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Differences of Alkali and Thermal Treatment on Cotton Residues Applicable to Green Composites

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Abstract

Natural fibers have been widely used in biocomposites because are renewable raw materials and improve mechanical performances. However, some components such as lignin reduce the biodegradation of these composites. This study evaluated the effects of two types of treatments (alkali and thermal) on superficial and composition of the cotton fibers. The samples were evaluated by Fourier-transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), contact angle measurement (CA) and X-ray diffraction (XRD). The alkali treatment removed impurities, hemicellulose and part of lignin (using 10% wt.%NaOH). There was also a change in the crystalline structure of cellulose. Treatment with higher temperatures increased the removal of hemicellulose residues and lignin. It also decreases oxidized cellulose, which increased wettability and hydrophilicity of the cotton fiber. The most effective treatment was with 10% NaOH and 60 or 90°C as studied with delignification, wettability, and thermal stability. This process should facilitate biodegradation.

Keywords: Cotton fiber, Alkali treatment, Thermal treatment, Natural fibers.

Introduction

The use of the biodegradable polymers can reduce the quantity of plastic wastes discarded in the environment. The incorporation of fibers in a polymeric matrix can modify their properties to improve biocomposites[1]. The fiber content (as reinforcement) can reduce the degradation time, density, and final cost in the composites [2]. However, a significant challenge is optimizing fiber use, adhesion of fiber with a matrix, and in biodegradation.

Natural fibers are used to both reduce the amount of energy necessary to produce products and to increase their mechanical and thermal properties. According to Albinante et al., the intertwined cells in natural fibers are responsible for density, tensile strength, modulus of elasticity and elongation at breakage [3]. Some studies can be incorporated at concentrations up to 50% wt%., by mass, to provide significant reductions in cost and degradation time. Of the natural fibers, cotton fibers have high strength and high cellulose content and present mechanical fragility without processing. Hence, they are mainly used to make textile thread [4,5].

Sanchez et al. showed that cellulose is the most important structural component of vegetable fibers and offers high molecular orientation and consequently better mechanical strength for fibers [6]. The primary cell walls of fiber contain different polysaccharides, and microorganisms play a role in the degradation process. In turn, the secondary cell wall contains lignin that is important for energy production by combustion of the composites [7].

Some authors have reported changes in the lignocellulosic structure of cotton fibers depending on the kind of the soil, growing region, harvest time and kind of fertilizer applied. The basic structure of cellulose and hemicellulose present in cotton are shown in Figure 1(a) and Figure 1(b), respectively [8,9].

According to Harkin et al., both aromatic rings and the methoxy groups content in lignin forms a crosslinked system, which determine the plant's stiffness. This lignin structure acts to link cells, generating a final fiber structure with higher resistance to impact, compression and bending [10]. In terms of degradation, lignin can be classified into two types: core and non-core. Lignin's basic structure is shown in Figure 1(c), and there are three monolignol monomers. These lignols are incorporated into lignin. The most commonly studied are: p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, see Figure 1(d) [11].

The structural changes in natural fibers alter the surface properties of the composites into which they will be incorporated including wettability, free energy, sorption, roughness and most importantly, biodegradation. These changes can make composites more accessible to microorganisms. A higher percentage of amorphous regions increase the rate of biodegradation. The intra and intermolecular hydrogen bonds formed between the long chains of cellulose originate microfibrils, which form a set of aggregates that are insoluble in water [12,13].

Although there are several studies related to modifications of natural fibers, there is a need for a deeper understanding of the

