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## Evaluation of physical properties of bleached eucalyptus fibers after thermal treatment

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### ABSTRACT

It has been shown that the thermal treatment (<100 °C) of cellulose fibers for periods shorter than 24 hours causes, additionally to the yellowing, the increment in tensile strength, elasticity modulus, toughness and resiliency, besides less plastic deformation in fibers after traction. These phenomena were interpreted from changes in hydrogen bonding monitored by FTIR. Aiming at evaluating changes in the mechanical strength of bleached eucalyptus fibers, samples were subjected to thermal treatment at temperatures ranging from 60°C to 100°C. The optical and mechanical properties, structure of linkages and crystallinity were monitored. Each year, new applications are developed by inserting the pulp as fibrous or not raw material, in increasingly diversified segments. The increase in the strength of the samples after thermal treatment has been justified by the increased interfiber interaction and possibility of formation of interplanar hydrogen bonding. The thermal treatment, in the settings used here, representing a good alternative for predicting the behavior of cellulose pulp optical properties.

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### KEYWORDS

Cellulose fibers;  
Thermal treatment;  
Bleached eucalyptus;  
Mechanical properties.

### INTRODUCTION

Cellulose is a linear β-1,4-glucan, and is the most abundant polymer available worldwide. Its strength, low density, biodegradability, high sustainability and easy conversion into other products<sup>[17, 21]</sup> can be considered. According to<sup>[22]</sup> these features have increased the interest in its incorporation in advanced materials such as composites, nanocomposites, biomaterials and engineering articles.

In fact, the cellulose is marketed in the form of fibers and the strength of these fibers is closely linked to peculiarities of the raw material and to forms of processing. Actually, the evaluation of the strength of the fibers<sup>[13]</sup> besides anatomical factors, their arrangement in the production of the samples is of great importance due to influencing the tropic state.

Many studies on the effect of heat on the structure of cellulose have been carried out in the recent literature in order to understand the pyrolytic process. The

main objectives are the controlling of thermal stability, mainly for wooden, paper, and textile materials<sup>[24]</sup>. Although many other recent studies on the thermal degradation of cellulose have been carried out, the detailed pathway of this process is not understood clearly as pointed out by<sup>[24]</sup>. Because the thermal degradation of cellulose occurs through a series of complex features, it is difficult to evaluate the mechanism of pyrolysis degradation. Low-temperature delays the initial process, corresponding to a reduction in the degree of polymerization and the formation of the so-called 'anhydrocellulose' or 'active cellulose'. High temperature pyrolysis of cellulose is expressed by two competitive degradation reactions: the first essentially to char and gas, the second to tars<sup>[20]</sup>.

Fiber strength of the natural fibers can be modified by thermal treatment<sup>[14]</sup>. Suggest the lack of interplanar hydrogen bonding in cellulose I<sub>β</sub> in crystal structure and hydrogen-bonding system in cellulose I from synchrotron x-ray and neutron diffraction<sup>[3,25]</sup>. Showed that the hydroxyl in (C6) undergoes changes due to heating, being essentially positioning perpendicularly to the scheme of the glycosidic ring. This repositioning enables the arising of interplanar bonding and consequent increase in the elasticity modulus of the fiber. Mechanical damages such as folds and collapsing also should be evaluated, once they change the effort distribution during the tests<sup>[1,4,6,18,19]</sup>.

Many works have been performed in order to describe the strength mechanisms in materials composed by a fibrous chain. These works have, in fact, culminated in the arising of two lines, being one based on structural models and the other one on molecular models. The structural models are more focused on the test mechanics, while the molecular models are based on assumptions related to the energies of the bonds. Each molecular or structural theory will fit better depending on way the effort is applied. However, both of them converge to a common factor, the interfiber interaction<sup>[15,16,18]</sup>.

