

Treatments of Jute Fibers Aiming at Improvement of Fiber-phenolic Matrix Adhesion

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Abstract: Composites based on a thermoset phenolic matrix and jute fibers were prepared and characterized. The fibers were alternatively treated with ionized air or aqueous alkaline solution (mercerization) with the aim of introducing changes in the morphology, dispersive component of surface free energy, γ_s^D (estimated by Inverse Gas Chromatography, IGC) and the acid/base character of their surfaces, shown by their AN_s/DN_s ratio (estimated by IGC), and their degree of crystallinity. The final objective was to investigate the influence of these modifications on the adhesion at the jute fiber/phenolic matrix interface in the composites. The untreated jute fiber showed 50% crystallinity, $\gamma_s^D=18 \text{ mJ m}^{-2}$ and $AN_s/DN_s=0.9$ (amphoteric surface), tensile strength = 460 MPa and maximum elongation = 0.7%, while the respective composite had an impact strength of 72.6 J m^{-1} . The treatments positively modified the fibers and the adhesion at the interface was better in the composites reinforced with treated fibers than with untreated fibers. The best set of results was exhibited by the fiber treated with 10% NaOH [46% crystallinity, $\gamma_s^D = 26 \text{ J m}^{-2}$ (phenolic matrix $\gamma_s^D = 32 \text{ J m}^{-2}$), $AN_s/DN_s = 1.8$ (surface predominantly acidic, similar to phenolic matrix, $AN_s/DN_s = 1.4$), tensile strength approximately 900 MPa, maximum elongation = 2%, impact strength of respective composite approximately 95 J m^{-1}]. The fibers treated for 5 h with ionized air exhibited favorable properties [(45% crystallinity, $\gamma_s^D = 27 \text{ J m}^{-2}$, $AN_s/DN_s = 2.1$ (acidic surface))] for further use as reinforcement of a phenolic matrix, but their partial degradation during the treatment decreased their tensile properties (395 MPa and 0.5% for tensile strength and maximum elongation, respectively) and their action as reinforcement (impact strength of the respective composite approximately 73 J m^{-1}).

Keywords: Phenolic matrix, jute fibers, ionized air treatment, mercerization, inverse gas chromatography.

Introduction

We report the preparation and characterization of composites based on a thermoset phenolic matrix and jute fibers. During two stages in the preparation of these thermoset composites, namely the impregnation of the fibers with the pre-polymer and the initial curing steps, the process of interdiffusion depends on the correlation between the cohesive energy of the pre-polymer and the surface energy of the fiber, among other factors. As far as phenolic pre-polymers and lignocellulosic fibers are concerned, the presence of low-polarity and nonpolar domains, as well as of polar groups, both in the pre-polymer and in the fibers, can facilitate the impregnation process and development of favorable interactions between them. However, matrix-fiber interactions could be further intensified, for example, by treating the surface of the fibers. In previous studies we have reported on chemical modifications of the surface of lignocellulosic fibers using furfuryl and polyfurfuryl alcohols, as well as using hydroxymethylated lignins^[1]. Treatment of natural fibers with an alkaline solution (mercerization) is widely used. This treatment can increase the fiber surface roughness, separate the fiber bundles and remove cell wall components^[1-6]. Usually, the wettability of the mercerized fibers is greater than that of unmodified fibers, thus improving strength of bonding between the fibers and the matrix^[7].

Aggregation involving fiber bundles can also be related to electrostatic interactions, which can be manipulated by specific treatments, such as the ionization of the surrounding air molecules. In the present study, the surface of jute fibers was treated with ionized air^[2,5,8,9]. Both of the treatments investigated here, namely mercerization and ionized air, can change the energy and the acid-base properties of the fiber surface, which in turn can affect the interactions at the fiber-matrix interface. The reinforcing efficiency of fibers depends largely on their own properties and the strength of the fiber-matrix interactions at the interface^[10]. The dispersive component of surface free energy (γ_s^D) and specific interaction parameters describing the ability of the surface to act as an electron acceptor (AN_s) or electron donor (DN_s) are used to quantify the properties of the polymer surface. These surface parameters can be estimated by Inverse Gas Chromatography (IGC)^[11,12]. In this study, IGC was used to characterize the surface properties of the fibers before and after modification (ionized-air and mercerization).

