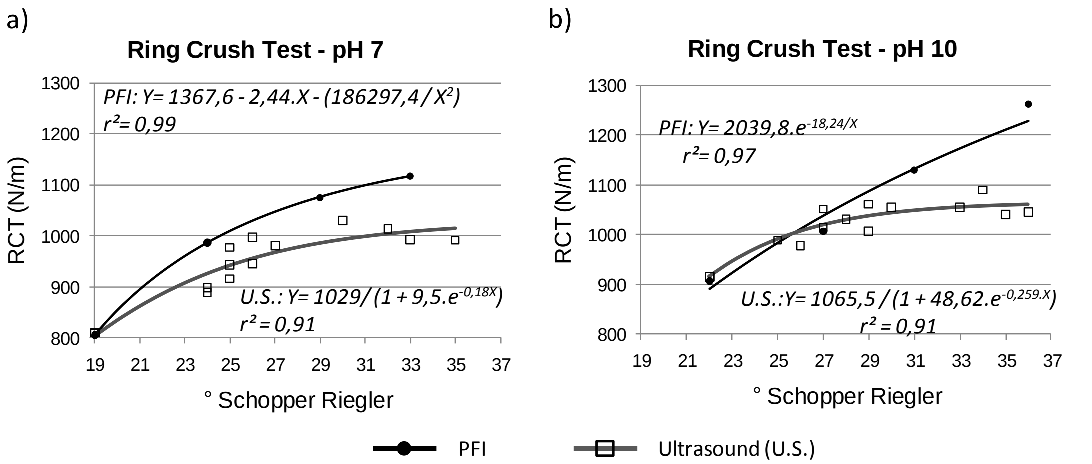

Figure 4. Effects of the ultrasonic treatment and PFI refine in the strength of the pulp in pH 7(a) and pH 10(b).

The Figure 5 shows that to the same effect in °SR the PFI refine increased more the tensile index of the pulp than the ultrasonic treatment. However, the ultrasonic treatment also resulted in a significant increasing of the tensile index.

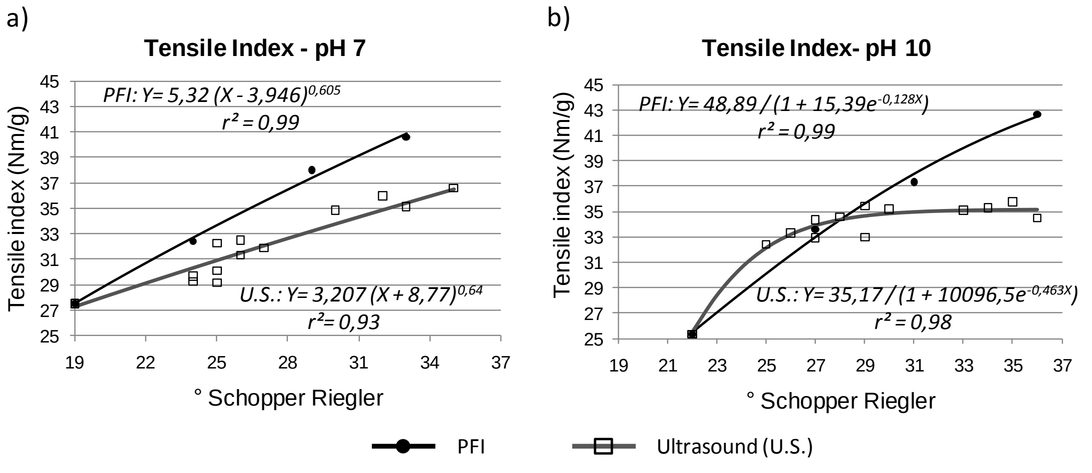

Figure 5. Effects of the ultrasonic and PFI refine in the tensile index of the pulp in pH 7(a) and pH 10(b).

The Figure 6 compare the effects of PFI refine and ultrasonification in the bulk. To the same increases in the °SR the ultrasonic treatment affected less the bulk than the PFI refine. The fact suggests that the ultrasonic treatment results in less fiber wall collapses or, and, less fines production than the PFI refine.