It is reasonable assume that the strength of chain of cellulose fibers is strongly influenced by the interfiber interaction, mainly hydrogen bonding. At the time of the fracture of the samples, these bonds are broken especially due to the magnitude of their energy when compared, for example, to the glycosidic bonding present

in the cellulose chain. However, the mechanics of each test may favor the loading of a particular group of bonding. In the tensile test, for example, the hydrogen bonds, the most important interaction between cellulosic chains, have an important role. On the hand, in the tensile test with zero spacing, the intramolecular bonding (hydrogen bonding, electrostatic interactions and covalent bonding) and structural defects start to play a more important role, once the fibers receive the effort directly from the testing machine. In addition, another important fact is that the intrafiber hydrogen bonding may be gradually broken considering that fracture does not occur obligatorily, but only a residual plastic deformation<sup>[5]</sup>.

Exposure to distinct environmental conditions may modify the properties of the cellulosic pulp causing changes in its appearance and in its intra and intermolecular bonding structure. These changes are related to hydrolytic, thermal, photo-induced and bacterial processes or to their combination. Such processes have the ability to modify the optical and mechanical properties of pulps, and the monitoring of each of these mechanisms would require a specific analytical route for their evaluation.

In the behavior of fiber properties over time, it is very common use incubator tests at high temperatures, ignoring the specificity of each method. This problem becomes very clear when obtaining predictive data regarding the mechanical properties. It is common to find, complementarily, information on physical properties derived from thermal tests even if they do not represent the reality to which the fibers are subjected over time. These findings generally point out the hysteresis process<sup>[11]</sup>, justifying the hysteresis effects on successive pulp drying and rehydration. Thus, few studies report<sup>[23]</sup> on the effect of thermal treatment about the strength of non-rehydrated fibrous materials, especially those composed of short fibers, such as eucalyptus fibers, information that would be very useful for inferences about the properties of materials.

Aiming at evaluating the changes in the strength of bleached eucalyptus fibers, fibers sheets were subjected to thermal treatment at temperatures ranging from 60°C to 100°C in our studies. Following, tensile strength, elasticity modulus, resilience, toughness and tensile zero span were evaluated. The variations in

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crystallinity and length of fibers after deformation in the tensile test were also evaluated. It is common knowledge that the cellulosic pulp exposure to different environmental conditions may modify its properties. The change modifications in the fibers properties are very important to pulp and paper industry in a general way. In addition, only some papers have reported the effect of thermal treatment on the strength of fibrous cellulosic materials.

## MATERIALS AND METHODS

### Materials

Bleached eucalyptus pulp (ECF) collected before the drying line at Celulose Nipo-Brasileira - Cenibra S/A. was used in this work. After sampling, the fibers were classified in a 60 mesh sieve to remove fines. Then, metals were removed by acid leaching (pH: 2.0; T: 25°C, 48 hours). In the end, the pulp was neutralized by using a diluted sodium hydroxide solution and centrifuged to 30% consistency. The cellulosic fibers sheets (grammage = 60g/sqm and 200 g/sqcm) were exposed to thermal treatments and analysis.

### Methods

The samples were thermally treated in a not sealed incubator with temperature control in periods ranging from 0 to 24 hours and sampling intervals of 6 hours. The temperatures used in the tests for each retention time were 60°C, 80°C and 100°C ± 0.2°C. Ten samples for fibers sheets were analyzed for each time-temperature set.

After treatment, the whiteness, CIELAB-b yellowness rate, tensile strength, tensile strength, tensile zero-span, tear rate and crystallinity were determined. The standards used are described: Preparations of Samples: Tappi T205 sp-02 and Tappi T220 sp-01; Tensile strength: Tappi T494 om-01; Tensile Zero Span: Tappi T231 cm-96; Tear Rate: Tappi T404 cm-92; Whiteness: Tappi T525 om-92 and CIELab: Tappi T524-om-94 and Tappi T1213 sp-03.

The interfiber interaction was based on equation 1 and toughness was obtained through the integration of the stress-strain curve of the tensile test<sup>[5]</sup>.

$$\beta = \frac{8ZT}{(8Z - 9T)}; Z - \text{Tensile Zero Span}, \quad (1)$$

km; T – Tensile strength, km

The crystallinity variations were evaluated through the ratio between the height of the infrared peaks in the 1,429 cm<sup>-1</sup> and 897 cm<sup>-1</sup> ( $A_{1429}/A_{897}$ ); 1,372 cm<sup>-1</sup> and 2,900 cm<sup>-1</sup> ( $A_{1372}/A_{2900}$ ) areas according to the methodology used by Åkerholm et al. (2004). The spectra were collected between 500 cm<sup>-1</sup> and 4000 cm<sup>-1</sup>, with 64 scans and 1,926 cm<sup>-1</sup> resolution by using a Nicolet thermo FC 330 FTIR.