Experimental

Jute fibers were soxhlet extracted with ethanol/cyclohexane (1:1 v/v; Synth 99%, 99%) for 50 h in order to remove extractives such as waxes and fats. After extraction,

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the fibers were stirred in water at room temperature, for 6 h, to eliminate water-soluble contaminants. The fibers were dried at 100 °C in an oven with forced air circulation, to constant weight. The chemical composition of these fibers was 15.9% total Klason lignin, 69.7% cellulose and 19.9% hemicelluloses^[2].

Alkali treatment: The jute fibers were cut into lengths of 40 mm and swollen using NaOH solution (10% and 5%) for 1h at 0 °C. The fibers were then exhaustively washed in distilled water to remove alkali and again dried to constant weight in circulating air at 100 °C^[2]. **Ionized air treatment:** The fibers were placed in a system based on a metal box containing air-injection channels on its lid, with electrodes near the outlets connected to a high-tension generator. In this study, an alternating current (AC) ionizer was used. In this type of ionizer, both positive and negative ions are generated in the air by applying a high voltage (7.5 kV) waveform to the series of electrodes at 5 mA. The fibers were then treated with a flow of ionized air blown the surface for 1, 3 and 5 h and immediately used to prepare the composite^[2,5]. **Fiber characterization:** The untreated and treated fibers were characterized by determining the crystallinity index of the cellulose and subjecting them to inverse gas chromatography (IGC), as described elsewhere^[1,12]. **Tensile strength:** Tensile strength was tested in fiber bundles 15 mm long and 0.5 mm in diameter, dried previously in a vacuum oven for 4 h, at 100 °C, and kept under vacuum, at room temperature. A Dynamic Mechanical Analyzer (model 2980) from TA Instruments was used in tensile mode, under the following conditions: 25 °C, 1 Newton/ min to 15 Newton. A minimum of thirty samples was tested for each material and average values are reported in the next section.

Pre-polymer synthesis: Phenolic pre-polymer was synthesized by mixing phenol (Synth, 99%), formaldehyde (Synth, 37%) and potassium hydroxide (Synth, 85%) (1.38:1.00:0.06) as described by Megiatto et al.^[1]. **Cure reaction and composite preparation:** Thermoset materials were prepared under conditions similar to those described by Silva et al.^[12]. Composites reinforced with jute fibers (chemically modified or unmodified) were produced by adding the fibers (18 g) to the pre-polymer (102 g), the mixture being subjected to mechanical stirring (50 °C, 30 min) to get optimal impregnation of the lignocellulosic materials by the pre-polymer. The curing procedure was the same as that used for thermoset preparation. Composites were made with randomly oriented fibers (near 40 mm length). **Composite characterization:** impact strength was tested in an Izod impact tester (CEAST Resil 25) and morphology analyzed in a Zeiss-Leica 440, SEM

microscope, with electron acceleration 20 kV. The specimens were prepared as described by Megiatto et al.^[1].

Results and Discussion

The treatments with ionized air (especially for 3 and 5h) and aqueous alkali solution (especially at 10%) led to a certain decrease in crystallinity (I_c) of the fibers. The alkali treatment can remove hemicelluloses of the jute fibers^[2], and, in the present study, the results indicated that in addition to hemicelluloses crystalline domains of cellulose may have been affected by this treatment. The cellulose lattice did not change from I to II (as it can be observed after mercerization) probably due to the conditions considered in the present study (low temperature)^[2]. The ionized air may have reached a small part of the crystalline domains of cellulose, thus disturbing the chains organization.

