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Structural Analysis of Kevlar Fabric Treated with Oxygen Plasma

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Abstract

The purpose of this work was to study the effects of low-pressure oxygen plasma treatment on the surface characteristics of kevlar fabric. For comparison purposes, samples treated with oxygenated plasma were prepared and characterised under different experimental conditions, i.e. a treatment time variation of 10, 30 and 60 minutes under a constant pressure of 4 mBar, using a pulsed current source. We analysed the effects of chemical and physical changes to the surface of the material aiming at improved hydrophilicity attributed to the formation of roughness on the surface of fibres, thus obtaining optimal parameters for future works. Changes in the chemical composition of the surface as well as in the superficial roughness of fibres before and after treatment were determined by FTIR, TGA, XRD and wettability testing. SEM was used as a complementary technique to monitor the changes triggered by the procedures using oxygen plasma.

Key words: kevlar fibre, plasma treatment, O₂ plasma.

the interfacial characteristics is required to obtain the best performance of composites [7, 8]. Several changes to the fibre surface through plasma treatment and chemical modification, among others [8, 9] have already been developed in order to improve the interface bonding of a composite fibre/matrix system using fibre.

In recent years, the use of plasma in the treatment of polymeric materials has become increasingly important [9, 10] as it can improve the quality of polymer surfaces without affecting their properties on a large scale. Plasma treatment modifies the highest atomic layers of the surface of the material without affecting its main characteristics. Most researchers employ the plasma treatment technique to increase fibre surface roughness [11] and, consequently, fibre/matrix adhesion, but sacrificing the resistance of the compound [12].

Fang Guo et al. [13] argues that the chemical compositions and surface properties of Kevlar fabric after treatment with air plasma were modified by the introduction of some active groups, generating increased surface fibre roughness and resulting in a better adhesion between the Kevlar fabric and phenolic adhesive. As a consequence, the tribological performance of the Kevlar fabric and plasma treated phenolic/Kevlar composite was significantly improved.

According to Joung-Man Park et al. [14], the interface shearing strength (IFSS) of plasma-treated Kevlar and PBO (p-phenylene-2,6-benzobisoxazole) fibres increased compared to untreated fibres.

The IFSS of the Kevlar/Epoxy fibre composite was higher than the PBO/Kevlar fibre composite for both treated and untreated conditions. This can be explained by the greater amount of hydrophilic functional groups in Kevlar fibre when compared to PBO fibre [15].

According to Min Su et al. [15], treatment with oxygen plasma has a great influence on the chemistry and morphology of Kevlar fibres, by which functional groups containing oxygen are introduced, as well as some small globular microstructures and obvious grooves present on the surfaces of Kevlar fibres; therefore, the roughness of the fibre surface is increased. Oxygen plasma treatment on Kevlar fibre shows an attractive potential for applications, considering that its aging behaviour was not severe.

This work aimed to study the effects of low-pressure oxygen plasma treatment on the characteristics of the surface of Kevlar-fibre fabric. For comparison purposes, samples treated with oxygenated plasma were prepared and characterised under different experimental conditions, i.e. treatment time variations of 10, 30 and 60 minutes, aiming at obtaining optimal parameters for future works. Changes in the chemical composition of the surface and in the superficial fibre roughness before and after treatment were determined by Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA), X-Ray Diffraction (DRX) and a wettability test. Scanning Electron Microscopy (SEM) was used as a complementary technique to monitor the changes triggered by the procedures using oxygen plasma on polymer fibre.

Introduction

Kevlar has been widely used in the manufacture of advanced composites in the aerospace, military, marine and sports fields, among others, due to its good mechanical properties, thermal stability and energy adsorption properties [1-4]. However, it is known that the mechanical properties of fibre-reinforced composites depend on the effectiveness of the interaction between the fibre and the matrix [5, 6]; therefore, adhesion between Kevlar fibres and most of the matrices is weak due to the high crystallinity, resulting in chemical inertia and a smooth fibre surface. Therefore, appropriate control of

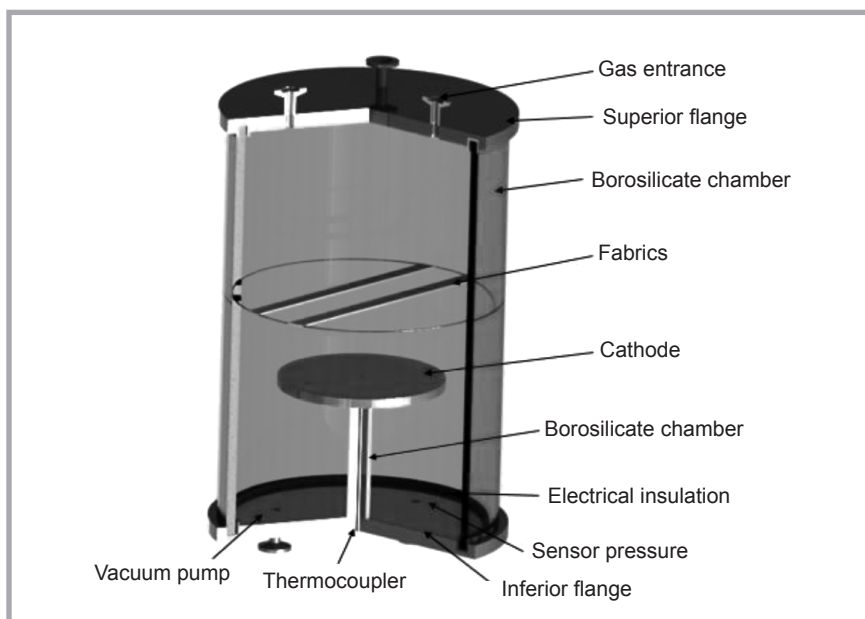


Figure 1. Representation of plasma reactor.