After the tensile test, fibers sheets were sampled in the fracture area and were exposed to 100°C during 24 hours in order to eliminate residual water for evaluation of the length of the fibers after the test. The verification of length of the fibers sampled was performed on the Ankersmid Cis 100 analyzer which evaluates the size of the particles through the incidence of a laser beam. The Threshold parameter was set to 235 and the number of scans 3000.

## RESULTS AND DISCUSSION

### Evaluation of optical properties

Whiteness is one of the most important parameters in the optical quality evaluation of bleached cellulose pulp and its stability has been object of study in many works. Consequently, the effect of heating on this property shall not be neglected<sup>[7,8,9,10]</sup>. The variance analysis of the results of pulp whiteness after thermal treatment has shown that both the time and the exposure temperature are significant ( $p < 0.05$ ). Another important indicator for the cellulose pulp optical quality is the yellowness rate, CieLab-b, obtained from the analysis of CIE Lab whiteness. As well as whiteness, this parameter has also shown dependence on time and temperature ( $p < 0.05$ ). The results show the pulp yellowing trend over time at the two temperatures, however more evidently at higher temperatures, as demonstrated in Figure 1a. Figure 1b shows the whiteness evolution over time at 80°C and 100°C temperatures indicating the declining trend due to the rise of time and temperature. This behavior is well known and has already been discussed in literature<sup>[9,10]</sup>.

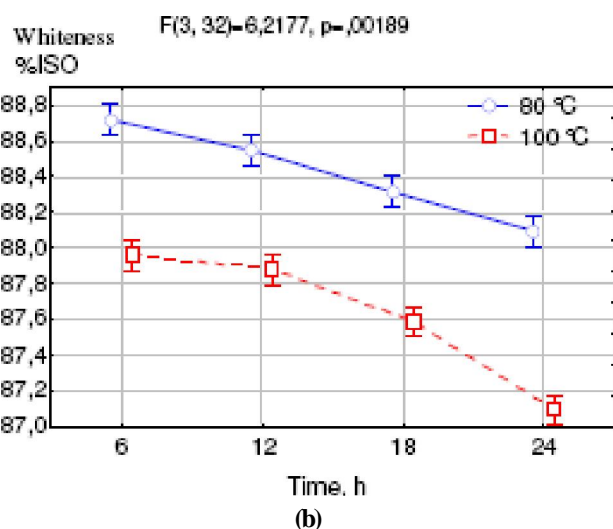
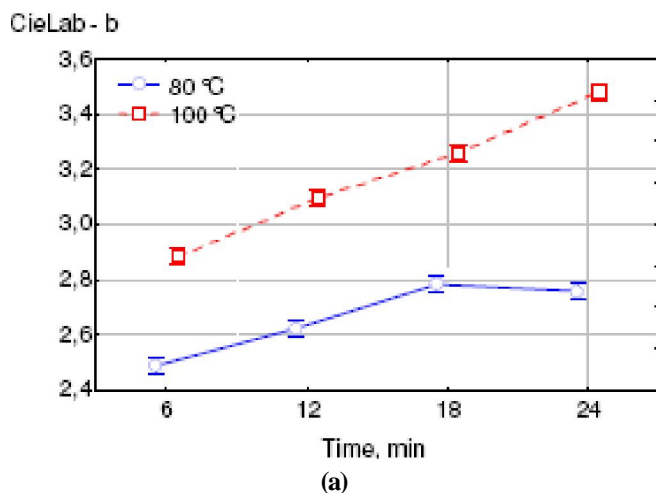


Figure 1(a) : Cielab versus exposure time to 80°C and 100°C temperatures and (b) Whiteness versus exposure time to 80°C and 100°C temperatures.

