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Effects of Methane Cold Plasma in Sisal Fibers

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Abstract. One of the main problems in using vegetable fibers as reinforcement in aggressive cement matrix is the penetration of alkaline products in the porous structure of the filaments, making them very fragile with the time. In this sense a series of physical and chemical methods of surface modification has been used in order to improve its characteristics. The plasma surface modification technique is a physical method surface modification that utilizes ionized gas at low pressure to change the chemical nature and the substrate surface morphology of both organic and inorganic materials without changing their intrinsic properties. This is considered an environmentally friendly process without generation of contamination and has a low operating cost compared to some chemical (such as silane based) treatments. In the present study, the sisal fibers were treated with methane plasma generated by direct electric current during 10, 20 and 30 min with gas flow of 5 cm^3/s and current of 0.10 A. The study presents some mechanical, physics and chemical characteristics of sisal fiber after being subjected to treatment with methane cold plasma. The results presented indicate that treatment with methane cold plasma induced changes in sisal fibers at all times of exposure to treatment (10, 20 and 30 min). However, the major changes in structural and mechanical components may be seen in fibers treated with 10 min of exposure to plasma.

Introduction

Currently the issue of economic, social and environmental sustainability is present in discussions of all sectors of industry, since it is a constant search by improvements in living conditions of the population, and by maintaining a safe environment for present and future generations.

Following this trend, the construction industry known for the massive use of non renewable natural resources, energy and ability to generate environmental impacts in all links of its chain, is being challenged to incorporate sustainability in the production processes. An example is the incorporation of vegetable fibers in the cementitious composites production to be used in many applications. Research related to the development of new cementitious products with natural fibers as reinforcement, need to be criated and improved so that these composites exhibit the characteristics of strength and durability similar to the materials set out in the market. While deficiency by these composites is associated to the hydrophilicity of natural fibers and consequently to reduce the durability of these compounds, researches of Tolêdo Filho et al.[1], Bilba and Arsene [2]; Tonoli et al. [3], have been conducted in order to fill the gap, as this limits their market inefficiencies and generates economic and environmental costs. The aim of this work is to present some mechanical, physics and chemical characteristics of sisal fiber after being subjected to treatment with methane cold plasma.

Natural fibers

The growing worldwide concern with the natural resources' preservation has intensified the interest of productive sectors on the use of renewable raw materials, for example, vegetable fibers, for the production of new composite materials and products. Thus, may be considered that these fibers are undergoing a high-tech revolution, in order to replace both synthetic and glass fibers in many applications in the automotive, packaging and construction industry [4,5].

This fact is mainly due to its intrinsic characteristics such as abundant availability, biodegradability, low density, non-toxicity, less abrasiveness to processing equipment, useful mechanical properties and low production cost compared to glass fibers and ohers derived from petroleum [6-8].

Using natural fibers also contributes to economic growth and social improvement of the producing region, since it raises employment and income in areas with low human development index, such as the Brazilian Northeast semi arid, which presents suitable conditions for growing sisal.

To the agricultural sector economy in the northeastern Brazil, the sisal fiber cultivation is indispensable once it generates employment and subsistence for thousands of people, providing income for the states of Bahia, Paraiba and Rio Grande do Norte. Bahia stands as the largest domestic producer of this plant, with more than 95% of fiber production [9].

The fibers are extracted from the leaves, which have 8 to 10 cm in width and 150 to 200 cm in length. During the process of improvement large amounts of solid and liquid are wasted, comprising on average 1% of short fibers, 15% of mucilage, and 81% of juice or sap chlorophyll [10].

However, Hill et al. [11] and Rowell [12] argue that, despite of the advantages that come by the use of natural resources, these fibers present a hydrophilic character, and consequently they swell and shrink according to the moisture content to which they are submitted. Besides, they are degraded by acids, bases and ultraviolet radiation with incremented effect under high temperature exposure.

Lignocellulosic fiber are considered natural composites, constituted by cellulose microfibrils embedded in a matrix of hemicellulose and lignin. Structurally vegetable fibers are composed by individual cells, called fibrils, which are composed of microfibrils arranged in layers of different thicknesses and with different orientation angles [12].

Lignocellulosic materials are composed primarily by cellulose, hemicellulose and lignin (Table 1).