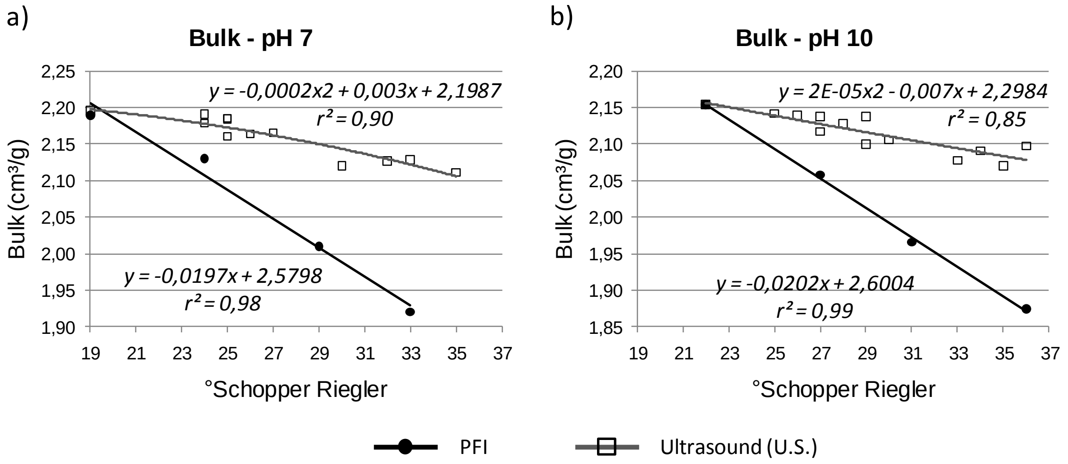

Figure 6. Effects of the ultrasonic treatment and PFI refine in the bulk of the pulp in pH 7 (a) and pH 10 (b).

The analyses of the fibrous material showed that to the same °SR the ultrasonic treatment produces more fines than the PFI (Figure 7). So, if to the same °SR the ultrasonificated pulp has more fines and nevertheless higher bulk, concludes that the fibers ultrasonificated are less collapsed than fibers refined.

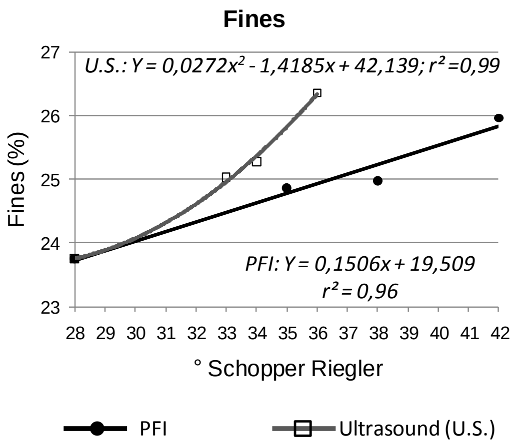

Figure 7. Fines rate of the ultrasonificated pulp and refined pulp

Based on the results and discussion above, the hypothesis created is that the ultrasonic treatment furthers the development of paper properties mainly by creating external defibrillation. This conclusion is similar to observation from other authors [3-7] that reporting that the ultrasonic treatment acts defibrillating the external layers of the fibers producing fine and increasing the paper strength.

Xylans addition

The results demonstrated that only a rate of xylans added was adsorbed for the fibers during the handsheet formation. This behavior was expected because the addition treatment was performed in condition able to exist in industries, differing that the optimal conditions to add xylans to the pulp.

The figure 8 indicates that refined pulp and ultrasonificated pulp retained more xylans than the original pulp (not refined and not ultrasonificated). When the pulp was previously treated for ultrasonic waves or refined in PFI the fiber have an external surface more defibrillated, creating more point to adsorb the xylans. More over, refined or ultrasonificated pulp have a fiber network less porosity during the drainage of the mass, what helps to retain more polymers of xylans. In the Figure 8 is also possible to notice that while the xylans dosage is increased more difficult becomes the xylans adsorption. The explanation for that is that while increasing the rate of xylans decrease the number of adsorption points result in higher difficult to xylans chains find a point to connect to the fiber.

