Superficial modification by alkalization of cellulose Fibres obtained from Fique leaf

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Abstract. The present study will focus on superficial modification by alkalization of cellulose fibres obtained from Fique leaf as reinforcement in polymer matrices to produce a natural fiber composite that can be suitable for industrial purposes. Fique fiber is a hard vegetable fiber derived from a Colombian plant (Agave furcarea). An appropriate treatment, namely alkalization, of the fiber was chosen and carried out, but will be customized for this specific study to be more environmental-friendly and economical. A higher fiber-to-solution ratio as well as a low concentration would decrease the price of the treated fibers. The changes introduced to the surface morphology by the abovementioned treatment is then examined using a scanning electron microscope (SEM), Thermogravimetric analysis (TGA), Differential scanning calorimetry (DSC) and FTIR analysis, and untreated and treated samples were.

1. Introduction
Due to the increase of the environmental consciousness around the world and with the purpose of diminish the damage to the environment, research of composite materials reinforced with natural fibers (NFC) has been boost, so that they can replace those of fossil origin, empowering the use of natural resources to accomplish this goal. Fique fiber is a hard vegetable fiber derived from a Venezuela and Colombian plant (Agave furcarea ssp.) whose production has expanded to other countries like Brazil, Ecuador, Cuba, Mexico, Costa Rica as well as other regions in Central and South America [1]–[3]. Since the fiber has high availability, low cost and is totally recyclable and biodegradable, it possesses technological, environmental and economic advantages. However, there are also certain limitations to its applications such as low mechanical properties and toughness; property variations; sensitivity to moisture, temperature and UV radiation; and fire resistance. Firstly, the fique fibers just like for other vegetable fibers, incorporation with an organic polymer matrix poses the greatest challenge due to the difference in surface nature. Polar OH groups are present in the chemical components, such as cellulose or hemicellulose, which makes these fibers highly hydrophilic. These hydroxyl groups and other oxygen containing groups are able to attract moisture through hydrogen bonding. Thus, they are prone to water absorption, leading to changes in fiber dimensions [4]. Since the polymer matrices are hydrophobic, good wetting of the fiber is hard resulting in poor adhesion at the fiber-matrix interface. The adhesion between fiber-matrix is the main factor that determines the mechanical properties of the composite material. Poor adhesion causes the load transfer from the matrix to the fiber to be ineffective, which leads to poor mechanical properties of the resultant composite [5], [6]. Application of chemical agents to the fiber and modification of the matrix could overcome this challenge [7]. Other disadvantages
associated with the use of fibers are quality variations and low thermal stability [8]. Several investigations concerning to realize superficial modification to the hard natural fibers of reinforcement have been realized in sisal fibers [9]–[14], jute [15]–[19], bamboo [20]–[23], kenaf [24]–[27] and hemp [28], [29].

1.1 Natural fibres (NF)

The natural fibers are composed mainly of cellulose (Figure 1), which is a high resistance and rigidity polymer, composite and other compounds such as lignin, waxes and water-soluble compounds. Among its advantages it highlights its low price and weight and high resistance, similar to the synthetic glass fibers. Disadvantages, the hydrophobic polar nature of the natural fibers causes a bad adherence with a thermoplastic matrix and low microbial resistance.

Cellulose serves as the main component and provides the strength and stability in the plant. The gluca (polysaccharide of D-glucose monomers) consists of β-(1 → 4) linked monomer units. Cellulose is highly anisotropic with a theoretical strength of 10 GPa in the chain direction due to the molecular linearity. The pyranose rings are in the C1 conformation, which means that the -CH2OH and –OH groups, as well the glycosidic bonds, are equatorial with respect to the mean planes of rings [30]. Natural fibers are composed of a hierarchical structure [31]:

i) Vascular bundles of elementary fibers (fibrils)

ii) Cellulose microfibril bundles consisting of packed bundles of cellulose chains, in a network of hemicellulose and lignin.

The microfibrils are helically wound along the fiber axis and form hollow cells. The tensile strength of natural fibers are mainly owed to these microfibrils and its cellulose type, because each type of cellulose has its own cell geometry.