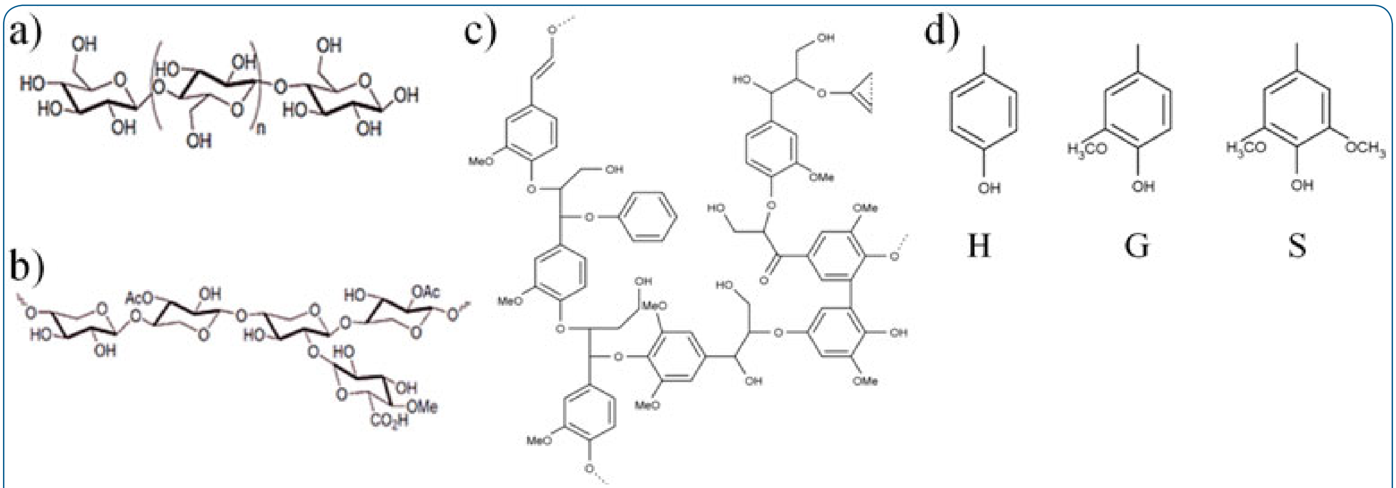


Figure 1: Structure of the chains: a) cellulose, b) hemicellulose, c) lignin and d) its p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units

structural and surface changes of cotton fibers promoted by different treatments. Thus, this study evaluated the structural, superficial and thermal properties as well as the physicochemical changes caused by treatment with alkaline solutions at 0, 5 or 10% wt%. NaOH was used followed by different treatments at 30, 60 or 90°C.

Materials and methods

Materials

We used natural cotton residues, separated from the boll and without dying. These were provided by the Cotton Institute of MatoGrosso (MT-Brazil).

Alkaline Treatment

The cotton fibers were chopped in a Croton TE625 rotary blade mill and sieved through 4mm mesh. The fibers were then immersed in a solution of 0, 5 or 10% wt%. NaOH under stirring at 30°C for 1 hour and were filtered and dried in a vacuum oven at 50°C for 48 hours.

Thermal Treatment

After alkaline treatment, the fibers were submitted to heat treatment by varying the temperature of the 10% wt%. NaOH solution (30, 60 or 90°C) and maintaining the same stirring and time conditions.

Fourier-transform infrared spectroscopy (FTIR)

The fibers were tested by FTIR using a Nicolet Nexus 4700 spectrometer by applying a scanning range of 400 to 4000 cm^{-1} and 64 scans.

Thermogravimetric analysis (TGA)

TGA was performed with a TA Instruments analyzer at a heating rate of 10 °C min^{-1} over 30-500°C with nitrogen flow of 50 $mL.min^{-1}$.

Contact angle (CA) analysis

The contact angle was measured using a DCAT tensiometer, with deionized water, by the sessile drop method. We calculated the hysteresis (Hi) and adhesion work (W_a).

X-ray diffraction (XRD)

The samples were characterized by an X-ray diffractometer (Bruker D8 Focus model) with a CuK source generating radiation with λ=0.15418 nm. The degree of crystallization (X_c) was determined using the crystalline peak of the cotton fiber at 2θ = 15°, 17° and 20°.