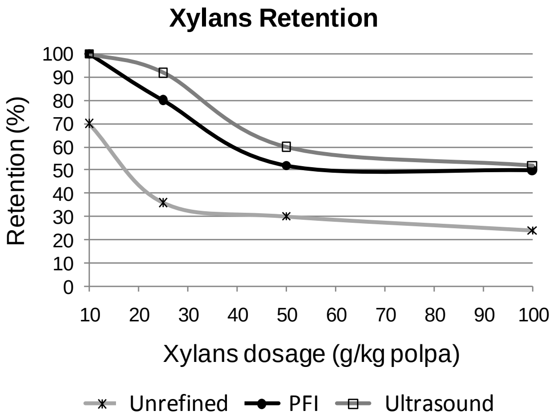

Figure 8. Xylans retention in original pulp, refined pulp and ultrasonificated pulp.

The addition of xylans even in low quantities increases the paper strength. The Figure 9 shows the effect of addition of xylans in the tensile index of the paper. The pulp refined in PFI for 200 revolutions had the maximum increase in the tensile index (42%). Even when was added only 1% of xylans (base pulp weight) the tensile index of the pulp refined (200 revolution), ultrasonificated (20 minutes) and original pulp (unrefined and not ultrasonificated) increased respectively 18%, 15% e 8%. The results suggest that is not necessary use high dosage of xylans.

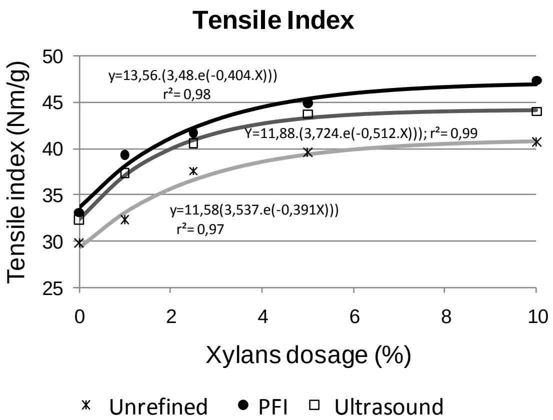

Figure 9. Effect of addition of xylans using different dosages on tensile index.

The paper resistance to compression forces (evaluated by the RCT) also was benefit for the xylans addition (Figure 10). In this case, the addition of 2,5% of xylans increased 46% the RCT resistance of the original pulp (unrefined and not ultrasonificated), even with only 40% of xylans retained (Figure 8). To the pulp previously refined was observed an increment of 90% in the RCT. To the ultrasonificated pulp the increment in RCT was 27% to dosage of 1% of xylans and 47% to dosage of 10% of xylans.

To evaluate the role of xylans as a fiber to fiber connector was performed a test where the tension is applied in the z-directon of the paper. The paper strength measured by this test is mainly influenced by the strength of the bonds between the fibers. The results confirmed that the xylans addition increase the strength of the bonds (Figure 11). The paper strength evaluated by this test increased 48% and 50% respectively in the original pulp and refined pulp after the addition of xylans. In the case of ultrasonificated pulp the increment was 43%. Even in low dosage, as in the case when the dosage of xylans was only 1%, the strength of the ultrasonificated pulp increased 27% while the strength of refined pulp increased 18% and the strength of the original pulp increased 17%. This higher increment of the paper strength observed in the ultrasonificated pulp can be explained for the lower strength of this pulp before the addition xylans. The original pulp was the material how had the lesser increment because it had the lowest adsorption of xylans.

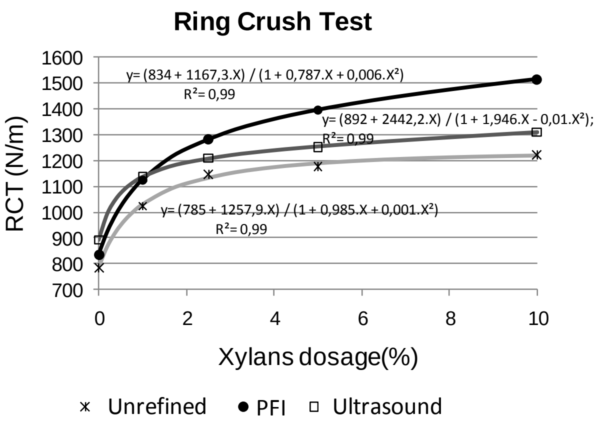

Figure 10. Effect of addition of xylans in the paper resistance to compression forces (RCT).

