

Alkali Treatment of Viscose Cellulosic Fibers from Eucalyptus Wood: Structural, Morphological, and Thermal Analysis

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ABSTRACT: The modification of viscose cellulosic fibers from eucalyptus wood was performed by alkali treatment to improve the surface properties of the fibers for subsequent incorporation as reinforcement into phenolic composites. The treatment was carried out at various NaOH concentrations (1–20 wt %) and soaking times (1 and 2 h). The structural transformations of the fibers were determined by Fourier transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD). Morphological observations of the fibers were performed using scanning electron microscopy (SEM), and wettability between the fibers and a resol-type phenolic resin was studied by contact angle measurements. Thermogravimetric analysis (TGA) was used to determine the thermal properties. The treatment of cellulosic fibers with 5 wt % NaOH for 2 h was selected as optimum. According to the analyses, these conditions increase the amorphous regions of the fibers (FTIR), reduce the crystallinity (XRD), swell the microfibers and fibers (SEM), and improve the wettability and the thermal stability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2198–2204, 2013

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INTRODUCTION

The use of cellulosic fibers as composite material reinforcement is an interesting alternative to traditional inorganic materials because such fibers exhibit good mechanical properties, are low in cost, are available in a wide variety of forms, and are recyclable. However, poor interfacial adhesion occurs between cellulosic fibers and most common matrix polymers. This issue must be resolved to obtain enhanced mechanical properties in the reinforced material.

The interfacial and mechanical properties of many natural fiber-reinforced composites have been studied. The fibers of interest include flax, hemp, henequen, jute, kenaf, ramie, and sisal in combination with thermoplastic matrices in particular.^{1–8} Some recent works have tested other natural fibers for potential reinforcement in composites, including artichoke⁹ and okra¹⁰. Few authors have used thermosetting matrices and only a minority has studied the behavior of cellulosic fiber-reinforced phenolic composites.^{11–14} In this study, cellulosic fibers are studied for potential use in thermosetting phenolic composites.

Despite the current interest in natural fibers, their uses are limited by poor sample reproducibility and the presence of defects

in the cell walls as a result of processing conditions. Such irregularities have been reported to reduce the stiffness of the resulting composite material and often lead to premature fracture, caused by the generation of localized stress points.^{15,16} Regenerated cellulosic fibers may be an interesting alternative with the ability to solve this problem because they have fewer defects. Although the use of regenerated fibers in composite materials is not widespread, some works employ different types of cellulosic fibers, such as lyocell,^{17,18} rayon,^{19,20} and viscose.^{21,22}

The hydrophilicity of the fiber and resin contributes to the degree of fiber–matrix adhesion. The highly hydrophilic nature of cellulosic fibers adversely affects their adhesion to hydrophobic matrices and may cause a loss of bond strength.^{23,24} Even if the matrix of the composite material is hydrophilic in nature, modification of the fiber surface is usually necessary to enhance fiber–matrix adhesion.^{12,14} Without such treatment, natural fibers embedded in a polymeric matrix generate weak and unstable interfaces, and the stress applied to the composite is not efficiently transferred from the matrix to the fiber. Moreover, strong fiber–fiber interactions resulting from intermolecular hydrogen bonds limit the dispersion of fibers within the matrix.²⁵ To reduce the hydrophilic character of cellulosic fibers

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and improve their adhesion properties, it is necessary to modify chemically the surfaces of the fibers.

A wide variety of fiber chemical modifications have been reviewed in the literature, including reactions with acid compounds and organosilanes in addition to alkali treatment.^{26,27} Alkali treatment with NaOH solutions has been the most widely used method in recent decades.^{28,29} However, many questions remain, especially with respect to changes in the crystal forms of cellulose. Moreover, each type of cellulose must be studied in detail to determine the most suitable conditions of alkali treatment.