Results and discussions

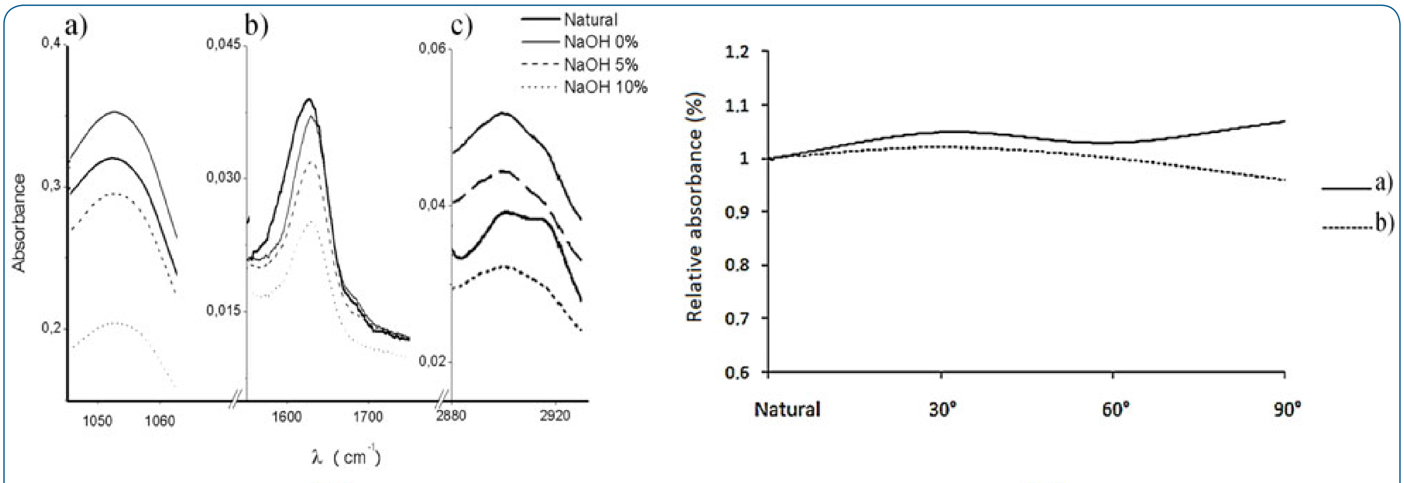
Fourier-transform infrared spectroscopy (FTIR)

Alkaline treatment: The main components of the untreated fibers presented overlapping absorption in the infrared spectrum because of the complex chemical structures of cellulose, hemicellulose, and lignin with distinct conformations and radicals. The spectra are shown in Figure 2 (A), considering only three regions. These refer to the main groups present in the cotton fibers: a) 1045-1065 cm^{-1}, b) 1500-1750 cm^{-1} and c) 2880-2930 cm^{-1}.

The FTIR results shown in Figure 2(A) compare the untreated fibers with those submitted to three different chemical treatments. Region (a), Figure 2(A), shows the absorption related to the ether group present in the hemicellulose. The results show that the ether group is sensitive to washing, and its absorbance decreases with increased concentration of NaOH. According to Zimmermann et al., the ether group is also found in cellulose; however, it has a crystalline structure, which can facilitate attack of waxes and oils with low molar mass [14].

Region (b), Figure 2(A), shows absorption data for carbon-carbon interactions related to the aromatic structures present only in the lignocellulosic structures. In this region, it is possible to observe a reduction in the absorption of samples that were submitted in higher concentrations of NaOH. According to some authors, however, this result is due to solubilization of the lignin by the alkaline solution, which promotes partial dissolution of lignocellulosic composites [5,15].

Region (c), Figure 2(A), refers to the absorption of methoxy groups that was characteristic of lignin. These show that these peaks were altered with washing. There is more absorption from the fibers treated without NaOH (0%) and NaOH 5% than natural fiber. This is because of removal of the less stable lignin. According to some authors, the O-β4 bonds between cyclic chains are less condensed and break more easily with simpler chemical pretreatment processes, but β-5', β-β', 5-5' and β-1' bonds are more condensed and resistant to chemical degradation [16,17]. This process can also cause yellowing of the fibers by



(A) (B)

Figure 2: (A) Spectra of the untreated and treated fibers divided into: a) 1045-1065 cm-1 b) 1500-1750 cm-1 and c) 2880-2930 cm-1. (B) Calculation of absorbance related to the monitoring of: a) cellulose and hemicellulose and b) lignin

intense exposure to alkaline solutions [18,19].