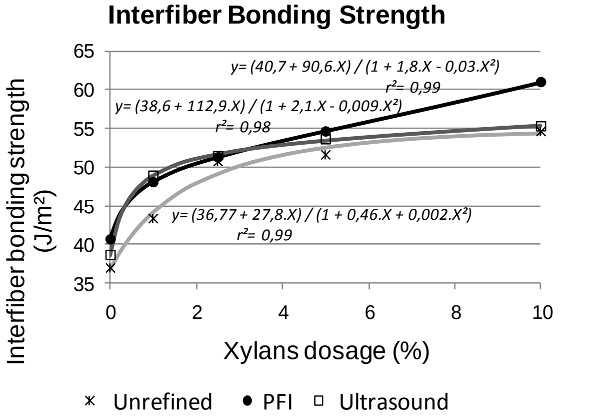

Figure 11. Effect of the addition of xylans in the strength of the fiber to fiber connections.

Another methodology used in this study with xylans was to add the same quantity of xylans in pulps refined at differs intensity or ultrasonificated at differs time, to evaluated the effect of these pretreatment of the pulp in the results of addition of xylans. The Figure 12(a) e 12(b) show the effect of PFI refine and ultrasonic treatment respectively, in the RCT of the pulps without addition of xylans and pulps that received the xylans,. The results showed that addition oh xylans is more efficient than the refine (until 600 revolutions) or the ultrasonic treatment (until 20 minute) to increase the RCT of the pulp. While just the addition of xylans increased the RCT of the original pulp in 53%, the PFI increased only 44% and the ultrasonic treatment increased 25%.

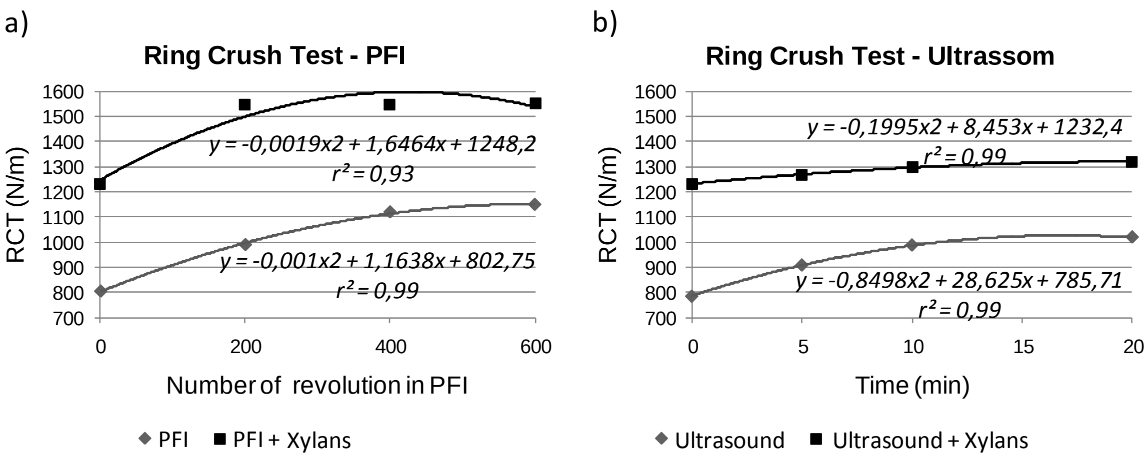

Figure 12. Effect of the addition of xylans, PFI refine and ultrasonic treatment in the RCT of the pulp.

The Figure 13 presents the effect of the addition of xylans on the tensile index of the paper. The addition of xylans was as efficient as the PFI refine until 600 revolution (Figure 13a) and more efficient than ultrasonic treatment (Figure 13b) to increase the tensile index of the pulp.

