Surface modification of kapok fibers by cold plasma surface treatment

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Article history:
Received 4 September 2019
Accepted 24 December 2019
Available online 8 January 2020

Keywords:
Kapok fiber
Cold plasma treatment
Kinetic studies
Surface activation.

This work evaluated the effects of cold plasma treatment on kapok fibers (Ceiba pentandra L.). Fourier-transform infrared (FTIR) spectra showed changes in characteristic absorption bands, indicating modification of the chemical composition of the fiber. Surface roughness, observed by field-emission gun scanning electron microscope (FEG-SEM), increased. Furthermore, the water uptake was significantly affected, the ability to uptake oil increased and a mechanism of reaction was suggested. The thermal behavior, analyzed by thermogravimetric analysis (TGA), was slightly altered and it was also shown that fiber surface was activated by the plasma treatment. Ultimately, cold plasma may prove as a feasible approach to improve fiber-matrix adhesion for the production of biodegradable polymer composites.

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1. Introduction

The use of vegetable fibers as composite reinforcement has increased due to their availability in nature, low cost, biodegradability and lightweight as compared to synthetic fibers. Cellulose fibers have good flexibility and elasticity when compared with mineral fibers, such as glass and carbon fibers, allowing them to keep high aspect ratio during manufacturing process [1,2].

Materials from renewable resources are of increasing interest due to the growing environmental awareness and new environmental regulations. Natural cellulosic fibers typically exhibit different contents of cellulose, hemicellulose, and lignin as main compounds. Cellulose is the main constituent of these fibers, which is lined up forming bundles, which are usually linked with the other constituents [3-6]. Kapok (Ceiba pentandra L.) is a cellulosic fiber with a high degree of hollowness (80-90 %), considered the largest among natural fibers.
These fibers are composed of two major layers with distinct orientations: the outer layer is composed of cellulose microfibrils, which are orientated transversally to the fiber axis, while the internal layer is parallel to fiber axis [7,8]. Another important characteristic of these fibers is the circular cross section [9,10]. Kapok fibers have been used as oil absorbent, especially for application in areas in which oil had been accidentally spread [11]. Tests for oil retention and oil absorption of kapok fibers have been reported elsewhere [12–14]. In addition, studies have been carried out in order to apply kapok fibers in composite manufacturing using recycled polypropylene. An increase tensile modulus with increasing kapok husk content has been reported in the literature in a study of green composites from kapok husk and recycled polypropylene [15]. Nevertheless, polymers and fibers normally have poor compatibility due to differences in polarity of each material, which can be improved by chemical modification or surface treatments of the fibers [16,17].

Plasma treatment may be used to modify polymers and natural fibers by changing fiber surface energy. The process causes surface crosslinking and can introduce reactive groups [18]. In addition, previous works reported that crosslinking at the fiber surface induces strengthening [19,20]. The surface modification by plasma treatment is a result of a sputtering effect at the fiber surface during the plasma bombardment of the material, which produces chemical modifications [3,20–22]. In a previous research, plasma process was shown to produce surface erosion of cotton fibers, thus resulting in weight loss and increase in the fiber carboxyl and carbonyl group contents [23]. Nevertheless, different vegetable fibers exhibit distinct mechanisms when subjected to plasma treatment, due to differences in composition and properties [3]. Thus, there is an interest in investigating the effects of plasma treatment on kapok fibers.

Chemistry of plasma reactions occurs in non-equilibrium conditions. Every plasma species, such as atoms in excited states, free radicals, metastable particles, electrons and ions can interact both chemically and physically with solid surfaces, starting reactions and changing surface structures [24]. X-ray diffraction analyses before and after plasma treatment have indicated no differences in crystallinity, thus confirming that plasma treatment induced decomposition only at the surface of cellulosic materials [25]. In addition, plasma has been used to change electrical resistivity of fabrics such as viscose and cotton [26]. Morphology studies of cotton fabrics have suggested that the surface of cellulosic fibers become rougher after plasma treatment with a significant amount of grooves and cracks [27–29]. Plasma treatment of cellulosic fibers can also improve fiber/polymer adhesion, as reported in a recent study [30].