The calculations (Figure 2(B)) were carried out for: a) oxidation of cellulose and hemicellulose [1720 cm^{-1}/2900 cm^{-1}], b) moisture [3330 cm^{-1}] and c) lignin removal [1640 cm^{-1}][20].

Curve (a) in Figure 2(B), shows an increase in oxidation of the chains, which does not have a significant variation with increasing NaOH concentration. This increase can be attributed to the breakdown of hemicellulose structures when the fibers were submitted in water or NaOH solution [21]. A little loss of lignins can be observed in curve (b) in Figure 2(B) corroborating the decrease in methoxyl, hydroxyl, and carbonyl groups as previously mentioned. The literature also shows that oxidation of the lignin fraction can increase the molar mass of the aldehydes groups. It is an indicator of the percentage of C9 units (H, G and S) in the fiber. This is directly related to the fiber's mechanical strength [11,22].

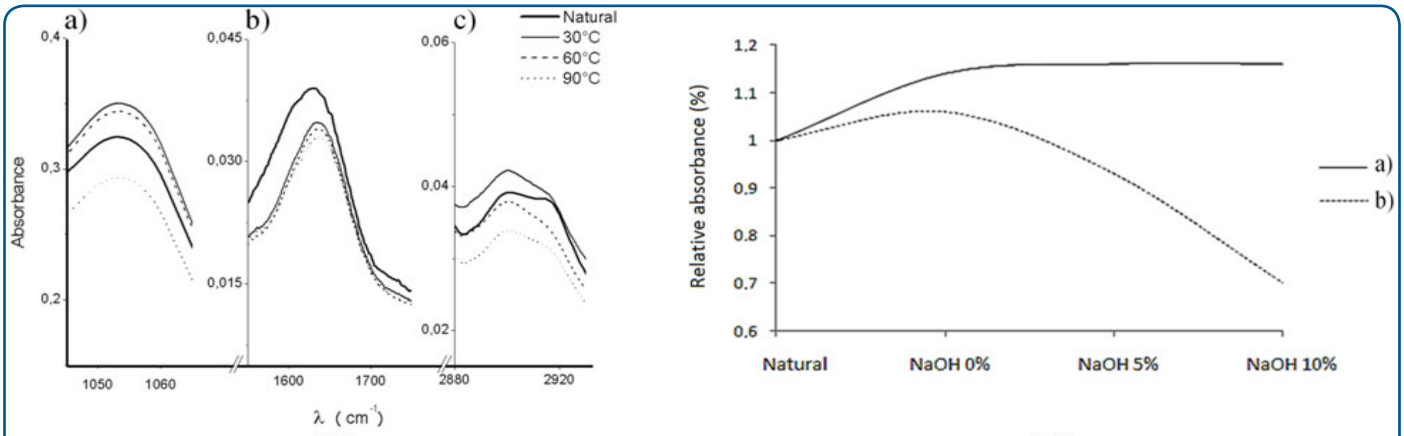
Thermal treatment: Figure 3(A) shows the spectra from the same three regions before analysis. It shows that the samples after heat treatment showed a less significant effect than samples treated only with the alkaline solution. According to the literature, this behavior is possible because the concentration of NaOH (10% wt%.) during treatment was high [23].

As shown in Figure 3(A)(a), there was a significant variation in the ether group with treatment at 90°C. This is probably due to the removal of the hemicellulose residue and oxidation of the cellulose. This would not occur in room temperature treatment. This change influences the structure of the fiber and hence the degree of swelling and crystallinity [19,21].

Figure 3(A)(b) shows the effect of the temperature in the reduction of the C-C (aromatic) bonds. There is no significant difference between the 60 and 90°C. According to Chenault*et al.*, rupture of this group in aqueous solution is accelerated by increasing temperature, and this behavior was less significant because of partial solubilization of the residual lignin in the cotton fiber [24].