The formation of oxidized structures, as those demonstrated by<sup>[10]</sup> and the content of transition metals and hexenuronic acid are often pointed out as being responsible for the whiteness reversion. In a recent work<sup>[7]</sup>, have correlated the whiteness reversion to the formation of organochlorinated compounds. The carbonyl groups are responsible for the whiteness reduction due the exposure to heat and light, while carboxylic groups cause reduction due to heat exposure. However, in this work, it is important to emphasize the transition metals, especially Cu, Mn and Fe, were removed at undetectable levels by atomic absorption spectrometry, being their influence minimized on the whiteness reversion processes observed.

### Mechanical properties

The thermal treatment was significant in the change of the tensile strength and tensile zero span according to the analysis of variance ( $p < 0.05$ ). Figures 2 show the evolution of the tensile strength and tensile zero span versus exposure time at 60 °C and 100 °C temperatures, demonstrating the increasing trend in both of them. The elimination of residual water molecules after thermal treatment could provoke a better inter-chain association between cellulose chains onto the cellulose fibers. The same trend was reported by<sup>[16]</sup> also working with unrefined pulps. It has also been noted that the effects are more pronounced at higher temperatures.

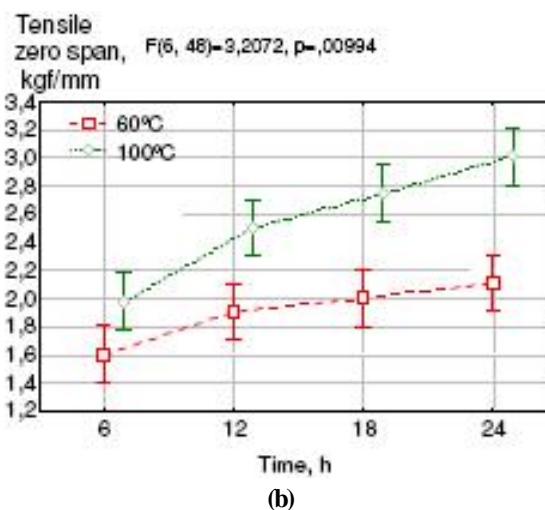
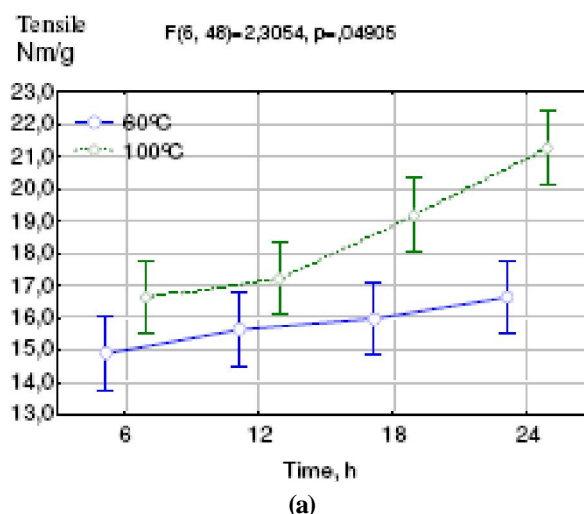


Figure 2 : Tensile strength versus time after exposure to 60°C and 100°C (a) and Tensile Zero span versus time after exposure to 60°C and 100°C (b)

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Figure 3 shows the interfiber interaction ( $\beta$ ) increase to 60°C and 100°C temperatures versus the exposure time, calculated according to equation 1. It should be taken into account that the rate is based on the structural theory proposed by<sup>[16]</sup>. As shown in Figure 3, the interfiber interaction showed a considerable increase after thermal treatment especially for treatment at 100 °C. This behaviour can be associated with an intensification of OH interactions between fibers after thermal treatment. He same way more hydrogen bonding ability when the fibers were treated at high temperature.