Table 1 Chemical composition of some Brazilian vegetable fibers [5]

Fiber	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Bagasse (sugarcane)	54.3 – 55.2	16.8 – 29.7	25.3 – 24.3
Coir	43.4 – 53	14.7	38.3 – 40.7
Curaua	70.7 – 73.6	21.1	7.5 – 11.1
Sisal	74 – 75.2	10 – 13.9	7.6 – 8

Cellulose is a natural polymer with crystalline properties, consisting of repetitions of glucose monomers (β - glucose), connected to each other in positions 1 and 4, as illustrated in Fig. 1. The hygroscopic hydroxyl groups (OH), which protrude from both sides of the chain form hydrogen bonds with OH groups of neighboring chains, resulting in the formation of bundles of parallel cellulose molecules held together by interconnections (Fig. 2) [13]. The links of hydrogen bonds between hydroxyls constitute the basic condition that prevents water from penetrating in the crystalline cellulose, since the OH group has become quite stable. Thus, the only hydroxyls that can bind chemically with water are those present on the surface of cellulose microfibrils [14].

Hemicellulose is a polysaccharide that presents usually linked to cellulose. Plants' hemicellulose fraction consists in several polymerized monosaccharides, with the lower degree of polymerization of cellulose [15]. Because of its heterogeneous and branched nature, Morsing [14] states that the hemicellulose forms a predominantly amorphous substance, which facilitates access to the hydroxyl groups and other reactive groups. Thus, it is relatively hydrophilic and sensitive to degradation by alkali and heat.

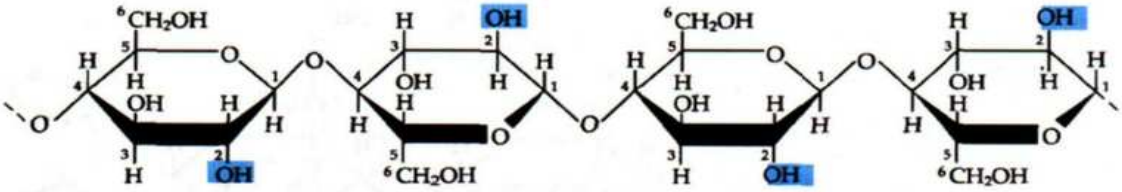

Fig.1. Cellulose molecule [13]

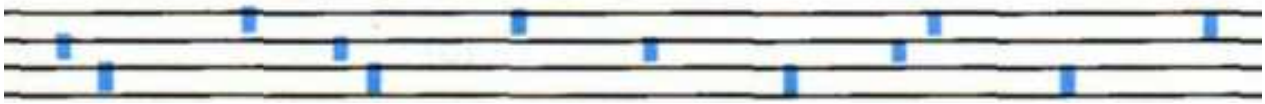

Fig.2. Cellulose molecules linked [13]

Lignin is a complex polymer amorphous, structure and chemical bonds still uncertain. It is understood that it is a three-dimensional polymer composed mainly by fenilpropane units, methoxy groups and other chemically active groups. Because of these connections lignin is relatively stable and hydrophobic, compared to hemicellulose [14]

Gram [16] reports that in an alkaline medium, the substances are easily destroyed, compromising the integrity of the fiber. However, studies of Mohr et al. [17] concluded that cementitious composites reinforced with unbleached wood pulp performed slower degradation during exposure to soak & dry cycles, compared to those produced with bleached wood pulp, in other words, with low lignin content. This suggests that the lignin in the unbleached fibers plays an important role in protecting the chains of cellulose, preserving them from an early degradation.

Regarding to the mechanical characteristics of natural fibers, due to the characteristics of polymeric fibers, their mechanical properties are determined by the resistance of inter and intramolecular bonds and the polymer chains formation [18].

Natural fibers reinforced cementitious composites

The cementitious composite is a material made from hydraulic cement and fibers randomly distributed, with no addition of small and/or large size aggregates. Nowadays, a variety of fibers can be used as cement reinforcement, such as fiberglass, carbon fiber, nylon fiber, polypropylene fiber and vegetable fiber [19].

Cementitious matrices are brittle, porous and susceptible to cracking. Fibers insertion is an important factor, as they lead to the improvement of mechanical properties that inhibit cracking. If the matrix cracks, the fibers begin to withstand the tensile stress acting on the composite close to the crack [20].

Aziz et al. [20] and Motta [21] argue that the fibers tend to increase not only the tensile strength in bending, but also the toughness of the hardened composite. If the fibers pull out of the matrix rather than break, with the consequent increase of energy absorption, toughness and impact resistance of the composite in comparison to the unreinforced matrix.