![Figure 1. Chemical structure of cellulose chain](image)

1.2 Treatment of natural fibers

There are several methods available to the enhance adhesion through chemical surface treatment of natural fibers involve silanization [32]–[39], Alkalization [5]–[7], [14], [29], [31], [32], [37], [40]–[42], [42]–[60], Esterification [6], [42], [61]–[64] benzoylation [10], [65]–[67], maleated coupling agents, isocyanate treatment, and grafting of synthetic polymers. The simplest way is by drying of the fiber before addition of the matrix. By doing so, the bonding of water molecules to the fiber surface is cancelled. More advanced treatments such as fiber surface modification, matrix modification, corona discharge, use of additives and coupling agents can enhance fiber-matrix adhesion. Surface modification by alkalization reduces the ability of cellulose to bond hydrogen, which also cancels the bonding of open hydroxyl groups with water molecules. In other words, it reduces the adsorption of water. Application
of additives can be done on the fibers or the matrices. Coupling agents are compatibilizers between fibers and matrix. These agents remove weak boundary layers and create a cross-linked region in which there are covalent bonds between the matrix and fibers [68]. These treatments are capable of changing the chemical composition, physical properties, thermal stability, and surface structure.

1.2.1 Alkalization. Alkalization, also known as mercerization or alkali treatment, is one of the most common treatments applied on natural fibers [23][25][64][69][6][41]. It is an irreversible process which involves the immersion of plant fibers in a relatively concentrated aqueous solution of a strong base for a set amount of time. The most commonly used base in this treatment is sodium hydroxide, NaOH. The treatment is mainly employed as a treatment of natural fibers that are to be used as reinforcements in a polymer matrix, thermoplastics and thermosets alike. The surface is cleaned by attacking non-cellulosic components in the fiber, which also increases the cellulose amount. Impurities and cementitious materials covering the external surface like lignin, wax, oils and residue from leaf not extracted previously are partly removed. Depolymerization of cellulose changes its fine structure and short length crystallites are produced. The surface roughness is increased through the disruption of hydrogen bonding in the network structure. More cellulose is exposed at the surface and there is an increase in fiber fibrillation. Thus, more reaction sites are produced, providing better mechanical interlocking with a matrix and, hence, better interfacial bonding. However, increased surface roughness could also promote the presence of voids in the resultant composites [42]. The treatment changes the fine structure, dimension, morphology and mechanical properties of the fiber. The mechanical behavior of natural fibers, more importantly the strength and stiffness, is significantly improved, which in turn also improves the mechanical properties of the resulting composite. Immersion of the natural fiber in aqueous hydroxide solution results in the ionization of the hydroxyl group to the alkoxide, which proceeds through the following reaction [4], [6], [7].

\[
\text{Fiber} - \text{OH} + \text{NaOH} \rightarrow \text{Fiber} - \text{O}^- \text{Na}^+ + \text{H}_2\text{O}
\]  

The effect on mechanical properties by alkali treatment can be further enhanced by the application of tensile load [31]. Tensile load application during the treatment induces changes in microfibril orientation, resulting in an improvement in structural and mechanical properties. The cellulose microfibrils are the main contributors to the tensile strength of natural fibers. In addition, the spiral angle affects the mechanical properties due to the highly anisotropic nature of cellulose. The mechanical properties (have been found to) become higher when the orientation of the microfibrils are along the axis of tension. Treatment with alkali solution while under tension leads to the rearrangement of the microfibrils in the direction of tensile application. There is a decrease in the spiral angle (angle between fibrils and fiber axis) and increase in molecular orientation, which in turn would cause better load sharing and higher stress development in the fiber. A study on Ramie fibers showed that treatment under 0.098 N of tension with 15 wt% NaOH solution for 2 h increased their tensile strength compared to untreated fibers whereas slack alkali treated fibers had a decrease of 1.8 % (15). This procedure could help achieve greater mechanical properties, but with lower concentrations of NaOH.

2. Experimental results and discussion
2.1 Materials
The fique fibers were provided by Cohilados Ltda. The chemical agents used in this study were: Sodium hydroxide pellets (99%, Emsure) and glacial acetic acid (100%, Emsure). Distilled water was used for preparation of sodium hydroxide and acetic acid solutions. Fique fiber was cut to a length of about 5 cm and a total amount of 8 g was placed inside the glass container. The ratio of fiber weight to alkali solution was set to 1:10 for all treatments. The fiber was immersed in NaOH solution at room temperature for 30 min. After the set immersion time, the spent solution was decanted and the fibers were repeatedly washed with distilled water containing a small amount of acetic acid to remove traces of alkali solution.
To speed up neutralization, the sample was washed under running water and thereafter rinsed with distilled water. In order to remove residual moisture, the treated samples were dried in an oven at 60 °C until constant weight was reached (~ 6 hrs). The treated samples along with samples not subjected to alkalization to the fiber at different stages of the alkalization process are presented in Figure 2. Some samples were subjected to a pretreatment using fabric softener to ease the removal of surface particles.