During treatment, the alkali penetrates into the swollen cellulosic fibers and causes a decrease in the cellulose crystallinity and an increase in its specific surfaces, making macromolecules more accessible for chemical interaction and mechanical interlocking with the composite matrix.^{30–32} The extent to which alkali treatment changes the properties of the fibers depends on factors such as the source of the cellulose, the concentration of the sodium hydroxide solution and the soaking time of the fibers in solution. For natural fibers, alkali treatment partly transforms the structure of native cellulose I to cellulose II. This transformation is generally known as mercerization. For regenerated fibers composed of cellulose II, the alkali treatment only increases the amorphous phase of the fibers.³³

In this study, the alkali treatment of viscose cellulosic fibers from eucalyptus wood was studied to improve their suitability as reinforcement in resol type phenolic composites. Alkali treatment was carried out by varying the NaOH concentrations and soaking times to improve the surface properties of the fibers. The optimal conditions of the alkali treatment were determined by studying the structural transformations of the fibers, observing their morphologies, and analyzing their thermal properties.

EXPERIMENTAL

Materials

Viscose fibers from eucalyptus wood were used in this study, supplied by Sniace (Spain). The linear density and length of the fibers were 1.7 dtex (0.17 g/1000 m) and 1.7–38 mm, respectively. Analytical grade sodium hydroxide (NaOH > 98%) was purchased from Panreac Química, S.A.U. Spectroscopic grade KBr (Scharlau Chemie) was used to prepare the Fourier transform infrared spectroscopy (FTIR) pellet samples.

Method

The cellulosic fibers were treated with 1, 5, 10, 15, and 20 wt % NaOH solutions (1 : 100 wt/wt) for 1 and 2 h at room temperature. The fibers were further washed with distilled water until pH 7 was achieved. Finally, the fibers were dried in an oven at 60°C for 24 h.

Testing

FTIR spectra of the fibers were recorded with a Mattson Satellite 5000 Spectrophotometer, using the KBr pellet method. Samples of finely divided cellulosic fibers (1 mg) were dispersed in a matrix of KBr (99 mg). The pellets were then formed by compression at 7 t for 30 s. The spectra were acquired over the spectral width of 4000–400 cm^{-1} for 32 scans at a resolution of

2 cm^{-1} . The variation of amorphous cellulose was calculated using the lateral order index (LOI), which is the ratio of the intensities of the bands near 1421 and 897 cm^{-1} .³⁴

X-ray diffraction (XRD) spectra of the fibers were obtained using a Philips X'Pert-PRO X-ray diffractometer (Cu $K\alpha$ radiation with $K\alpha_1 = 1.540598 \text{ \AA}$ and $K\alpha_2 = 1.544426 \text{ \AA}$). The 2θ scan range was from 4 to 80° with a step size of 0.0501° and a step time measurement of 200 s. An amorphous substance within a mixture of phases can be identified as an amorphous “hump.” Accordingly, instead of the characteristic diffraction peaks that originate from crystalline compounds, X-rays incident upon amorphous materials are scattered continuously over a broad 2θ range. The crystallinities were calculated with the X'Pert HighScore software as the ratio between the crystalline region and the sum of the crystalline and amorphous regions. The constant background intensity was specified in advance.

Scanning electron microscopy (SEM, JEOL JM-6400) was utilized to observe the surfaces of the cellulosic fibers. The sample surfaces were sputtered with graphite and gold to enhance electrical conductivity. The operating voltage of the microscope was 40 kV.

Contact angles between a resol-type phenolic resin and the cellulosic fibers were obtained using the sessile drop method with a Dataphysics OCA-20 contact angle analyzer. The drop images were processed with the SCA 20.2.0 software, which calculated both the left and right contact angles from the shape of the drop with an accuracy of $\pm 0.1^\circ$.

Thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo TGA/SDTA 851°. In each analysis, 12 mg of previously milled cellulosic fibers was ramped at 10°C/min from 30 to 900°C under inert atmosphere ($\text{N}_2 = 20 \text{ mL/min}$). The thermal stability of the fibers was calculated in terms of temperature at 10% weight loss (T_{10}).