The matrix fiber strengthening increases the versatility of the mortar as a building material, providing an effective method to overcome its characteristic fragility [23].

However, natural fibers may undergo many degrees of degradation when subjected to high pH environment as the solutions generated by cement hydration reducing the durability and strength of reinforced composites them [25]. This fact is directly associated to the reduction of fibers pullout strength (fiber pull out), due to a combination of mechanical strength loss to the mineralization and the change in volume by high water absorption by the fibers.

Gram [16], studying the fibers degradation mechanisms, found that the main cause of the change in their enhancement characteristics is related to the lignin and hemicellulose (present in the middle lamella) dissolution and the filling of the lumen by calcium hydroxide. To control the alkali attack to the fibers is suggested the use of arrays of low alkalinity, carbonation of the matrix, treatment of the fibers, etc [26].

Cold methane plasma treatment for natural fiber

Plasma is a partially ionized gas, considered the fourth state of the matter, which constitutes more than 99% of the universe. It consists in electrons, ions and neutrons in the fundamental and excited states [27,28].

The term plasma, also known as glow discharge, electrical discharge or gas discharge, defines a partially ionized gas composed of a neutral species mixture (atoms, molecules and free radicals), electrically charged species (electrons, positive and negative ions) and photons. It is produced by an electromagnetic field applied under appropriate pressure and appears electrically neutral. In other words, the number of electrons equals the number of ions [29].

The plasma treatment has been considered a quick and safe alternative for the fibers surface modification, since it is a clean process, without using pollutant inputs and without generation of hazardous wastes, and with low operating costs [27,30,31]. In addition to eliminating human security risks associated with hazardous chemicals, the plasma treatment minimizes the generation of environmental problems and the disposal of liquids and solids. Therefore, it is considered as an environmentally friendly process by the U.S. Environmental Protection Agency [32].

There are two kinds of plasma, cold and hot. The hot plasma is considered the thermodynamic equilibrium plasma, as the electron temperature is close to the gas temperature. The cold plasma is a non-equilibrium thermodynamics plasma, where the electron temperature is higher than the temperature of the other species in the plasma and it is possible to work with atmospheric pressure. They are initiated and obtained through the use of a continuous power source, radio frequency and microwave. In this process, the electrical discharge is maintained by collisions between electrons and other species present in plasma.

Navarro et al. [31] reported that the cold plasma treatments are characterized by low levels of ionization and therefore are suitable for organic substrates modification., It is a convenient method for surface modification of solid materials, by having a low penetration depth and, therefore, without changing the volume of the substrate.

In the vegetable fibers, the low-temperature plasma surface causes a change known as plasma polymerization [33], which allows the formation of a highly crosslinked film with thickness of approximately 50 nm to 1 μm, and with a high degree of compliance [34].

The plasma polymerization is a specific type of chemistry plasma, which involves reactions between plasma species, plasma species and the fiber surface species, and between itself surface species [33].

In the present study, the methane monomer is used for providing the hydrophobic alkane radical formation in order to maximize the desirable surface hydrophobic characteristics of the vegetable fiber. This polymerization allows the polymeric film formation based on carbon, and deposited on the fiber surface [35], protecting it from cementitious matrix alkaline attack.

Material and methods

Material. Sisal (*Agave sisalana*) fibers were extracted from the waste of baler twine cordage, provided by the Associação de Desenvolvimento Sustentável e Solidário da Região Sisaleira (APAEB - Valente, Bahia State, Brazil) which were treated as received without any previous conditioning.

Methods. Cold plasma treatment with methane gas: The sisal fibers were treated in cold plasma reactor vacuum with methane gas (Fig. 3), generated by direct electric current during 10, 20 and 30 min with flow of gas of 5 cm^3/s and current of 0.10 A.