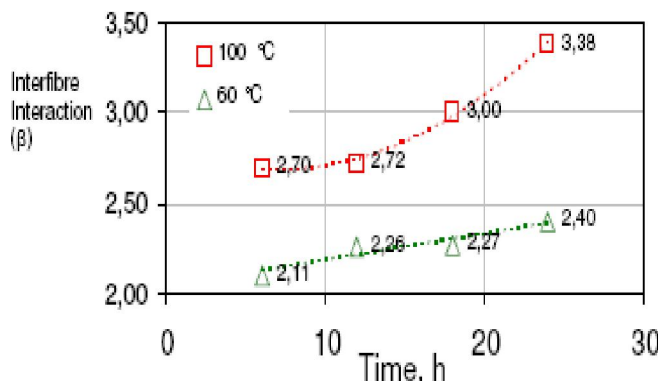


Figure 3 : Interfibre interaction. Sample exposed to 60°C and 100°C

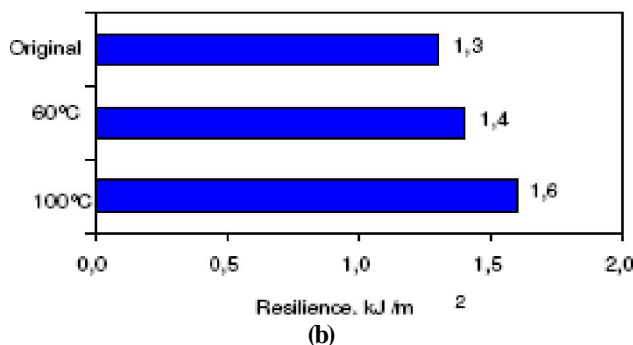
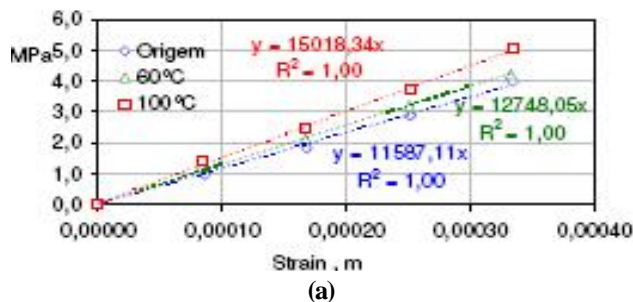


Figure 4(a) : Stress-strain in the elastic zone for the sample with no exposure to temperature and exposed to 60°C and 100°C during 24h and (b) Resilience for the sample with no exposure to temperature and exposed to 60°C and 100°C during 24h.

Figure 4a shows the stress-strain behavior in the elastic area during the tensile test on the samples with no exposure to heat and exposed during 24h to 60°C and 100°C. The results show a 29.5% increase in the elasticity modulus after thermal treatment. It may also be observed that the elastic zone was not changed, remaining at 0.33 mm. As a result of the elasticity modulus increase, there was also resilience increase (Figure 4b).

It is noted in Figure 5a that longer strain values were obtained after thermal treatment, with a significant increase in rupture stress for thermal treated samples. As observed for the elasticity modulus, the results originated from samples exposed to greater temperatures were higher. Figure 5b shows the toughness of the samples and it can be noted higher values for this parameter after thermal treatment as consequence of fiber interaction modification provoked by higher temperatures.

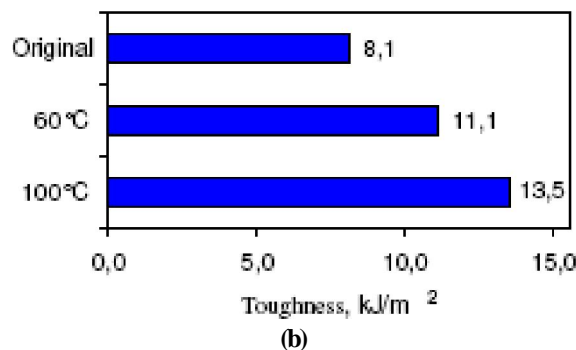
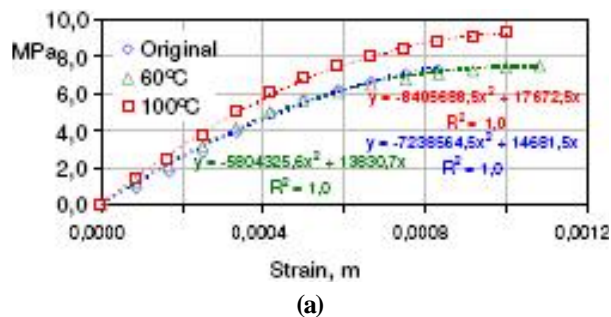


Figure 5(a) : Stress-strain behavior for samples before and after exposure to 60°C and 100°C during 24h and (b) Toughness for B sample with no exposure to temperature and exposed to 60°C and 100°C during 24h.