RESULTS AND DISCUSSION

FTIR Analysis

FTIR analysis was used to analyze the structural changes that occur on the cellulosic fibers during alkali treatment. To understand the effect of this treatment, it was necessary to know the structure of the viscose fibers. Infrared spectra in the 4000–400 cm^{-1} region of the raw viscose fibers and the fibers treated with 5 wt % NaOH for 2 h are shown as examples in Figure 1. The bands near 2890 (CH stretching), 1638 (OH bending of adsorbed water), 1200 (COH bending in plane at C-6), and 897 cm^{-1} (COC stretching at the β -(1 \rightarrow 4)-glycosidic linkage) are characteristic of cellulose II, which predominates in the viscose fibers studied. The absence of the characteristic bands of cellulose I, such as 2945 (CH stretching), 1455 (COH bending), and 1282 cm^{-1} (COH bending), indicates that the cellulose I content in the viscose fibers from eucalyptus wood is negligible.^{35,36}

The lateral order index (LOI) was calculated as the ratio of the intensities of the bands at 1421 and 897 cm^{-1} . The band near 1421 cm^{-1} corresponds to the symmetric bending δ_{CH_2} of cellulose II and amorphous cellulose, while the band 897 cm^{-1} is

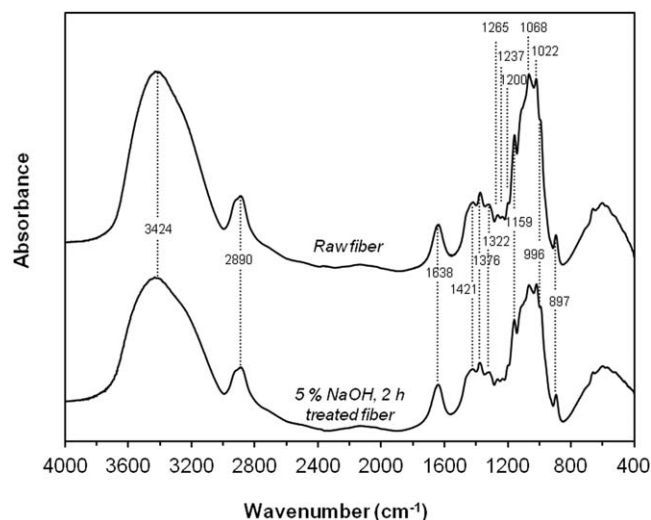


Figure 1. FTIR spectra of the raw viscose fibers and the fibers treated with 5% NaOH for 2 h.

characteristic of symmetric stretching in plane γ (COC) of the cellulose II. Thus, the LOI represents the variation of amorphous cellulose in the viscose fibers and, therefore, the efficiency of the alkali treatment. The LOI variation, as a function of the NaOH concentration for both studied soaking times, is shown in Figure 2. The alkali treatment of the fibers was not extended beyond 2 h because treated fibers do not present changes in properties after this point. The value of the raw fiber is plotted on the y -axis.

The LOI values for the fibers treated with 1 and 5% NaOH are higher than that of the raw fibers. During treatment with NaOH solutions at low concentrations (1 and 5 wt %), swelling of the cellulosic fibers occurs, and the amorphous regions of the viscose fibers are increased. We observed the formation of a gel following treatment with NaOH concentrations equal to or greater than 10%, which was attributed to partial dissolution of the viscose fibers. In these cases, the amorphous phase fraction of the samples, and therefore the LOI values, was reduced because part of the amorphous phase fibers was washed off by water. Colom and Carrillo³⁷ observed a similar dissolution behavior with viscose fibers, which was achieved with NaOH concentrations higher than 14 wt %.

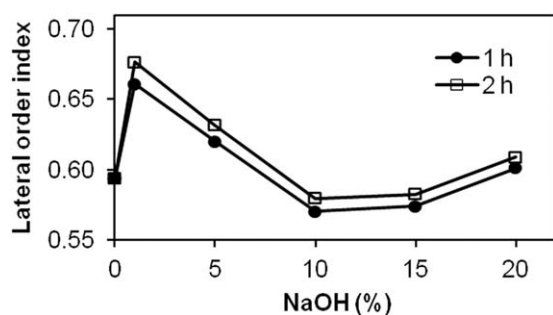


Figure 2. Lateral order index of the viscose fibers versus NaOH concentration at different soaking times.

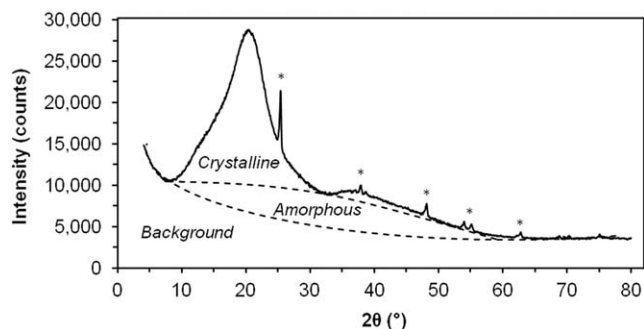


Figure 3. XRD spectrum of the raw viscose fibers.