Liquid sorption properties of vegetable fibers influence their adhesion to a polymer and are key to some manufacturing operations of fabrics, such as dyeing, and finishing. The ability of wood materials to uptake water is improved after plasma treatment, as shown in a previous study [31].

Thermal stability is also an important characteristic of vegetable fibers intended to be used as reinforcement in polymer composites since traditional processing – such as extrusion or injection – may involve high temperature. If the thermal stability is not known, fibers may degrade during processing [32,33]. Mathematical models have been developed by researchers, based on reactions that occur during heating [34]. Models to describe thermal behavior and thermal degradation kinetics of lignocellulosic materials usually follow iso-conversional principle. However, there are results based on Prout-Tompkins integral solution, in which the activation energy is calculated as a global average of degradation process rather than energy values in specific conversion rates. Common mathematical expressions for calculating kinetics parameters based on TGA analysis are those by Friedman, Kissinger and Flynn-Wall-Ozawa as reported in the literature [32,35,36]. Other methods for estimating lignocellulosic components decomposition have also been reported [37].

It has been reported in the literature that pyrolysis reaction of cellulose and lignin follow first-order kinetics and generate low-density volatile components. However, the prediction of the exact behavior of each component in plant fibers is not simple due to the unlimited possibilities of growth, that make each material virtually unique with respect to their crystalline structure and chemical composition [33,38]. The activation energy have been used as a method for evaluating the purity of cellulose, which is an important characteristic for the use of these fibers as reinforcement or filler in polymeric matrices [33,36]. The decomposition reaction of the fibers can be modeled using activation energy data, Arrhenius pre-exponential factor and the reaction model, usually referred to as kinetic triplet [39].

The aim of this work was to evaluate the effect of cold plasma on the chemical, morphological and thermal properties of the kapok seed fibers. The fibers were activated under cold plasma treatment.

2. Experimental

2.1. Material

Kapok fibers were obtained from the fruits of the kapok tree, collected in the State of Paraíba, Brazil. The fruit of kapok contains husk, fibers and seeds and this research focused on the fibers, only. The fruits were first dried at room temperature. Then, the fibers were obtained by opening up the fruit and isolating it from both seeds and husk, and later dried in an oven at 60 °C for 24 h. Neither chemical nor washing processes were used. The fibers were kept under vacuum in an oven at 30 °C until plasma treatment.

2.2. Plasma treatment

Plasma treatment was carried out to induce modifications on fiber surface and improve wettability as well as improvements in fiber-polymer interface for further composite preparation. The plasma equipment consists of a chamber in which coaxial electrodes were used for electrical discharge. Details of plasma equipment used (Fig. 1) has been reported elsewhere [40]. The electric current was controlled over the range of 0.09–0.12 A and voltage from 400 to 500 V. The samples’ temperature was 72 °C, the flow rate was 10 cm³.min⁻¹ of gas and the work-distance was set to 4.0 cm. The pressure inside the reactor was 1.5 mbar. Oxygen gas was used and exposure times were set
to 30, 45 and 60 min, respectively, in order to study the effect of time on the plasma treatment. The chamber was evacuated until $7 \times 10^{-3}$ mbar using a vacuum pump prior to refilling with oxygen gas. Approximately 5 g of fibers for each analysis were placed in the sample holder prior to starting the treatment.

The plasma equipment is designed to maintain all sample surface under the same connections, being uniform throughout all surface. Thus, is reasonable to assign about the reliability of induced changes. In addition, this study applied a small amount of fiber spread over the sample-holder.