TABLE 1 : Length of fibers

	Before Traction	After Traction
Origin	0.7476 mm	0.8703 mm
100°C and 24h	0.7476 mm	0.8396 mm

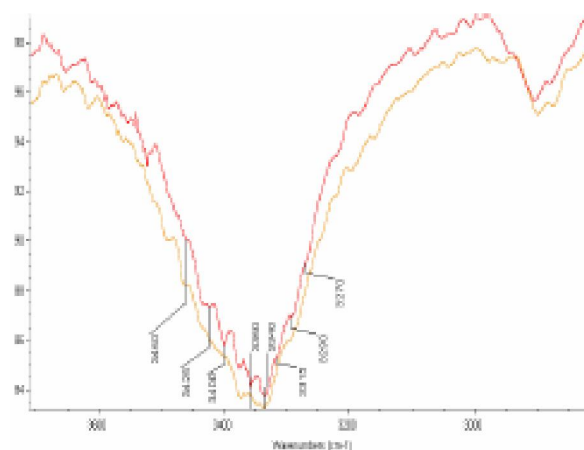
TABLE 1 shows the medium length of the fibers before and after the traction tests. It's clear that the lengths of the fibers are higher after the test. The thermal treatment reduced the ductility of the fibers as consequence of the modification of fiber interaction as showed in Figure 3. Data presented on fiber length after traction are statistically different according to the Tukey test at 95% confidence (TABLE 1).

The elasticity modulus and the strength to rupture may be changed by the formation of higher density of intra and intermolecular interfiber bonding and larger crystal packaging that would restrict the movement of the fibers, microfibrils and crystal planes during the test. Therefore, some hypotheses may be raised to explain the increase in the tensile strength with the thermal treatment. The first one is the increase of the crystallinity, considering the amorphous area as the place of higher fragility and less packaging, causing thus a premature fracture. Another possibility is the modification of the hydrogen bonding, enabling the increase in the interplanar and interfiber interaction, mainly reflected in the tensile strength. A third hypothesis is the transition between the  $I_{\alpha} \rightarrow I_{\beta}$  crystalline forms, once  $I_{\beta}$  is thermodynamically more stable.

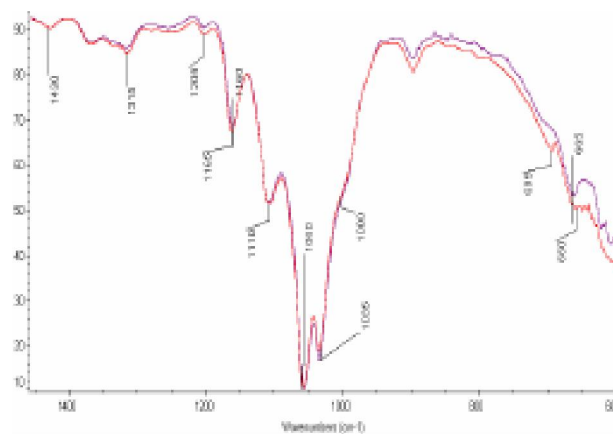
The first two hypotheses were evaluated by using the spectroscopy in the infrared area. Figures 6a e 6b shows the infrared spectrum with Fourier transformation (FTIR) for the sample with no (red) and with (yellow) thermal treatment to 100°C during 24h. In Figure 6b there is change (disappearance) in the absorption band at 3,270  $\text{cm}^{-1}$ , where there is intermolecular C2OH—O6 and intramolecular C3OH—O5 hydrogen bonding. Great change has also been observed between 3,340  $\text{cm}^{-1}$  and 3,360  $\text{cm}^{-1}$  concerning the hydrogen bonding in the carbon six hydroxyl. According to<sup>[26]</sup>, changes in 3,270  $\text{cm}^{-1}$  and 3,340  $\text{cm}^{-1}$  often occur when exposed to heat. According to Maréchal & Chanzy (2000), the 3,340  $\text{cm}^{-1}$  area associated to the 1,060  $\text{cm}^{-1}$  area indicates strong hydrogen bonding in secondary alcohols, however these areas may be modified by heating below 120°C, which does not indicate its breakdown, but the arising of the weaker bonding.