The effect of the basic solution soaking time of the fibers on the lateral order index is lower than that of the alkali concentration. The trend described above for the variation of LOI with the NaOH concentration is consistent with the soaking times of 1 and 2 h. The LOI values of the fibers treated for 2 h are slightly higher ($\sim 2\%$) than that of the fibers treated for 1 h.

The alkali treatment conditions that led to the increased LOI values of the fibers (and consequently, the increased amorphous fractions) are the sodium hydroxide concentrations of 1 and 5 wt % with any of the studied soaking times.

XRD Results

The crystallinities of the raw and treated fibers were determined by XRD. Figure 3 shows an example XRD spectrum of the viscose fibers used. The crystalline and amorphous regions and the baseline (background) are identified on the raw viscose fiber spectrum. The strong and well-defined peaks marked with asterisks correspond to an opacifying and bleaching agent that is widely used in the production of regenerated fibers. This agent is titanium dioxide, namely, in its crystalline anatase form.

The crystallinities of the viscose fibers from eucalyptus wood before and after treatment with NaOH are given in Table I. The crystallinities of the NaOH-treated fibers are lower than that of the raw fibers. During the alkali treatment, the amorphous regions of the fibers (LOI) increase at the expense of fiber crystallinity. The soaking time influences the crystallinity values of the fibers more significantly than their LOI values, and the optimal soaking time is 2 h. This time provides lower values of crystallinity than the soaking time of 1 h, which is associated with the increasing amorphous region of the fibers with prolonged alkali treatment. Thus, the crystallinity of the fibers

Table I. Crystallinity (%) of Raw and NaOH Treated Fibers Obtained by XRD

Soaking time (h)	NaOH (%)					
	0	1	5	10	15	20
0	76	-	-	-	-	-
1	-	72	74	74	75	75
2	-	65	63	68	67	67