2.3. Chemical analysis

Changes in chemical groups of both untreated and plasma treated fibers were observed using Fourier transform infrared (FTIR) spectroscopy in an IRTtracer-100 spectrometer. Samples were analyzed in ATR mode and scanned over the frequency range from 4000 to 500 cm$^{-1}$ with resolution of 4 cm$^{-1}$ and 20 scans per sample. No signal correction process was carried out to avoid loss of data.

2.4. Morphological characterization

Morphology of fiber surface before and after plasma treatment was analyzed using a Field-Emission Gun - Scanning Electron Microscope (FEG-SEM) - ZEISS Auriga, operating at 2.0 kV with tungsten filament. Prior to the FEG-SEM analyses, all samples were coated with a thin layer of gold for 60 s in a Sputter Coater BAL-TEC SCD 005 using argon atmosphere under vacuum, in order to avoid charging sample while scanning.

The roughness of the fiber surface was analyzed using an AFM Shimadzu Model SPM 9700, dynamic mode over an aluminium sample-holder.

2.5. Absorption testing

Absorption properties of the fibers were determined using water (polar molecule) and lubricating oil (nonpolar molecule). The measurements were conducted using fiber samples before and after plasma treatment. For the treated fibers, only those exposed to plasma treatment for 60 min were evaluated since no considerable chemical changes were observed by FTIR for the fibers treated for 30 and 45 min. Two Beckers were used: one filled with oil and the other filled with distilled water, both at room temperature. Prior to the absorption measurements, samples were conditioned in an air-circulating oven at 60 °C for 8 h. Approximately 1.0 g of fiber was immersed in the liquid (water or oil) for 15 min. The fibers were then removed from the liquid bath and weighed after 25 min. Absorption of oil or water was calculated using Eq. 1. Five samples for treated and untreated fibers were used for calculating average and standard deviation.

$$\text{Abs}(%) = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100\% \quad (1)$$

2.6. Thermal characterization

Thermogravimetric analyses (TGA) of untreated and treated fibers were carried out in a PerkinElmer STA 6000 apparatus to evaluate the effect of the plasma treatment on the thermal degradation. The samples were scanned over a temperature range of 30–600 °C under a dynamic flow atmosphere of Nitrogen (99.5 % purity) at a flow rate of 50 ml.min$^{-1}$. Four heating rates were used for the thermal decomposition kinetics studies (5, 10, 15 and 20 °C.min$^{-1}$).

3. Results and discussion

3.1. Chemical analysis

Plasma treatment was performed to induce changes in chemical bonding and, thus, FTIR spectroscopy analysis was conducted aiming to identify these bonds before and after plasma treatment. The infrared spectra and some characteristic absorption band peaks are shown in Fig. 2 and Table 1, respectively.

Fibers treated for 30 and 45 min remained practically unchanged in comparison to untreated fibers. Thus, these exposure times were insufficient for changing chemical groups of these fibers and no further characterizations of these samples were performed. Nevertheless, the plasma treatment duration of 60 min has changed some chemical bonds, as shown in Fig. 2.

The spectrum of untreated fibers is typical of lignocellulosic fibers. Cellulose is identified by some chemical groups, such as C–O–C stretching, at 2125 and 1157 cm$^{-1}$, while the peak at 3355 cm$^{-1}$ is related to the stretching of OH group, which represents mainly the hydroxyls of cellulose. Besides, the peak at 1645 cm$^{-1}$ is related to the O–H deformation, which might be of cellulose and water. The peak at 1373 cm$^{-1}$ is characteristic of C–H deformation, related to cellulose, lignin and hemicellulose. A peak at 1238 cm$^{-1}$ is C–O stretching vibration band of hemicellulose and lignin. Furthermore, the
peak observed at 1733 cm⁻¹ is attributed to the C=O stretching, characteristic of hemicellulose linkage, that is, it represents the C=O of carbonyl structure. The peaks at 1108 and 1036 cm⁻¹ are also C–O stretching, linked to hemicellulose and lignin. Lignin is identified by C=C bonds, being stretching in 1507 cm⁻¹ and aromatic skeletal vibration in 1458 cm⁻¹. Thus, the main components of lignocellulosic fibers – cellulose, hemicellulose and lignin – were identified.