Table 1 also shows the values of γ_s^D and acid/base parameters obtained by IGC^[1,11,12], for the untreated and treated fibers.

The dispersive component (γ_s^D) was calculated from the retention times (t_R) of nonpolar n-alkane probes on the gas chromatograph (GC) column filled with jute fibers (untreated or treated). The lower the polarity of the fiber surface, the stronger was the interaction with the nonpolar probes, which led to an increase in t_R and consequently, in $\gamma_s^{D[1]}$. Thus, γ_s^D is a measure of the nonpolar character of the surface. In the present study, all treatments led to higher values of γ_s^D , compared to the untreated fiber (Table 1), which indicated that the treatments led to less polar fibers. This suggests that the treatments (particularly ionized air for 5h and NaOH at 10%) may have removed and/or rearranged some layers of the surface of the fibers, possibly enriching the surface with less polar domains, such as aromatic rings. The γ_s^D of the phenolic thermoset matrix was determined in a previous study as 34 mJ m^{-2[1]}. This value of the dispersive component results, at least partially, from the large number of aromatic rings present in its crosslinked structure. Thus, the increase in the nonpolar character of the fibers (Table 1), by the surface treatments should favor interactions with the nonpolar domains of the matrix.

The ratio AN_s/DN_s can be taken as an indication of the predominance of acidic ($AN_s/DN_s \geq 1.1$) or basic ($AN_s/DN_s \leq 0.9$) sites at the surface of the fibers^[1]. Amphoteric surfaces have AN_s/DN_s values between 0.9 and 1.1^[1]. Acidic sites predominated ($AN_s/DN_s \geq 1.1$) after the treatments with 10% alkali and 5 hours of ionized air (Table 1). The enrichment of the surface of these treated fibers with aromatic rings, as mentioned above, suggests that these surfaces could be rich in structures typical of lignin, where

Table 1. Crystallinity index (I_c) of jute fibers^[2] and dispersive component of surface free energy (γ_s^D) and acid-base (AN_s/DN_s) parameters of the jute fiber surface, at 30 °C.

Treatments	Untreated	NaOH		Ionized air		
		5%	10%	1h	3h	5h
I_c (%)	50	48	46	47	43	45
γ_s^D (mJm ⁻²)	18	22	26	21	23	27
AN_s/DN_s	0.9	0.9	1.8	0.9	0.9	2.1

many aromatic rings are phenolic groups. The acidity of the phenolic hydroxyls would thus explain the acidic surface observed on these fibers. The surface of the fibers treated with ionized air for 5h exhibited the most strongly acidic character ($AN_s/DN_s=2.1$) (Table 1). The longest treatment with ionized air (5h) may have oxidized some -OH groups on the surface of the jute fiber to the carboxylic acid group (-COOH), increasing the acidic character of the surface. It is important to highlight that this treatment only affected the surface of the fibers, making it hard to detect the presence of the carboxyl groups, for instance by FTIR or solid NMR, owing to the very low concentration of the acid groups. The other treatments led to fibers with AN_s/DN_s equal to that of untreated fiber (Table 1), so that these fibers can be considered practically amphoteric.

The AN_s/DN_s ratio for the phenolic matrix was 1.4, as determined in a previous study^[1]. The predominance

of acidic sites on the phenolic polymer is probably a consequence of the acidity of the phenolic hydroxyl groups present in the structure of this matrix. Thus, the acidic character of the surface of the fibers treated with 10% NaOH or ionized air for 5h would favor fibers-phenolic matrix interactions at the interface.