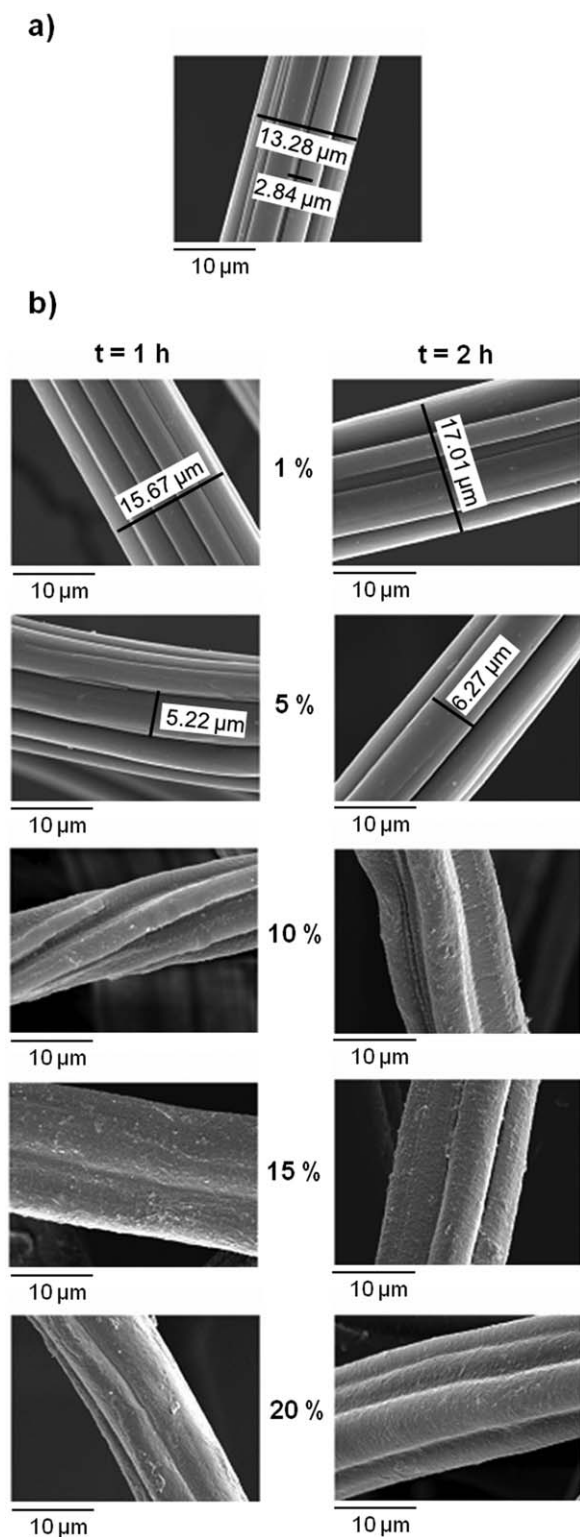


Figure 4. SEM micrographs of (a) raw fiber and (b) NaOH treated cellulose fibers for 1 h (left column) and 2 h (right column) at different concentrations.

treated with NaOH for 1 h varies between 72 and 75%; however, for the fibers treated for 2 h, the crystallinity varies between 63 and 68%.

With respect to the influence of sodium hydroxide concentration on fiber crystallinity, the values are reduced by us much as 16% at low concentrations (1 and 5%) in comparison to the crystallinity of the raw fibers. This fact is due to the above-mentioned increase of the amorphous phase in the alkali-treated fibers. Increasing the NaOH concentration above 5% leads to insignificant reductions in crystallinity for fibers treated with NaOH for 1 h as well as an increase in crystallinity for the fibers treated with NaOH for 2 h. Therefore, NaOH concentrations $\leq 5\%$ are preferable for use.

The increase in crystallinity observed upon increasing the NaOH concentration from 5 to 10% for the soaking time of 2 h coincides with the partial dissolution and removal of the amorphous phase when washing with water for the 10% NaOH-treated fibers. Thus, it was determined that fiber crystallinity is affected by two opposing factors, including the increased amorphous phase of the fibers following NaOH treatment (crystallinity reduction) and the removal of the amorphous phase with the wash water in partially dissolved samples (crystallinity increment).

The predominance of one of these factors depends on the NaOH concentrations selected for the treatment and the type of fiber studied. Thus, while Colom and Carrillo³⁷ found a reduction in the crystallinity of lyocell cellulosic fibers after alkali treatment, Rusznak et al.³⁸ described an increase in crystallinity of viscose fibers after the treatment. In this study, a shift from the dominance of the two factors described above was found because a wide range of NaOH concentrations were studied.

Morphological Observations and Contact Angle Measurements

SEM micrographs of the viscose fibers from eucalyptus wood treated with different concentrations of sodium hydroxide (1–20%) and soaking times of 1 and 2 h are shown in Figure 4. An image of a raw cellulosic fiber is also included [Figure 4(a)]. The fiber diameter increases from 13.28 μm in the raw fiber to 15.67 and 17.01 μm in the fibers treated with 1% NaOH for 1 and 2 h, respectively. The microfibril diameter increases from 2.84 μm in the raw fiber to 5.22 and 6.27 μm in the fibers treated with 5% NaOH for 1 and 2 h, respectively. The increases in both fiber and microfibril diameters are attributed to the swelling of the fibers as a result of the alkali treatment. It also can be observed that the fibers treated with sodium hydroxide concentrations of 10% or higher begin to degrade regardless of the soaking time studied [Figure 4(b)].

Figure 5 shows in detail the degradation of the fibers mentioned above. Figure 5(a) exhibits well-differentiated microfibrils in cross-section following treatment with 1% NaOH. The second image [Figure 5(b)] corresponds to a 10% NaOH-treated fiber in which the microfibrils of the cellulosic fibers are degraded and swollen. Figure 5(c) shows another SEM image of the 10% NaOH-treated fiber but at lower magnification. Both the degradation and partial dissolution of the cellulosic fibers can be clearly observed. This effect also occurs with sodium hydroxide concentrations above 10%.