Decreasing in peak intensities at 3350 cm⁻¹ was observed in treated fibers. This stretching vibration band is characteristic of bonding of hydroxyl groups of fatty acids, commonly found on the surface of vegetable fibers, especially kapok due to its oleophilic characteristic. The height of this peak was reduced after 60 min of treatment, suggesting a reaction with oxygen provided by plasma, while another absorption band at 1645 cm⁻¹, linked to O–H stretching has disappeared. These changes take place at the most external bonds and they are related to fats. In addition, the peak attributed to the OH groups of cellulose on the fiber surface (1645 cm⁻¹) exhibited reduced intensity after plasma treatment. This was associated to a reaction with oxygen while removing fatty acids and waxes during the plasma treatment. A summary of possible reactions that occur during the plasma treatment is shown in Fig. 3.

Plasma treatment reduced that intensity, also confirming the modification at the fiber surface. Other authors [15] also attributed these absorption bands to changes in OH groups. The existence of oxygen induces the presence of hydrogen bounds and the reduction of free OH at the fiber surface [9,10].

An absorption band with peak at 1597 cm⁻¹ was also found. Bands at around 1600 cm⁻¹ are related to insaturation (C=C) and they were changed after treatment most likely due to reactions between oxygen coming from plasma and this double bond. These bands were attributed to the presence of lignin, which was also changed due to the treatment. These existent bonds are linked to traces of oils that were partially removed with treatment [41]. Another way to confirm this is the increase in peak height around 1733 cm⁻¹, attributed to carbon and oxygen [42]. These bonds at the fiber surface are important because, while in process with a polymeric matrix, carboxyl group (C=O) may react with carbons near to back-

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Table 1 – Summary of analyzed FTIR bonds.

<table>
<thead>
<tr>
<th>Peak (cm⁻¹)</th>
<th>Relative bonding</th>
</tr>
</thead>
<tbody>
<tr>
<td>3355</td>
<td>O–H stretching (OH group)</td>
</tr>
<tr>
<td>2924</td>
<td>C–H stretching of aliphatic (–CH₂ and –CH₃)</td>
</tr>
<tr>
<td>2847</td>
<td>C–H stretching (–CH₂ groups)</td>
</tr>
<tr>
<td>2125</td>
<td>C–O–C stretching (β-glucoside linkage)</td>
</tr>
<tr>
<td>1733</td>
<td>C=O stretching (hemicellulose linkage) / C=O from carbonyl structure</td>
</tr>
<tr>
<td>1645</td>
<td>O–H deformation (H₂O and cellulose)</td>
</tr>
<tr>
<td>1597</td>
<td>C=C aromatic skeletal vibration (Lignin)</td>
</tr>
<tr>
<td>1507</td>
<td>C=C stretching (Lignin)</td>
</tr>
<tr>
<td>1458</td>
<td>C=C aromatic skeletal vibration (Lignin)</td>
</tr>
<tr>
<td>1421</td>
<td>C–H deformation (Cellulose and lignin linkage)</td>
</tr>
<tr>
<td>1373</td>
<td>C–H deformation (Cellulose, hemicellulose and lignin linkage)</td>
</tr>
<tr>
<td>1328</td>
<td>O–H in plane deformation (cellulose)</td>
</tr>
<tr>
<td>1238</td>
<td>C–O stretching (Hemicellulose and lignin)</td>
</tr>
<tr>
<td>1157</td>
<td>C–O–C asymmetric stretching (Cellulose, hemicellulose and lignin linkage)</td>
</tr>
<tr>
<td>1108</td>
<td>C–O stretching (Hemicellulose and Lignin)</td>
</tr>
<tr>
<td>1036</td>
<td>C–O stretching (Hemicellulose)</td>
</tr>
<tr>
<td>660</td>
<td>C–OH bending</td>
</tr>
<tr>
<td>595</td>
<td>C–OH bending</td>
</tr>
</tbody>
</table>

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Fig. 2 – FTIR spectra of untreated and treated kapok fibers.