The tensile strength and percent elongation at break of the untreated fiber were 460MPa and 0.7%, and, for the 10% NaOH-treated fibers, approximately 900MPa and 2%, respectively. Probably, the treatment with the most concentrated aqueous alkaline solution introduced modifications in the internal parts of the fibers, rendering the interfibrillar region less rigid and giving the fibrils greater freedom to align with the direction of deformation. The treatment with ionized air for 1 and 3h, as well as that with 5% NaOH, did not lead to significant changes in these parameters, relative to the untreated fiber. However, the

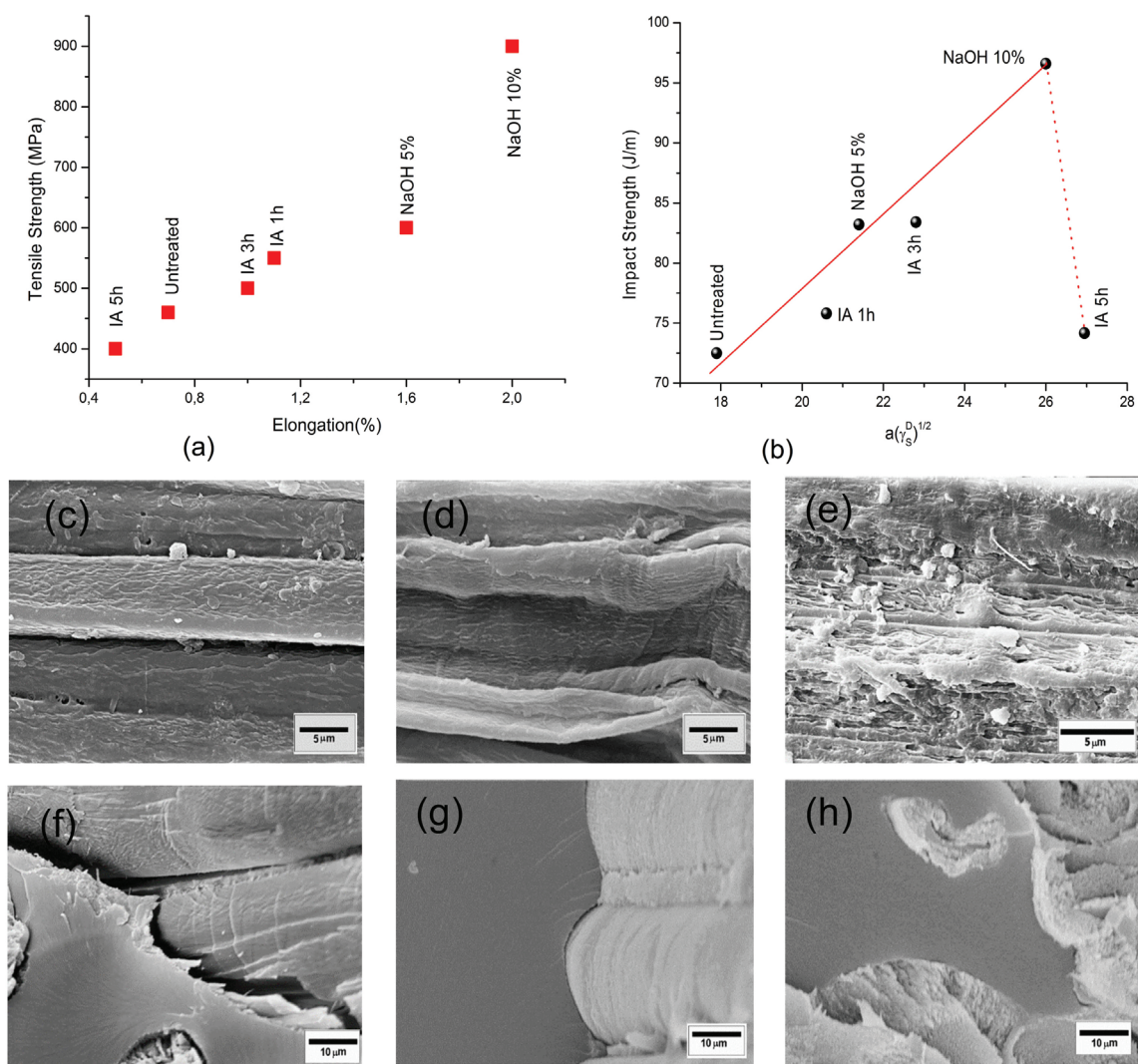


Figure 1. (a) Tensile strength of untreated and treated jute fibers plotted against elongation at break. (IA= ionized-air treatment) (errors approximately 9% for all measurements); (b) Impact strength (errors approximately 6% for all measurements) of phenolic composites reinforced with untreated and treated jute fibers plotted against fiber surface energy. SEM images of the surface of jute fibers: (c) untreated; (d) alkali treated (10% NaOH) (e) IA-5h. SEM images of the impact fracture surface of phenolic composites reinforced with jute fiber (f) untreated; (g) IA-3h; (h) alkali treated (10% NaOH).

fiber treated with ionized air for 5h showed a tensile strength of 395MPa and 0.5% maximum elongation, suggesting that the mechanical properties of the fiber were affected by longer ionized air treatment, which was also reflected in the performance of the fiber as reinforcement, as will be discussed later (Figure 1b).

When Figure 1d is compared with 1c (untreated fiber), it can be seen that the alkaline treatment led to a certain separation of fiber bundles. The treatment with ionized air (5h, 1e) led to a rougher surface, compared to the untreated fiber (1c). Both observed effects may have facilitated the impregnation of the fiber by the phenolic pre-polymer and further by the matrix. The other treated fibers (5% NaOH, ionized air for 1 and 3h; figures not shown) exhibited surfaces with features intermediate between those shown in Figures 1c, 1d and 1e.