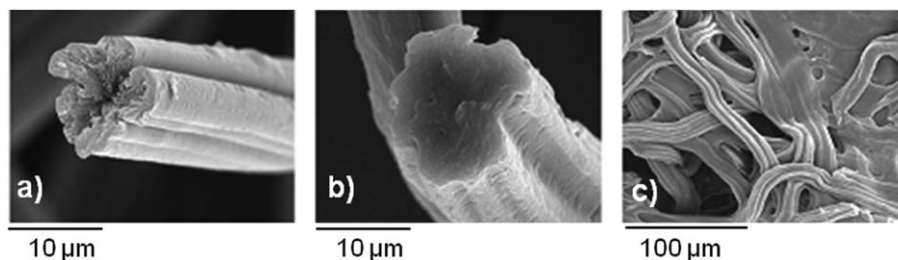


Figure 5. SEM micrographs of 1 h viscose treated fibers. Cross section of (a) 1% NaOH treated fibers and (b) 10% NaOH treated fibers. (c) Degradation detail of 10% NaOH treated fiber.

Contact angles between the cellulosic fibers (reinforcement) and a resol-type phenolic resin (matrix) were measured to probe the effect of the alkali treatment on the wettability of the fibers. The dynamic acquisitions of the contact angle values for the raw fibers, fibers treated with 1% NaOH for 2 h, and fibers treated with 5% NaOH for 2 h are shown in Figure 6. The contact angles decrease from 40.4° in the raw fibers to 38.7° and 37.9° in the fibers treated for 2 h with 1 and 5% NaOH, respectively. The NaOH treatment reduced the contact angle between the cellulosic fibers and the phenolic resin due to the improvement in the fiber wettability.

TGA Analysis

The thermograms obtained by TGA for the raw fibers and fibers treated with 5% NaOH for 2 h are displayed in Figure 7. The fibers treated with 5% NaOH for 2 h are taken as the example because all of the thermograms of the treated fibers showed similar behavior. Three steps can be observed in each thermogram. In the first step, a small amount of fiber mass is lost (<10%) up to approximately 250°C for the raw fibers and up to 300°C for the NaOH-treated fibers, which is related to the loss of moisture and volatile species in the fibers. After, the degradation of the cellulose polymer occurs at two different rates. In the second step of the thermograms, the fast decomposition of cellulose bulk ends at approximately 350°C . The third step begins above 350°C and slowly completes the breakdown of cellulose.

The temperatures at 10% weight loss (T_{10}) of the eucalyptus wood cellulosic fibers treated with different NaOH concentrations and soaking times are shown in Figure 8. The T_{10} of the

raw fiber (287.7°C) is also included. Alkali treatment of the fibers increases their T_{10} values, and consequently their thermal stabilities, with respect to raw fibers by values between 9 and 12%, up to the concentration of 10% NaOH. From this concentration, the T_{10} value remains approximately constant in the $319\text{--}321^\circ\text{C}$ range. The thermal stability (T_{10}) of the fibers increased as a result of NaOH treatment due to the removal of waxes and other surface impurities contained in the fibers.³⁹ These substances decompose earlier than cellulose; hence, their removal leads to improvements in fiber thermal stability.

The thermal stability of the fibers treated with NaOH for 1 h is slightly higher than that of the 2 h treated fibers, for NaOH concentrations of 10% or less. The observation of decreasing thermal stability of the fibers as a result of prolonging the NaOH treatment from 1 to 2 h may be related to the observed increase of the amorphous phase and corresponding reduction of crystallinity. The decrease in the thermal stability of the treated fibers following reduced crystallinity has been reported by others.^{40–42}

Optimal Conditions of the Treatment

The most significant characterization results of the alkali-treated cellulosic fibers from eucalyptus wood are summarized in Table II. The targets of each technique and treatment conditions that led to the best fiber properties are specified.

In view of the results provided by the techniques discussed here, a concentration of 5% NaOH and a soaking time of 2 h were selected as the optimal conditions for the alkali treatment of cellulosic fibers. These conditions increased the amorphous

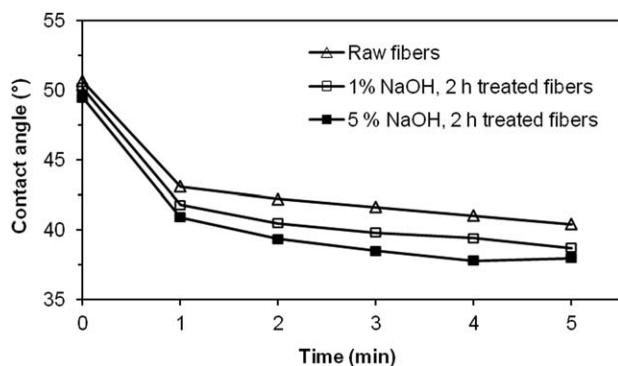


Figure 6. Contact angles for the raw cellululosic fibers, fibers treated with 1% NaOH for 2 h, and fibers treated with 5% NaOH for 2 h.