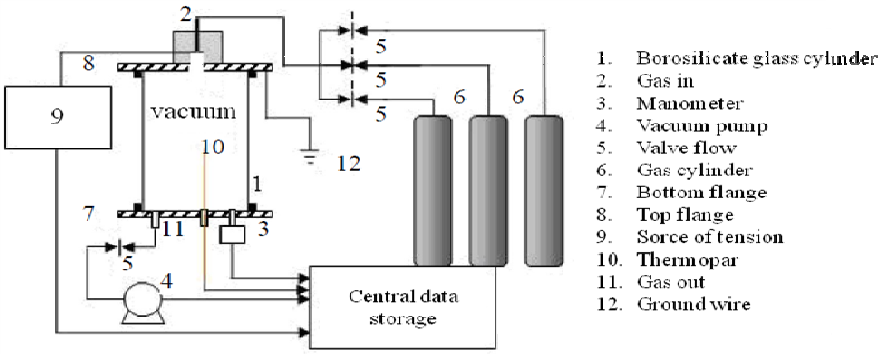

Fig.3. Cold plasma reactor vacuum [39]

Mechanical tensile test: For the mechanical direct tensile analysis, the fiber samples were placed in the universal testing machine EMIC DL 30000, with load cell capacity of 1000 N, 2000 N pneumatic grips and test speed 0.4 mm/min. The test speed was established from Motta [21] and the distance between the grips match the useful length of the fiber to be tested. The fiber was conveniently fixed in the paper mask apparatus, according to the scheme of Fig. 4, in the attempt to avoid tension concentration or eccentricity during the development of the test.

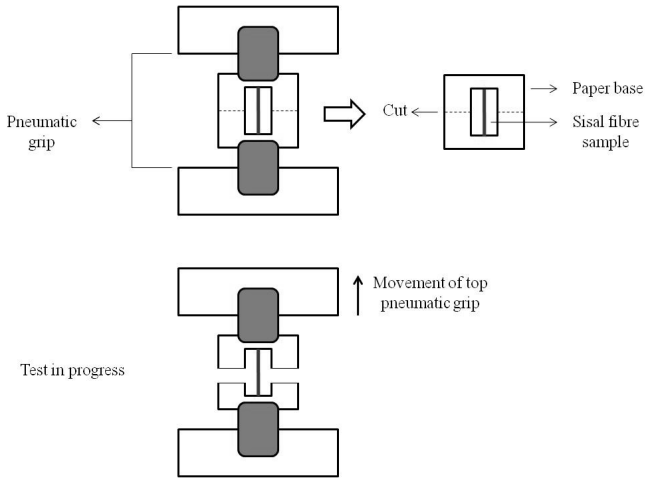

Fig.4. Mechanical tensile test in sisal fibers (without scale)

X-ray diffraction: For the X-ray measurements, the sisal fibers were cut in small pieces and then, fixed in a small plate with inert paste, in order to interact with the beam. The X-ray diffractogram patterns were obtained by the X-ray generator Theta-Theta from RIGAKU with cooper tube (alpha radiation). The beam angle varied from 10 to 30 (2 theta).

Fourier transform infrared spectrum: Infrared spectra (FTIR) of films were recorded between 4000 and 600 cm^{-1} at 2 cm^{-1} of resolution, with a Spectrum One (Perkin Elmer) spectrometer, supplied with a universal attenuated total reflectance (UATR) accessory. For each spectrum, six scans were co-added. A small amount of fibers were carefully placed over the cell and pressed conveniently in order to maintain the same pressure, for the reflectance operation mode. Measurements were performed at room temperature.

Results and discussions

Mechanical characterization. The use of natural fibers as reinforcement depends, among others, of their mechanical properties, thus, an improved mechanical behavior of these fibers is necessary for the development of new composite materials.

Table 2 presents the mean values, with the respective standard deviations, for the sisal fibers tensile strength under different time exposition to the treatment with methane cold plasma.

Table 2 Tensile strength of sisal fiber under different times of exposition to the methane cold plasma

Condition	Tensile strength (MPa)
Reference (no treatment)	197 (42.0)
10 min treatment[1]	278 (68.1)
20 min treatment	208 (51.5)
30 min treatment	230 (47.5)

[1] Methane cold plasma

Observing the average value of tensile strength obtained for untreated sisal fibers, it can be seen that this is below those reported in the literature (Table 3). This fact can be explained by the type of fiber used in the study to be waste of baler twine cordage, which suffered twisting during the production process.

Table 3 Distinct values for tensile strength of sisal fibers, as reported in the literature

Tensile strength (MPa)	Reference
324-329 / 577	Satyanarayana et al. [5]
467	Motta [21]
513	Martin [36]

Another factor that may affect the fiber strength is its morphology. Rowell et al. apud Martin [36] stated that the natural characteristics of the fibers such as knots and lumps can act as points of stress concentration along the axis of the fiber and consequently reducing the mechanical resistance.