Figure 1b shows that jute fiber is a good reinforcing agent for the phenolic matrix, because the impact strength increased from 12.6 Jm⁻¹ (unreinforced thermoset) to 72.6 Jm⁻¹ (composite reinforced with untreated jute). The mechanical properties of the fibers have an influence on their action as reinforcement in composites. In addition, the impregnation of the fibers by the pre-polymer, as well as the strength of interaction between the two, can further influence the load transfer at the interface, and thus the mechanical properties, such as impact strength, of the composite.

The greater separation of fiber bundles (Figure 1d) and roughness (Figure 1e), as well as the lower degree of crystallinity (Table 1) of the treated fibers, led to an increase in the wettability of the fibers by the pre-polymer, further improving the fiber/matrix binding at the interface. Figures 1f, 1g and 1h show SEM images of the fractured surfaces of the composites reinforced with untreated fibers and fibers treated with 10% NaOH and ionized air for 5h, respectively. These images confirm that the adhesion at the interface was improved when the fibers were treated. The fractured surface of the other composites (figures not shown) exhibited interfaces intermediate between those shown in Figures 1f and 1g, 1h. Figure 1b shows that the impact strength of the composites increased with the dispersive component (γ_s^D) of the fibers, except for the fiber treated with ionized air for 5h.

The results plotted in Figure 1b confirm that the treatments strengthened the fiber/matrix interactions at the interface. However, although the treatment with ionized air for 5h led to a decrease in crystallinity (Table 1), to a rougher surface (Figure 1e) and a higher value of γ_s^D , that is, to properties that favor the adhesion at the fiber-matrix interface, the tensile properties of the fibers indicated that the treatment weakened the fiber (Figure 1a). Thus, although the load transfer from the matrix to the fibers was promoted by the very good adhesion at the interface of this composite (Figure 1g), the load was transferred to a weakened fiber, resulting in lower impact strength than other composites. The best result of impact strength was exhibited by the composite reinforced with the fibers treated with 10% NaOH (Figure 1b), which also exhibited the best tensile properties (Figure 1a). The AN_s/DN_s and γ_s^D of this fiber

and the phenolic matrix were, respectively, 1.8 (Table 1) and 1.4^[1], 26 mJm⁻² (Table 1) and 34 mJm^{-2[1]}, which points to good interactions between both the nonpolar and polar domains of the fibers and the phenolic matrix.