The absorption data in (c) (Figure 3(A)) was assigned to the methoxy group. It experienced a smaller change with increasing temperature versus NaOH treatment at 30°C. This is because lignocellulosic structures such as guaiacyl (G) and syringyl (S) are more stable [14]. Heating at 90°C, near the glass transition temperature (T$_g$) of lignin (90 to 180°C), may also have favored the oxidation of lignin in the core. These were not oxidized at lower temperatures [25].

Increased temperature favors the oxidation of cellulose groups or



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hemicellulose groups (Figure 3(B)(a); unlike the literature). This behavior was not observed when the samples were treated with the alkaline solution in lower temperature [15]. The decrease in the relative absorbance of lignin, Figure 3(B)(b), can be attributed to the acceleration of extracting the residual lignin fraction from the fiber [26].

Thermogravimetric analysis (TGA)

Alkaline treatment: The results of the thermograms are shown in Figure 4 and indicate the thermal stability and ash content of the fibers. The results suggest that the aqueous treatment promoted greater thermal stability and show the increase in degradation onset temperature of the fiber similar to Albinante et al. The authors argue that swelling of the cellulosic structure in the presence of water changes the organization (from monoclinic to polymorphic) and that water washing can promote treatment similar to that of weak acids [5].

A reduction in the thermal stability was observed when the fibers were treated with NaOH perhaps due to removal of impurities, hemicellulose and part of the lignin. The fibers treated with 5% wt%. NaOH showed a change in initial temperature of TGA curves (in 10% mass loss) but they also left more waste and ash. For fibers treated with 10% wt%. NaOH, the effect on thermal stability was more significant demonstrating greater removal of lignocellulosic components. These results corroborate those of Albinante et al., who showed that the alkaline treatments cause an increase in amorphous cellulose. However, the crystalline structure depends on the type and concentration of the alkaline solution [5].

Thermal treatment: Figure 5 presents the thermograms of samples subjected to heat treatment. The thermograms from samples treated at 30 and 60°C were similar. The sample treated at 90°C shows less thermal stability. However, the temperature promotes a higher thermal stability for the fiber than the samples treated only with alkaline solution. According to Pires et al., alkali treatment can partially remove hemicellulose and lignin, but temperature changes this process. The results presented in Figure 5 suggest that temperatures of 30 and 60°C caused no significant effect on the removal of lignin but caused fiber swelling. The presence of excess ions in alkaline solution (10% wt%. NaOH), according to Sanchez, promotes rupture of secondary bonds and contributes to the removal of cellulosic chains; temperature helps this process [6,15].

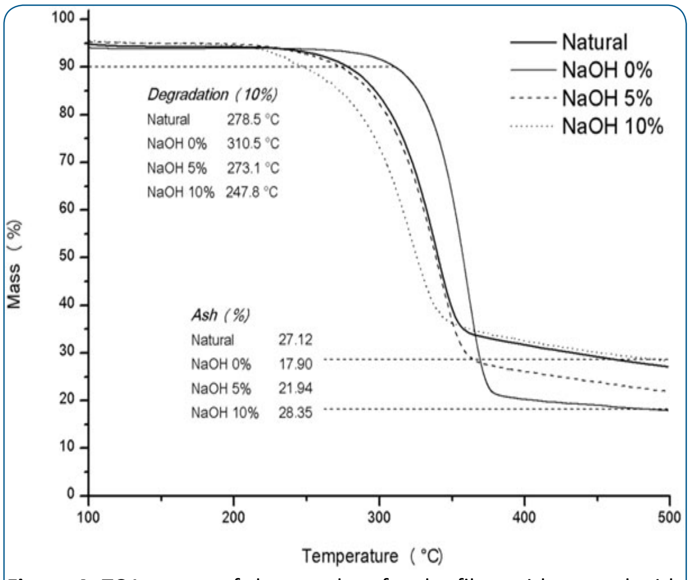

Figure 4: TGA curves of the massloss for the fiber without and with alkaline treatment with 0, 5 and 10%wt%. NaOH solution

The increased thermal stability of heated cotton fibers is due to the change in crystallinity caused by alkali treatment. These increase the degree of organization and provide greater thermal stability (see the XRD results). On the other hand, when treated at 90°C, the cellulose should undergo increased oxidation and consequently disrupts the chains [27].