Fig. 3 – Schematic representations of (a) typical cellulose fiber, (b) kapok fiber, (c) plasma treatment, and (d) suggested mechanism of plasma reaction.
bone chains and a strong bonding may be obtained, resulting in a strong interface [23].

The absorption band at about 2847 cm⁻¹ for treated fibers has changed in comparison to untreated fibers. This might be attributed to changes in lignin structure –CH₃ also observed at about 2937 cm⁻¹ in a previous study, in which two kinds of lignin were analyzed [43]. In this work, the peak was found at 2924 cm⁻¹.

The presence of water was identified by peaks at 1645 cm⁻¹, which are also associated with –OH bonds of cellulose groups. The free hydroxyl groups on the cellulose chains have been associated to sites where the absorption of water occurs [44]. An absorption band with peak at 1421 cm⁻¹ characteristic of CH₂ bonding was observed and linked to both cellulose and lignin. The changes in bands around 1328 cm⁻¹ after plasma treatment were also connected to OH bonding in cellulose groups. The in-plane OH bending absorbance is observed for the untreated fibers. Fibers treated for 60 min exhibit a considerably reduction in that peak, as shown in Fig. 2. This behavior may be related to the plasma action onto the surface cellulose bonds, since the inner portions of the samples are not affected by the plasma treatment. Fibers treated for 60 min exhibited reduction in heights of peaks around 660 and 595 cm⁻¹, which means reductions in the amount of C–OH bonding. This might be attributed to reactions involving C–OH group and oxygen.

No atmosphere corrections were performed after recording data in order to check hydrophobic/hydrophilic characteristic of samples before and after treatment. Absorption bands with peaks around 2350 cm⁻¹ have been predominantly attributed to moisture in the sample. These bands were not observed in the untreated samples. In contrast, the treated samples have this peak, indicating a reduction in pseudo-hydrophobicity as well as increasing in wettability.

The liquid uptake capacity of fibers is related to the contact between the liquid and the fiber surface. Plasma treatment removed part of fatty acids and wax from the fiber surface, thus allowing contact between fibers and the surrounding liquid (polar or nonpolar). That is, plasma treatment improved the wettability of fibers. The new absorption peaks after plasma treatment may be related to reactive sites that can improve reactions with polar and nonpolar liquids. Thus, while the hydroxyl groups on the fiber surface increase wettability by water, the remaining oily components renders the fibers wettable by oil. Furthermore, the plasma treatment induces surface erosion of the fibers opening up channels for liquids to penetrate into surface pores. Therefore, there is a possibility of improvement in wettability by different liquids. This characteristic is relevant for further use of these fibers in composites’ manufacturing.

The structure of a typical cellulose fiber and kapok fiber are presented in Fig. 3a and in Fig. 3b, respectively. The representation of plasma treatment is summarized in Fig. 3c and a suggested reaction mechanism that occurs during plasma treatment is presented in Fig. 3d.

3.2. Morphological analysis

Differences in morphology of untreated and treated fibers were evaluated using FEG-SEM images. External and internal diameters, wall thickness and surface fiber roughness were parameters observed before and after treatment. The most samples kapok fibers showed external diameter ranging from 12 to 15 μm, on average, and wall thickness of about 1.5 μm. However, samples with diameter from 10 to 27 μm were also observed. Fig. 3 shows the actual morphology of the fibers with the characteristic smooth appearance (Fig. 4a) and hollowness (Fig. 4b). The hollowness of 80–90% of kapok fibers reported in a previous work [45] is seen in the FEG-SEM images of Fig. 4.