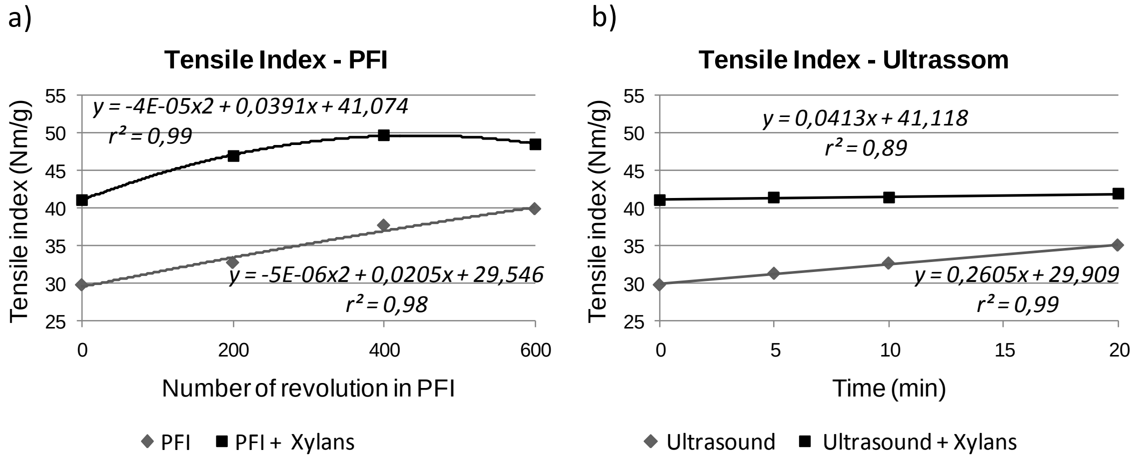

Figure 13. Effect of the addition of xylans, PFI refine and ultrasonic treatment in the tensile index of the pulp.

The results showed that the addition of xylans contributes significantly to increase the paper strength. This effect happens mainly due to the xylans ability for increase the strength of the fiber to fiber bonds. The tensile index of the pulps refined for 200 revolutions and refined for 600 revolution was the same after the addition of xylans. This facts indicates that when xylans is add the intensity of refine is lower to reach some value of tensile index.

As presented in the Figure 12 (b) and 13 (b), the value of the properties of the pulp not ultrasonificated (time 0) and pulps ultrasonificated for 5, 10 and 20 minutes were very similar after the addition of xylans (ultrasound + xylanss). It means that the previously ultrasonification of the pulp didn't further the positive effects of the addition of xylans as observed with the previously PFI refine.

Conclusions

The ultrasonic treatment of the pulp showed be efficient to develop the mechanical properties of the recycled paper. The effects of the ultrasonification of the pulp are higher when the treatment is performed in alkaline condition. The pulp consistency didn't affected the action of the ultrasonic waves.

The mechanical refine can be replaced for the ultrasonic treatment resulting in recycled papers with a higher bulk to a same strength.

Add xylans to the pulp even in low dosage increase significantly the recycled paper strength. The development of paper properties due to the addition of xylans was similar to the development achieved by the refine in PFI and higher than the observed due to ultrasonic treatment.

The retention of xylans is favored for a previously PFI refine or ultrasonification of the pulp.

Treat the pulp with ultrasonic waves or add xylans to the pulp increase significantly the recycled paper.

References

1. Brazilian Association of Pulp and Paper (BRACELPA). <http://www.bracelpa.org.br> (2009)
2. Minor, J. L. and Atalla, R. H. Strength loss in recycled fibers and methods of restoration. In: Material research society symposium, Pittsburgh, pp. 215-228 (1992)
3. Laine, J. E.; Macleod, J. M.; Bolker, H. I.; Goring, D. A. I. Application of ultrasound in pulp and paper technology. Paper Ja Puu: Paper och Trä, Specialnummer, Helsinki, v. 59, pp. 235-247 (1977)
4. Laine, J. E. & Goring, D. A. I. Influence of ultrasonic irradiation on the properties of cellulosic fibres. Cellulose Chemistry and Technology 11 (5), pp. 561-567 (1977).
5. Peixoto, R. S. Utilização de vibrações ultra-sônicas para o refino de celulose kraft de eucalipto. Master Thesis, Universidade Federal de Viçosa, Viçosa Brazil, (2009)
6. Tatsumi, D.; Takashi, H.; Kawamura, S.; Matsumoto, T. Ultrasonic treatment to improve the quality of recycled pulp fiber. Japan, Journal of Wood Science 46 (5), pp. 405-409 (2000).
7. Won, J-M; Lee, M-K. Effect of ultrasonic treatment on the pulp properties. Journal of Korea Tappi 28 (2) (1996).