In addition, the disappearance of the peak at 3,400  $\text{cm}^{-1}$  may also be seen in Figure 6a, concerning intermolecular hydrogen bonding in C6OH-- and the signal

intensification of the weak hydrogen bonding at 3,460  $\text{cm}^{-1}$ . No change was observed in the intermolecular hydrogen bonding among C6OH—O3. The only change observed in the spectrum of Figure 6b is the disappearance of the peak at 695  $\text{cm}^{-1}$ , concerning the OH stretch outwards the scheme. The results show that the exposure to heat causes restructuring in hydrogen bonding more bonding ability with possible consequences on the mechanical properties of the fibers at high temperature.



(a)



(b)

Figure 6(a, b) : FTIR spectra before treatment (red) and after exposure to 100°C during 24h with different ranges.

Figure 6a showed changes in the area concerning the hydrogen bonding in the hydroxyl at C6 (3,400  $\text{cm}^{-1}$  – 3,460  $\text{cm}^{-1}$ ) indicating that such modification may have occurred<sup>[3, 26]</sup>. Showed that the hydroxyl in (C6) undergoes changes due to heating, being essentially positioning perpendicularly to the scheme of the glyco-

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sidic ring. This repositioning enables the arising of interplanar bonding and consequent increase in the elasticity modulus of the fiber.

The modification of hydrogen bonding may also cause major changes in crystallinity. Figure 7 shows the ratio between the peak heights at 1,372  $\text{cm}^{-1}$  and 2,900  $\text{cm}^{-1}$ , and between the peaks at 1,429  $\text{cm}^{-1}$  and 897  $\text{cm}^{-1}$ .<sup>[2, 23]</sup> Showed ratio between the height proportion of these infrared peaks and cellulose crystallinity. Figure 7 showed increasing trends versus the exposure time to 100°C, and it is an indication of possible rise in the cellulose crystallinity due to degradation of the amorphous areas or restructuring.

According to<sup>[21]</sup>, crystallinity affects the tensile properties of the fibers in a way that the elasticity modulus and hardness increase and the flexibility decreases with the increase of crystallinity index.

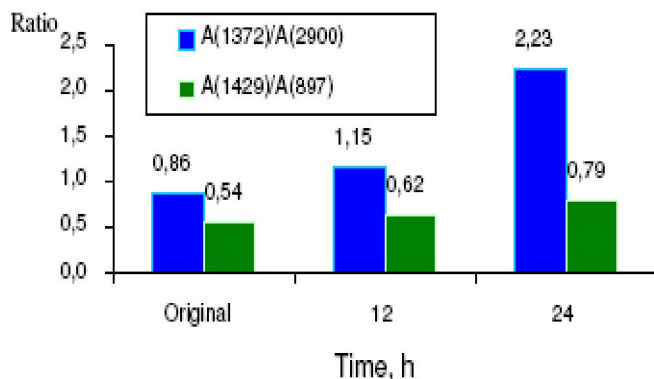


Figure 7 : Ratio between the height of 1372/2900 and 1429/897 peaks versus the exposure time to 100°C.

## CONCLUSION

It has been demonstrated in this study that the thermal treatment (<100 °C) of cellulose fibers in periods shorter than 24 hours causes, additionally to the yellowing, the increment in tensile strength, elasticity modulus, toughness and resilience, besides less plastic deformation in the fibers after traction. The increase in the strength of the samples after thermal treatment has been justified by the increased interfiber interaction and possibility of formation of interplanar hydrogen bonding. The thermal treatment, in the settings used here, although representing a good alternative for predicting the behavior of cellulose pulp optical properties over time, does not provide subsidies for the same analysis regarding mechanical properties.

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