Images before and after treatment (Fig. 5) were carried out in order to observe any modification on surface roughness produced by the plasma treatment. Fig. 5a exhibit a fiber before plasma treatment while the plasma treated fiber is shown in Fig. 5b. According to the images in Fig. 5, the plasma has induced changes on the fiber surface, increasing roughness.

The surfaces of fiber samples were investigated by Atomic Force Microscopy in order to determine if plasma treatment induced considerable changes onto the surface. Results indicated a roughness of 142 nm for raw fibers, while for plasma treated this roughness was 265 nm, which means an increase of about 86 % in the roughness, thus indicating considerable changing in the roughness pattern, as presented in Fig. 6.

3.3. Absorption testing

According to the measurements, plasma treatment produced a significant effect on water and oil uptake of kapok fibers. Oil absorption was increased from 5047 to 7385 wt.%, and water uptake was increased from about 36–9438 wt.%, as compared to untreated fibers. Cellulose fibers are typically semi-crystalline, with free hydroxyl groups throughout the amorphous portion. These groups attract water molecules forming hydrogen bonds. In addition, the higher level of polar carboxyl and carbonyl groups generated during plasma treatment leads to more polar - and consequently more wettable - fibers, as reported elsewhere [23].

Kapok fibers are naturally oleophilic [13] and the plasma treatment increased the wettability of the fibers in nonpolar liquids, such as oil, as a result of surface erosion, which exposes the natural hydrophobic groups on the fiber surface and opens up spaces for liquids to penetrate. A recent study reported that calotropis (Calotropis procera) – a fiber similar to kapok – also showed improvement in the oil-absorbing performance [46]. This result may be used in further studies of plasma treated fibers using polymeric resins for the production of fiber-reinforced composites. The wettability of the fibers by a polymeric matrix during impregnation is essential for the use of these fibers in composite manufacturing. The increment in water uptake may be related to the efficiency of plasma processing for removing oils and waxes from the fiber surface, thus opening up channels for moisture uptake, in addition to changes in surface roughness. In addition, the removal of waxes makes filling of tube-like fiber structure possible. Waxes and fats at the surface of untreated fibers are known to affect wettability. Therefore, plasma treatment has induced reactions and promoted breaking of some fatty acids on the fiber surface, as confirmed by FTIR, thus reducing pseudo-hydrophobicity characteristic.

Changes in relative peaks in FTIR spectra as well as a more irregular surface texture shown in SEM images (Fig. 5) and AFM images (Fig. 6) confirm the plasma modification of the fiber
surface. The adsorbed water or oil induced fiber swelling. Fig. 7 describes in details a diagram of untreated and plasma treated fibers exposed to water and oil, respectively.

Different from common vegetable fibers, such as cotton, kapok shows a combination of two features: it has excess of oil on its surface, which difficult liquid sortion, in general, and its hollowness is considered the largest among vegetable fibers (near to 90%). Thus, after plasma treatment, it is reasonable expect that any liquid might penetrate into fiber cavity. Furthermore, cellulosic fibers are naturally hygroscopic and when oils are removed from the surface, water penetrates the internal structure of the fibers. The combination of the characteristic smoothness and hollowness of kapok fibers with air entrapped in the fiber lumen hinders water absorption for raw fibers.

After plasma treatment, the increase in fiber surface roughness increased and partial oil removal facilitates water filling of the lumen. It is important to note that the inner structure of fibers has less oil in comparison to fiber external surface, what turns into possible liquids to go through. However, the access of liquids to the tube-like structure depends on amount of oil onto surface. Unless the oil (or at least part of) is removed, water might not access. Besides, plasma treatment occurs at the surface and the inner portions of the fibers remain unaffected. Thus, the lipophilicity of fibers is not reduced after the treatment. In addition, the oil that was removed (or at
Thermal degradation data were also evaluated from TGA thermograms obtained using different heating rates. The results were used for the determination of kinetic parameters and changes in thermal degradation, as a function of heating rate.