Conclusions

Jute fibers were subjected to treatments of ionized air and mercerization (aqueous alkaline solution), which resulted in changes in the morphology, dispersive energy and acidic character of their surfaces, as well as reducing the fiber crystallinity. These changes led to an increase in the wettability of the fiber by the phenolic pre-polymer, as well as to enhancing the fiber/matrix interactions at the interface of the composites. In general, these treatments improved the fibers properties, the adhesion at the interface was stronger in the composites reinforced with treated fibers, than in the one reinforced with untreated fibers. However, the set of results indicated that, when fibers are subjected to these treatments, there should be a balance between the positive changes in their properties, such as the surface energy and acid/base character, and the preservation of their mechanical properties. The fiber treated with ionized air for 5h exhibited some favorable properties for its use as reinforcement in the phenolic matrix, but the partial degradation of the fibers during the treatment impaired their tensile strength, and thus their action as reinforcement of the matrix.

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References

- Megiatto Jr., J. D.; Silva, C. G.; Rosa, D. S. & Frollini, E. - Polym. Degrad. Stabil., **93**, p.1109 (2008). <http://dx.doi.org/10.1016/j.polymdegradstab.2008.03.011>.
- Razera, I. A. T. & Frollini, E. - J. Appl. Polym. Sci., **91**, p.1077 (2004). <http://dx.doi.org/10.1002/app.13224>.
- da Silva, C. G.; Grelier, S.; Pichavant, F.; Frollini, E. & Castellan, A. - Ind. Crops Prod., **42**, p.87 (2013). <http://dx.doi.org/10.1016/j.indcrop.2012.04.040>.
- Almeida, E. V. R.; Morgado, D. L.; Ramos, L. A. & Frollini, E. - Cellulose., **20**, p.453 (2013). <http://dx.doi.org/10.1007/s10570-012-9802-5>.
- Faulstich de Paiva, J. M. & Frollini, E. - Macromol. Mater. Eng., **291**, p.405 (2006). <http://dx.doi.org/10.1002/mame.200500334>.
- Dufresne, A. & Belgacem, M. N. - Polímeros, **23**, p.277 (2013).
- Teodoro, K. B. R.; Teixeira, E. D. M.; Corrêa, A. C.; Campos, A.; Marconcini, J. M. & Mattoso, L. H. C. - Polímeros., **21**, p.280 (2011). <http://dx.doi.org/10.1590/S0104-14282011005000048>.
- Takeshita, H.; Ishida, K.; Kamiishi, Y.; Yoshii, F. & Kume, T. - Macromol. Mater. Eng., **283**, p.126 (2000). [http://dx.doi.org/10.1002/1439-2054\(20001101\)283:1<126::AID-MAME126>3.0.CO;2-#](http://dx.doi.org/10.1002/1439-2054(20001101)283:1<126::AID-MAME126>3.0.CO;2-#).
- Zang, X.; Fukuda, E. K. & Rosen, J. D. - J. Agric. Food Chem., **46**, p.2206 (1998). <http://dx.doi.org/10.1021/jf980332b>.

10. Ramires, E. C.; Megiatto Jr., J. D.; Gardrat, C.; Castellan, A. & Frollini, E. - *Polímeros.*, **20**, p.126 (2010). <http://dx.doi.org/10.1590/S0104-14282010005000016>.
11. Belgacem, M. N.; Czeremuskin, G.; Sapiaha, S. & Gandini, A. - *Cellulose.*, **2**, p.145 (1995). <http://dx.doi.org/10.1007/BF00813015>.
12. Silva, C. G.; Oliveira, F.; Ramires, E. C.; Castellan, A. & Frollini, E. - *TAPPI J.*, **11**, p.41 (2012).

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