Contact angle (CA) analysis

The results of contact angle (CA), surface hysteresis (H) and work of adhesion (W_a) are presented in Table 1. This analysis shows the differences in wettability of natural cotton fiber and fibers treated under different conditions.

The contact angle measured in the untreated cotton fibers indicates their hydrophobic character (CA>90°), and consequently lower affinity for water. This results in a low work of adhesion. The natural fiber surfaces are impregnated with apolar oils and have high entanglement, which can explain their higher hydrophobicity and high hysteresis [28,29].

The submission of the fibers in the water increased the contact angle, which was reduced with increasing NaOH concentration during mercerization. In a study of surface treatment with NaOH, Sirvaitiene et al. showed that the samples submitted in alkaline solution promoted fiber cleaning with a lower content of lignin and produced more hydrophilic fiber surfaces. In this work, the results are due to removal of a small portion of hemicellulose and lignin. However, the wettability of natural fiber is also related to its degree of entanglement and twisting (twist level). Cotton fibers have a high aspect ratio, and this factor as well as spatial orientation makes their conformation sufficiently compact to decrease their affinity for the medium [30].

The heat treatment with 10% wt%.NaOH solution showed a continued reduction of the contact angle without reducing the hysteresis angle. The treatments with 10% wt%.NaOH at 60 and 90°C showed higher efficiency in a gain of hydrophilicity with high

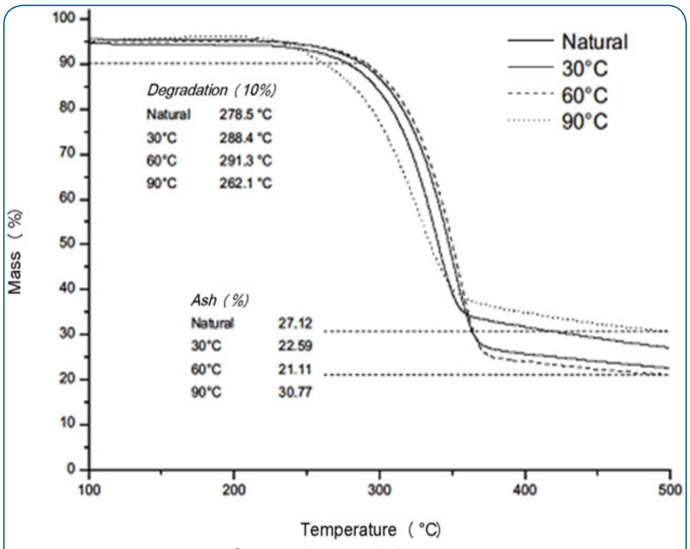

Figure 5: TGA curves of mass loss with heat treatment at 30, 60 and 90°C (10% wt%. NaOH)

Table 1: Parameters of wettability: contact angle (CA), hysteresis (Hi) and work of adhesion (W_a) for cotton fiber with and without treatment

Fibers	CA (°)	Hi(°)	W_a(%)
in natura	123.6	11.2	22.3
$0\%_{NaOH}$	131.1	4.0	17.1
$5\%_{NaOH}$	120.1	7.6	25.0
$10\%_{NaOH}$	107.0	5.5	35.4
30°C	126.7	6.0	20.1
60°C	76.0	7.6	62.1
90°C	73.7	7.3	64.0

hysteresis by oscillations of the surface free energy. According to Bonetti et al., the energy dissipated in the system is affected by the volume of material (ΨΩ) in contact with the medium [31]. This result confirms the increased removal of lignocellulosic as also were shown by the FTIR and TGA. The results in Table 1 show a small increase of hysteresis. This result could be relevant by explaining a possible stronger mechanical anchoring of the fiber in polymer matrixes or adhesion of microbes and biofilms [31]. This result is important because it could facilitate biodegradation of fibers treated with hot alkaline solutions [32].

X-ray diffraction (XRD)

The X-ray diffraction data are shown in Table 2 and Figure 6(a) for samples after alkaline treatment; Figure 6(b) is after thermal treatment.