| Samples of fiber | Treatment (softener) | Concentration wt% NaOH | Reaction time (h) |
|------------------|----------------------|------------------------|------------------|
| Sample A         | Untreated            | 0                      | -                |
| Sample B         | Treated              | 0                      | 24               |
| Sample C         | Untreated            | 2.5                    | 1/2              |

2.2 Thermogravimetric (TGA) and Differential scanning calorimetry (DSC) Analysis

In order to know the thermal stability of the fique fibers, it proceeded to measure the behaviour of the mass of the fibers in function of the temperature, it’s measured the fique natural fiber, the fique fiber that passed through concentrations of NaOH and the fique fibers passed through softener. All the measures were realized at a speed of 10°C/min. The samples (see table 1) were submitted to controlled heat from 25°C to 500°C until the process of degradation and combustion of the solid residues initiates, finally remaining the generated ashes.

As examples are shown in figure 2, the TGA and DSC analysis for the natural fique fibers (sample A) it’s noted that as the fibers is heated, when it reaches ~150°C it has already lost approximately 7.045% of its weight, which can be attributed to the humidity in the material, once this humidity no longer existed, the fibers do maintain steady until approximately 280°C, temperature at which the process of decompose of the fique fibers starts, losing 71.34% between 280°C and 380°C, once 380°C is reached it initiates the degradation and combustion process, leaving 20% of the initial weight. DSC analysis was carried out to observe the behavior of the natural fique fibers (sample A), it presents a transition step type around -7.02°C which it is attributed to the vitreous transition of the fiber with an energetic requirement of 2J/g, then it is observed a transition of endothermic character that initiates at 10°C and finalizes around 130°C which can be attributed to dehydration of the fiber with a required energy of 247,3 J/g and ends with a transition of exothermic character around the 301.28°C with an energy liberation of the order of 15.93 J/g, that can be attributed to a possible combustion of the material for the high temperature reached. Mostly the thermal behavior of fique fibers presents three lose weight regions, which are show in Table 2.

The natural fibers fique (sample A) and treated fibers fique (Sample B) using softener has a maximum degradation about 360 °C and 355 °C respectively, whereas the fique fiber after 30 minutes of immersion in alkali solution (Sample C) has a maximum degradation al 337 °C. From figure 2.b), it can be seen that the treated fiber with fabric softener starts to lose weight earlier that samples B and Sample C. This may be attribute to the using fabric softener to ease the removal of surface cellulose particles. For the untreated fique fibers (without NaOH) two obvious peaks can be observed. The first peek at 240 °C corresponds to the decomposition of hemicellulose while the second peak at 355°C is due to the decomposition of cellulose.
Figure 2. TGA/DTG and DSC curves a) natural fibers fique (sample A), b) treated fibers fique using softener (Sample B), c) fique fiber after 30 minutes of immersion in alkali solution (Sample C)

Table 2. Thermogravimetric results

| Samples of fibre | T₁ (°C) | T₂ (°C) | T₃ (°C) | Temp. T₁(°C) | Temp. T₂(°C) | Temp. T₃ (°C) | Mas weight loss(%) | Max. temp degradation |
|-----------------|---------|---------|---------|--------------|--------------|--------------|------------------|---------------------|
| Sample A        | 240     | 332     | 380     | 7.980        | 29.26        | 81.32        | 81.86            | 361                 |
| Sample B        | 176     | 280     | 385     | 7.045        | 32.15        | 79.86        | 83.26            | 355                 |
| Sample C        | 236     | 255     | 365     | 7.323        | -            | 65.753       | 70.15            | 337                 |
2.3 **FTIR Analysis**