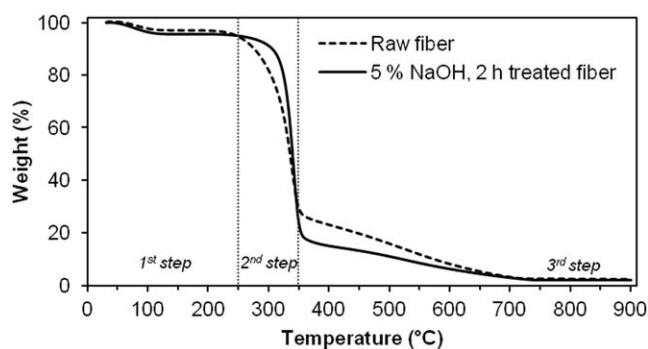


Figure 7. TGA thermograms of the raw cellululosic fibers and the fibers treated with 5% NaOH for 2 h.

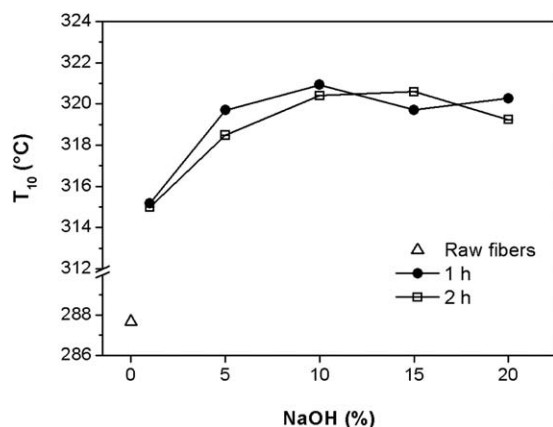


Figure 8. Values of T_{10} for NaOH treated fibers at different soaking times.

regions of the fibers (FTIR) at the expense of their crystallinities (XRD) and caused fiber swelling (SEM). Furthermore, these treatment conditions improve the thermal stability of the fibers, according to the TGA results.

CONCLUSIONS

The alkali treatment conditions of viscose cellulosic fibers from eucalyptus wood were studied to improve the surface properties of these fibers for their potential use as reinforcement in phenolic composites. The treatment of cellulosic fibers with 5 wt % NaOH for 2 h was selected after characterizing the alkali-treated fibers with FTIR, XRD, SEM, and TGA techniques. These conditions increase the amorphous region of the cellulosic fibers, reduce their crystallinity, swell their microfibers and fibers, and improve the wettability and the thermal stability of the fibers. Swollen NaOH-treated fibers exhibit increased accessibility and reactivity in comparison to raw fibers. Moreover, the NaOH-treated fibers possess a bigger effective surface area, which is the area available for chemical interaction and mechanical interlocking with the matrix in composite materials.

Although this study reveals the surface modifications that occur in the cellulosic fibers after alkali treatment, nonetheless in the future, extensive characterization of reinforced phenolic composites should be performed to verify the treatment effect. Additionally, it would be beneficial to study the mechanical and thermal properties, as well as the morphology of the phenolic composites reinforced with NaOH-treated fibers. Finally, it

Table II. Summary of Results Obtained in the Alkali Treatment of Viscose Fibers from Eucalyptus Wood

Technique	Target	Treatment conditions
FTIR	High LOI.	≤5% NaOH, 1 and 2 h
XRD	Low crystallinity.	≤5% NaOH, 2 h
SEM	Swelling of the fibers. Minimum dissolution.	≤5% NaOH, 2 h
TGA	High thermal stability.	5–10% NaOH, 1 and 2 h

would be beneficial to compare these findings with those of raw fiber-reinforced composites.

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