The weight-loss curves of untreated fibers exhibited a trend of small increase in $T_{\text{ONSET}}$ (Fig. 9a) and maximum degradation peak (Fig. 9b), as the heating rate increased. For treated fibers, other changes in weight-loss curves were observed below the $T_{\text{ONSET}}$, as the heating rate increased (Fig. 9c). These changes were attributed to a reaction mechanism, influenced by oxygen provided by the plasma treatment.

New bonds, as observed in FTIR spectra, may affect thermal degradation. Thus, the treated fibers subjected to slower heating rate have decomposed a bit faster than those exposed to higher heating rates. After $T_{\text{ONSET}}$, the behavior of untreated and treated fibers was similar until final thermal degradation. In addition, the portion affected by plasma was almost entirely consumed below $T_{\text{ONSET}}$. Free oxygen at the fiber surface may react faster than cellulose. This explains the changes in thermal behavior of plasma treated fibers at temperatures below $T_{\text{ONSET}}$. Free oxygen reacts before reaching this temperature. Thus, the thermal decomposition behavior remains unchanged above $T_{\text{ONSET}}$, as shown in Fig. 9d.

Thermal decomposition behavior of untreated and treated kapok samples were also evaluated using DTG peaks for each heating rate studied. Results are presented in Table 2. An increase of about 5% in activation energy ($E_a$) of plasma treated fibers was observed in comparison to untreated fibers. This was attributed to oxygen at the surface of treated fibers, since higher temperatures increases reaction with oxygen, generating residues of incomplete decomposition reactions. Both CO and CO$_2$ are obtained. This shifting can be subtle and hard to detect without a specific study of releasing gases by TGA decomposition. Thus, TGA is associated to FTIR for immediate analysis while thermal decomposition occurs.

In general, thermal behavior is not altered significantly by increasing heating rate, but a shift of DTG peaks is observed. The first peak in thermal decomposition is attributed to hemicellulose decomposition. In this work, $E_a$ of 103 KJ. mol$^{-1}$ was obtained. Other cellulose-based fibers show similar values, as reported in the literature [47].

Conversion of cellulose followed a first order reaction and the corresponding reaction energy was 184 KJ. mol$^{-1}$. The maximum percentage of weight loss occurred over the range 330–360°C. Previous studies have reported values ranging from 160 KJ.mol$^{-1}$ (Wood-pine) to 183 KJ. mol$^{-1}$ (Jute), or Rice straw (197 KJ. mol$^{-1}$) [33,47,48].

TGA experiments combined with mathematical models have been applied by many researchers [33,47,49] to measure activation energy ($E_a$). A previous study of thermal decomposition kinetics for determining activation energy of the main components of kapok fibers – cellulose, hemicellulose and lignin – the degradation of lignin structures was linked to dehydration, generating products with unsaturated chains and release of water, yielding carbon monoxide, carbon dioxide and methane [50].

Thermal decomposition kinetics pattern for untreated and treated fibers were determined from TGA data. Friedman method was used to evaluate reaction order in various steps.

3.4. Thermal characterization

Thermogravimetric analyses were carried out in both untreated and plasma treated kapok fibers. The main difference between thermogravimetric curves of treated and untreated fibers at 10°C.min$^{-1}$ was the loss of moisture over the range 30–100°C, which has been attributed to moisture uptake. Plasma treated fibers are more likely to exhibit free oxygen or weak bonds, resulting in changes in polarity and improving wettability to some liquids. Above this temperature range, the thermal behavior was not modified by the plasma treatment, as shown in Fig. 8.
The actual reaction mechanism is deeply dependent on how fast the components react. For untreated fibers, first-order reactions are observed over 10–80% conversion, as shown in Fig. 10a. On the other hand, plasma treated fibers exhibited first-order reactions in 10% and over 40–80% conversion, as shown in Fig. 10b. The thermal degradation over the range of 20–30% of decomposition has changed to second-order reaction at a temperature range of 280–315°C. The reaction observed at 280°C corresponds to hemicellulose degradation and at 315°C is related to the degradation of some parts of cellulose and lignin structures. Hence, these changes were attributed to fiber activation, since oxygen provided by plasma has contributed to accelerate reaction. However, as oxygen is consumed, the reaction tends to go back to the original first-order behavior. Even though the reaction was faster of degradation. Friedman method is the simplest model for obtaining thermal and kinetic behavior. The thermal degradation in each step of conversion was evaluated and suggested the presence of different materials with distinct reaction mechanisms.
for the treated fibers when compared to untreated, this difference is not significant for the bulk decomposition of both since plasma activation affects the fiber surface only, and the bulk properties remain unaltered.