Table 2: Crystallinity index ($\%X_c$) calculation and desviation (SD) for cotton fiber with and without treatment

Fibers	$\%X_c$	SD value
in natura	82.2	3.4
$0\%_{NaOH}$	79.6	2.6
$5\%_{NaOH}$	84.6	2.2
$10\%_{NaOH}$	88.1	1.9
30°C	87.9	3.1
60°C	91.4	2.5
90°C	90.2	3.5

The results in Table 2 show that the water treatment does not increase the crystallinity. An important increase was observed when the sample was treated with 10% wt%. NaOH solution. The removal of the lignin is likely less significant (by water treatment). However, it is higher than when the higher concentration of alkalis solution was used. In general, the XRD results of the fibers submitted to alkali treatment does not present a change in the crystal structure of cellulose. According to Borysiak, this confirms that the polymorphic transformation of cellulose depends on the concentration of hydroxide sodium [33].

The thermal treatment diffractograms of the 90°C sample show an increase in the polymorphic transformation of cellulose (I into II) as well as the presences of additional peaks while the cellulose intensity decreases.

Conclusion

This work showed that exposure of cotton fibers to water does not cause a significant change in the chain organization and offers improved thermal stability but with reduced wettability. The alkali treatment reduced the thermal stability and caused some changes in the chemical structure of the fiber. In other words, it accentuated the removal of impurities, hemicellulose, and some lignin. At higher concentrations, the alkali behavior was intensified. The temperature increase removed the hemicellulose residue and the lignin and changed the fiber structure, this increased the thermal stability. The samples submitted in higher temperatures show a reduction in contact angle (without reducing the hysteresis angle). There is also an increase in wettability, which facilitates the biodegradation process of the fiber.

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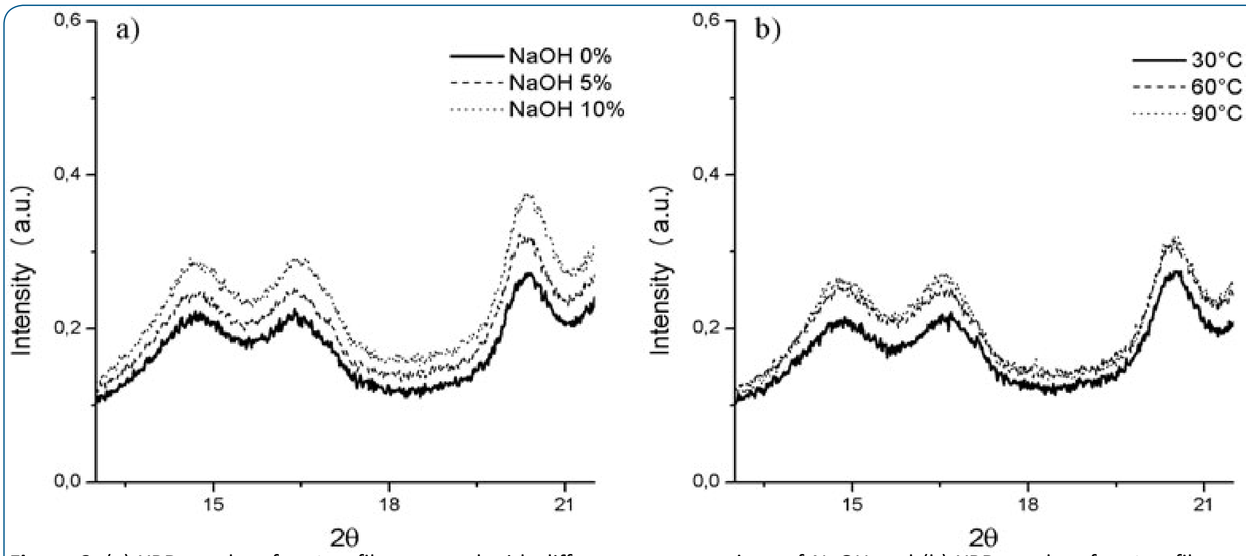

Figure 6: (a) XRD results of cotton fiber treated with different concentrations of NaOH and (b) XRD results of cotton fiber treated with and without heat treatment

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