Furthermore, the tensile strength decreases with the increasing of the diameter. Tomczak et al. [7] reports that this influence can be explained by the structural properties of the fibers. As the diameter increases there is a greater possibility of variations in the number of unitary cells, changing structural parameters such as helix angle, volume of constituent cells and number of defects (Table 4).

Table 4 Minimum and maximum values of the sisal fibers diameters and their respective tensile strength

Condition	Diameter min and max (μm)	Tensile strength (MPa)
Reference (no treatment)	169.6	279
	231.3	136
10 min treatment[1]	181.5	378
	215.0	177
20 min treatment	194.5	312
	289.8	135
30 min treatment	239.1	309
	344.5	161

[1] Methane cold plasma

According to Table 4, there is great variability in diameter of the fibers. This morphological difference, that is usual among the vegetable fibers, can be responsible for the high standard deviation values found not only for untreated fibers, but also for the fibers under the different treatment conditions.

The average tensile strength of the fibers after treatment with methane cold plasma indicates that, numerically, all the treated fibers perfomed a greater resistance compared to the untreated fibers (Fig. 5).

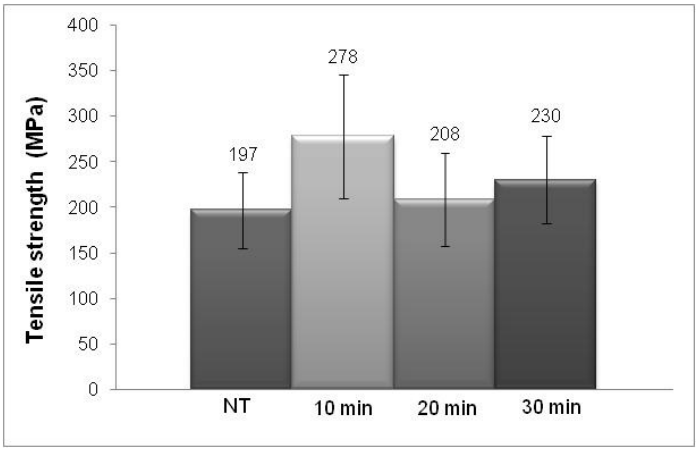

Fig.5. Average tensile strength (with bars of+/- standard deviation) of untreated sisal fiber (NT) and treated fibers under different times of exposition to the methane cold plasma: 10, 20 and 30 min

The Tukey test applied to the comparison of means (each one based on 14 repetitions) of tensile strength indicated that the fibers treated for 10 min with the methane cold plasma performed a statistically significantly (5% of error probability) higher tensile strength in relation to the untreated fibers and fibers treated for 20 and 30 min as depicted in Table 5.

Table 5 Tukey test applied to the comparison of average tensile strengths of sisal fiber under different times of exposition to the methane cold plasma

Condition	Tensile strength (MPa)
Reference (no treatment)	197 a
10 min	278 b c d
20 min	208 a e
30 min	230 a e

** Numbers followed by the same letter have no significant difference between them at 5% of probability

Sao et al. [37] and Rowell et al. apud Martin [36] stated that the mechanical properties of the lignocellulosic fibers are directly related to the crystallinity index (Ci). In other words, the mechanical performance has direct relation with the cellulose amount present in the fibers.
The crystallinity index is calculated by Eq 1 based on the X=ray diffraction (XRD) patterns as depicted in Fig. 6. As indicated in Table 6, there was an increase in the crystalline portion of the fibers treated with 10 min of methane cold plasma.

$$Ci\ (\%) = 1 - \frac{Ia}{Ic} * 100 \quad (1)$$

where,
Ci = Crystallinity index
Ia = Amorphous peak intensity (2θ = 18º)
Ic = Crystalline peak intensity (2θ ~ 22º)

Table 6 Cristallinity index of sisal fibers under different times of exposition to the methane cold plasma

Condition	Ci (%)
Reference (no treatment)	50.9
10 min treatment	51.7

Physical and chemical characterization

X ray diffraction. Through X-ray diffraction (XRD) it can be determined the influence of treatments on the increase, maintenance or reduction of crystallinity of the fibers.