Kissinger and F-W-O methods resulted in similar activation energy ($E_a$). These two models are similar regarding to thermal considerations and were used to determine the actual activation energy for untreated and treated fibers. Thermal properties of untreated and treated kapok fibers are shown in Fig. 10. For untreated fibers, $E_a$ values decrease from 10 to 30 % of conversion. This behavior is observed over the temperature range of 293–327 °C, as presented in Fig. 10a for untreated fibers and in Fig. 10b for treated fibers. This temperature range corresponds to hemicellulose degradation.

For plasma treated fibers, an increase in activation energy was observed up to 30 % conversion - related to hemicellulose - and followed by a decrease until the reaction was complete. In addition, a significant variation in lignin and cellulose degradation was observed. Exothermic reactions between oxygen and cellulose/lignin components at the fiber surface generated higher $E_a$ values. Furthermore, for these fibers, the $E_a$ were shifted when compared to pristine fibers, indicating changes in thermal behavior under plasma surface activation, as shown in Fig. 10 for Kissinger (Fig. 10c) and F-W-O methods (Fig. 10d).

An increase in $E_a$ means higher energy needed for the degradation reaction. Hence, components with higher $E_a$ values are more likely to remain safe while processing at high temperatures. This is an important attribute if the fibers are intended to be added to polymers that are processed at higher temperatures. Difference in peak temperature as well as $E_a$ values are shown in Table 2.

Lower energies in thermal degradation process were related to lignin degradation. These events occurred from 300 to 350 °C temperature range, which is usually reported as being lignin degradation [47]. Thermal degradation curves of lignin can be overlapped by those of cellulose and hemicellulose. Thus, due to the similar activation energies for the thermal decomposition of lignin, hemicellulose and cellulose, a reliable model for evaluating energy of each component separately becomes more complex [33]. The authors attribute this to the complexity of natural components, such as soil properties, moisture availability and external factors as sunshine exposure.

4. Conclusion

Plasma treatment was successfully applied for the surface activation of kapok fibers. Changes in relative peaks in FTIR spectra as well as a more irregular surface texture shown in
SEM images confirm the plasma modification of fiber surface. The plasma treatment removed oils and wax from the fiber surface improving their wettability. The surface erosion produced by plasma treatment was found to expose the natural hydrophobic groups on the fiber surface while opening up spaces for liquids such as oils to penetrate. The open pores and partial removal of oils and waxes also facilitate water uptake and absorption by the cellulosic fibers. Thus, absorption testing indicated an increase in water and in oil uptake in comparison with untreated fibers. Activation energy data were successfully obtained from thermogravimetric analysis experiments combined with mathematical models. This approach proved successful as an alternative for the determination of the cellulose content. Plasma treatment has the advantage of producing changes at the fiber surface only, increasing the activation energy in comparison to untreated fibers. Ultimately, plasma treatment proved as a feasible approach for surface activation of kapok fibers, thus improving matrix/filler adhesion.

Conflict of interest

The authors state that there is no conflict of interest

Acknowledgements

This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior - Brasil (CAPES) - Finance Code 001 and Embrapa Agroindústria Tropical (Fortaleza, CE – Brazil) for providing TGA tests.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jmrt.2019.12.077.

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