8. Brodeur, P. H.; Gerhardstein, J. P. Overview of applications of ultrasonics in pulp and paper industry. In: Ultrasonics Symposium (1998).
9. Milanez, A. F.; Barth, P. P. O.; Pinho, N. C.; Vesz, J. B. V. Influência das hemiceluloses nas propriedades óticas e físico-mecânicas da polpa. In: 15th Pulp and Paper International Congress and Exhibition, São Paulo, pp. 155-170 (1982).
10. Molina, E. M. A.; Mogollón, G.; Colodette, J. L. Efecto de las hemiceluloses en la refinabilidad y propiedades físico-mecánicas de pulpa kraft de eucalyptus spp.. In: Iberoamerican Congress in Pulp and Paper Research, CIADICYP, Mexico (2008).
11. Molin, U. and Teder, A. Importance of cellulose/xylans ratio for pulp strength, Nordic Pulp and Paper Research Journal 17 (1), pp. 14 (2002)
12. Schönberg, C.; Oksanem, T.; Suurnäkki, A.; Kettunem, H.; Buchert, J. The importance of xylan for the strength properties of spruce kraft fibres. Holzforschung 55, pp. 639-644 (2001)
13. Anjos, O.; Santos. A.; Simões. R. Efeito do teor de hemiceluloses na qualidade do papel produzido com fibra de Eucalipto. In: 5th National Forest Congress (2005)
14. Annergren, G.; Rydholm, S.; Vardheim, S. Influence of raw material and pulping process on the chemical composition and physical properties of paper pulps. Svensk Papperstidning 66 (6), pp. 196-210 (1962)
15. Bhaduri, S. K.; Ghosh, I.N.; Deb Sarkar, N. L. Ramie hemicelullose as beater additive in paper making from jute-stick kraft pulp. Industrial Crops and Products 4, pp. 79-84 (1995)
16. Sihtola, H. and Blomberg, L. Xylans precipitated from steeping liquor in the viscose process as additives in papermaking. Cellulose Chem. and Technology 9 (5), pp. 555-560 (1975)
17. Sjöberg, J.; Kleen, M.; Dahlman, O.; Agnemo, R.; Sundvall, H. Analysis of carbohydrate and lignin in the surface and inner layers of softwood pulp fibers obtained employing various alkaline cooking process. Nordic Pulp and Paper Research Journal 17, pp. 295-301 (2002)
18. Spiegelberg, H. L. The effect of xylans on the mechanical properties of individual pulp fibres, Tappi Journal, 49 (9), Atlanta, pp. 388 (1966)
19. Köhnke, T.; Pujolras, C.; Roubroeks, J. P.; Gatenholm, P. The effect of barley husk arabinoxylan adsorption on the properties of cellulose fibres. Cellulose 15 (4), pp. 537-546 (2008)
20. Aurell, R. Increasing kraft pulp yield by redeposition of xylans. Tappi Journal 48 (2), Atlanta, pp.80-84 (1965)
21. Hansson, J. A. and Hartler, N. Sorption of xylans on cellulose fibers. Svensk Papperstidning 72 (17), pp. 521-530 (1969)
22. Linder, A.; Bergman, R.; Bodin, A.; Gatenholm, P. Mechanism of assembly of xylan onto cellulose surfaces. Langmuir 19 (12), pp. 5072-5077 (2003)
23. Yllner, S. and Enström, B. Studies of the adsorption of xylan on cellulose fibres during the sulphate cook. Part. 1, Svensk Papperstidning 59 (6), pp. 229 (1956)
24. Yllner, S. and Enström, B. Studies of the adsorption of xylan on cellulose fibres during the sulphate cook. Part. 2, Svensk Papperstidning, 60 (6), pp. 449 (1957)

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