Fig. 6 shows the XRD patterns of untreated sisal fibers and 10 min treated fibers. There was a larger increase in the peak amplitude of the fiber treated with cold plasma of methane for the angle $2\theta = 22^{o}$, in relation to the corresponding peak of the untreated fiber. The referred peak is associated with the crystalline region of the fiber [7], which increased from 850 (untreated) to 1246 (10 min treatment).

In addition, one can observe an increase in the peak amplitude of lower intensity $2\theta = 18^{o}$ (from 417 to 601), corresponding to a region of semi-crystalline and amorphous structure. This increase can be attributed to the increase in the fraction of semi-crystalline over amorphous components of the fiber.

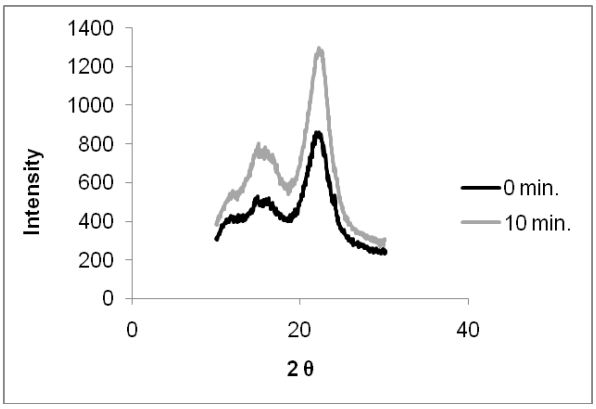

Fig.6. XRD pattern of sisal fibers untreated (0 min) and methane cold plasma treated (10 min)

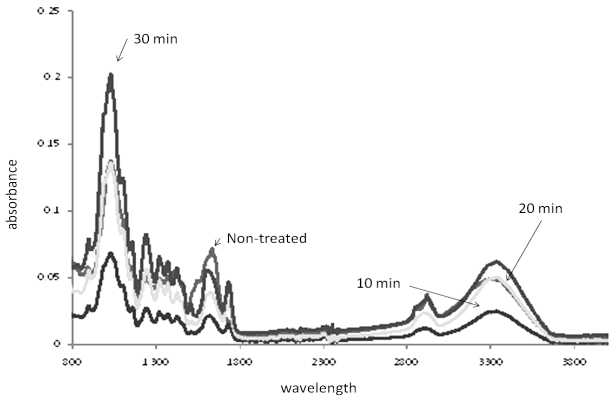

Fig.7. FTIR spectra of sisal fibers treated with methane cold plasma

Fourier transform infrared spectroscopy

Fig. 7 shows the Fourier transform infrared (FTIR) spectra of sisal fibers untreated and treated with methane cold plasma. The spectra show some changes induced by the cited treatment in a region composed of some complex structures such as semi-crystalline, secondary structures and carbonyl groups and alcohol.

Lopes et al. [38] reported important changes in the spectra of the sisal fibers treated by acetylation, especially in the carbonyl groups. The bands corresponding to 1636-1750 cm^{-1} are characteristic of these groups and the bands around 3300-3500 cm^{-1} are related to the axial vibrations of hydroxyl (OH). The peak near 1017 cm^{-1} is attributed to strong vibrations of hydrogen.

The peaks of the treated fibers referring to the region between 1100 and 950 cm^{-1} are similar to those found in structures of starch and are considered by Van Soest et al. [40] as the effect of re-crystallization of part of the structure of starch. As the spectra formed by the fibers studied resemble the spectra of starch-based films, Van Soest et al. [40] and Bergo et al. [41] attribute the changes observed in this region to the increase of the fraction of semi-crystalline structures, in relation to the amorphous phase.

Changes between 1800 and 1500 cm^{-1} may be associated with the onset of some specific structures induced by the plasma, apparently absent in the untreated fibers. The results also suggest a possible condition of equilibrium after 10 min of treatment.

Conclusion

The results presented indicate that treatment with methane cold plasma induced changes in sisal fibers at all times of exposure to treatment (10, 20 and 30 min). In mechanical terms, there was an increase in tensile strength of the treated fibers, however, only fibers exposed to 10 min of treatment had significantly higher values than the untreated fibers and treated with 20 and 30 min. With regard to the structure of the fibers were also observed important changes in the fibers treated with

10 min, whereas the fibers exposed to the times of 20 and 30 min tended to reach an equilibrium condition. Thus, one can conclude that treatment with 10 min exposure to the cold plasma of methane is more efficient since it induced significant changes in a short period of time.

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