Fig. 3 shows band intensities in the infrared spectra of natural fique fibers untreated (sample A) and fique fiber treated with NaOH (sample C). It is well known that natural fiber mainly consists of cellulose, hemicellulose and lignin. Hemicellulose and lignin are soluble in alkali solutions; therefore, it is likely that a part of both components were dissolved during alkali solution treatment. Careful examination of the spectra revealed that several changes did occur. The vibration peak at 1731 cm\(^{-1}\), assigned to a C=O stretching vibration of carboxylic acid or ester, disappeared due to the removal of hemicellulose. Second, the vibration peak at 1240 cm\(^{-1}\), which belongs to a C-O stretching vibration of the acetyl group in lignin component, was reduced. Third, a vibration peak at 2915 cm\(^{-1}\), belonging to the C-H stretching vibration in cellulose and hemicellulose, decreased after alkali solution treatment indicating that part of the hemicellulose was removed. On the other hand, in both spectrums appear typical vibrations for fique fibers, for example the peak at 3330 cm\(^{-1}\) due to water molecules absorbed on the cellulose structure. The band located at 2850 cm\(^{-1}\) is associated with the C-H stretching vibration from CH and CH2 in cellulose and hemicellulose components. The vibration peak at 1026 cm\(^{-1}\) corresponding to the vibration of C–O–C (glycosidic linkage).

![FTIR spectra for treated (top) and untreated (bottom) fique fiber](image)

**Figure 3.** FTIR spectra for treated (top) and untreated (bottom) fique fiber

2.4 **Surface Morphology**

The effect of alkali concentration on surface morphology was examined using SEM. The effect of fabric softener on as-received fibers before alkalization were also studied. Two different concentrations of NaOH solution were employed in this study. SEM was mainly used for observation of the surface morphology as it provided more details.

2.4.1 **Effect of fabric softener.** The figure 4 show thee fiber surface of the untreated Sample A is seemingly smooth and intact, although loose helical fibrils can be found occasionally. This could be due to damage during the fiber extraction. The fiber also has a uniform diameter throughout its length. However, the thickness varies between each fiber in the interval 150 – 200 µm. Here it is easier to identify the cells walls. At these magnifications, the surface does not seem very smooth, although the roughness also seems to vary from fiber to fiber. Figure 5 shows that Sample B an increased surface roughness, even more so than the as-received Sample A. The rectangular cell wall edges are slightly more pronounced. One would think the contrary was the case since the individual fiber of Sample E do
not adhere to each other. This hints at low mechanical interlocking which should be the case for a smooth surface, which is obviously not the case for Sample B.

**Figure 4.** SEM micrographs of untreated fiber fique as received magnified at 200 (left) and 500 times (right)

![SEM micrographs of untreated fiber fique as received magnified at 200 (left) and 500 times (right)](image)

The surfaces of pretreated samples appear to be rougher, which is expected as the pretreatment alone had already increased the surface roughness as shown in Figure 6. Like Sample B, the fiber bundles of these pretreated mercerized samples are loosely bound. It is therefore possible that this observation is related to the chemical changes on the surface brought about by the fabric softener. The fiber-fiber adhesion of non-pretreated samples is not solely mechanical but also chemical.

**Figure 5.** SEM micrographs of fique fiber pretreated with fabric softener in 30 min magnified at 200 (left) and 500 times (right)

![SEM micrographs of fique fiber pretreated with fabric softener in 30 min magnified at 200 (left) and 500 times (right)](image)
3. Conclusions
In general, in the TGA analysis of all the treated and non-treated samples it can be noted that it presents two temperatures of weight loss that are appreciable. Making a comparison of the thermograms, it can be noticed that the fique fibers submitted to a previous washing process are thermally less stable that the rest of the fique fibers, remaining more stable the fibers treated previously with NaOH.

The use of alkali solution had successfully changed the surface morphology of the as-received fique fiber as proven by Scanning Electron Microscopy (SEM) and examination of the FTIR spectra. The concentrations 2.5 wt% NaOH resulted in a greater extent of fiber alkalization where helical fibrils were exposed in addition to increased surface roughness.

The use of fabric softener on as-received fibers resulted in increased surface roughness. Despite this fact, there is less mechanical interlocking of individual fibers compared to the as-received samples natural fibers. This property was preserved even after drastic changes on the fiber surface following alkalization.

For future prospects, thermoset and thermoplastic polymers could be used as the composite matrix. Moreover, the several variables such as fiber type, length, orientation, loading and fiber dispersion could be varied to study their effect on the composites properties.

Acknowledgments
This work was supported by the DIT under grant Nº 025-0716-2600; this financial support is gratefully acknowledged. The authors would like to express their gratitude to GiDeTechMA Research Group of Faculty Mechanical Engineering, Universidad Pontificia Bolivariana, Bucaramanga.
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