Table 1. Specifications of Kevlar-49 Fabric. Source: MAXEPOXI.

Fabric characteristics	Kevlar fabric
Surface density, g/m ²	200 ± 20
Length, cm	130 ± 3
Linear meters per coil, m	50 ± 3
Linear meters per coil, m ²	65 ± 8
Width, mm	0.34 ± 0.50
Warp's theoretical ultimate load, Kg/cm	207 ± 9
Weft's theoretical ultimate load, Kg/cm	207 ± 9
Pattern type	Screen
Fabric type	Woven

Materials and methods

This section describes the materials and methods used in the treatment, as well as the physical and chemical analyses carried out on the material.

Materials

Flat Kevlar-49 bidirectional fabric, supplied by MAXEPOXI, with the technical specifications described below, was used in this study (Table 1).

O₂ plasma treatment

Developed at UFRN's Plasma Materials Processing Laboratory, the plasma apparatus (presented schematically in Figure 1) used in this work is constituted by a continuous power source of 1kW, connected to a reactor. This source had a maximum voltage of 1200V. The reactor utilized in this work is the same as described by Feitor et al. [16].

The sample was attached to the inside of the reactor with a circular copper wire at

a distance of 5 cm. The sample treatment was carried out using oxygen gas with a flow of 10 sccm at maximum temperatures of 52 °C, 88 °C and 182 °C for 10, 30 and 60 minutes treatments, respectively. Those times were chosen because Feitor et al. [16] proved there is an aging time for poly (Ethylene Terephthalat) treated by plasma. During the process, the voltage and pressure parameters were controlled at 600 V and 4 mbar, using a pulsed current of 0.1 A. After the completion of each treatment, the samples were conditioned in humidity and contamination free containers, thus ensuring the integrity of testing and characterisation.

Physical chemical tests

To evaluate the effects of O₂ plasma treatment on Kevlar fabric, some methods were used for characterisation through physical chemical testing, such as wettability, which aimed to assess the occurrence of structural modifications to the material when exposed to different treatment times with O₂ plasma.

The wettability test was used to describe the tissue's ability to absorb liquids, realised in accordance with the AATCC TM79-2018 standard. For this purpose, the samples were weighed before and after immersion in water (25 ± 2 °C) in a time interval of 30 s. Water absorption was observed and calculated according to the following Equation (1):

$$\text{Water absorption (\%)} = \frac{(m_0 - m_i)}{m_i} \times 100 \quad (1)$$

Where, m_i and m₀ are the weights of the sample before and after immersion, respectively.

Infrared spectroscopy (FTIR) was performed using a Bruker FT-IR Vertex 70 Spectrometer, at a spectral range of 400-4000 cm⁻¹. Transmission spectra were obtained at a resolution of 4 cm⁻¹ and for 16 scans per test, and then processed by a Bruker FT-IR Vertex 70 data manager. FTIR permits the consideration of possible variations with regards to O₂ exposure time and the intensity of characteristic absorptions of the fabric before and after treatment, as well as the presence of new chemical groups.

Thermogravimetric Analysis (TGA) was used both quantitatively and qualitatively by changing the mass of a substance according to the temperature and/or time through controlled programming. This type of analysis has advantages in small sample studies at an extensive scale of programmed temperatures in a defined atmosphere [17]. An SDTQ600 simultaneous thermogravimetric analyser and differential scanning calorimeters were used for experimental analysis where small sections of the sample (mass = 4 mg) were arranged in an alumina crucible, using nitrogen as a purge gas at a flow rate of 50 ml/min, with a temperature variation of 10 °C/minimum up to 700 °C maximum.

The X-Ray Diffraction (XRD) was performed on a Bruker D2 Phaser, through the θ-2θ rotation technique. The source used was copper (λCu Kα = 1,54060Å) (Cu 40KV/45mA). The 2θ scan was performed with a pitch of 0.02° within an angular range of 3° to 70°. OriginPro 9.0 software was used in the analysis of the diffraction curves.

As Kevlar is not metallic and semi-crystalline in some parts of its structure, complete image capture is impaired. In order

to help capture and ensure a clear image, a carbon tape is required. The scanning electron microscopy (SEM) used to analyse the topography surface of the samples was a Hitachi TM3030 Plus.

■ Results and discussion

This section presents the results obtained throughout the study, as well as their analysis.

Evaluation of physico- chemical characteristics

Wettability

The following shows a quantitative analysis of Kevlar fibre fabric wettability.

Note that the untreated fabric presented 80% water absorption, whilst absorption in the oxygen plasma treated samples reaches approximately 295%. These results evidence that the treatment is effective in improving absorption, as all samples presented water absorption greater than 80%. Therefore, the material gets more hydrophilic after testing.

The improvement in wettability may have occurred due to the creation of superficial roughness resulting from O₂ plasma treatment. As oxygen is a highly reactive gas, when it collides with the surface it promotes the tearing of atoms, causing erosion or incorporation thereof, thus forming micro-porosity and, therefore, an increased contact area [18]. As a result, water will permeate better.

Through analysis of the chart in **Figure 2**, it was noted that with an increase in treatment times, there was a simultaneous increase in water absorption. This increase is expected because there is an erosion of the amorphous areas of the sample treated at lower treatment times, as atoms in that region are connected by a lower energy than those in crystalline and semi-crystalline zones, and therefore they are less bundled [19].

Hence, with regards to the wettability test, the best treatment time for the material used is 60 minutes, as it presents greater water absorption compared to other samples.

Scanning Electron Microscopy (MEV)

According to the images captured by scanning electron microscopy (SEM), we observe a degradation of the fibre during exposure to oxygen plasma for 10 min,

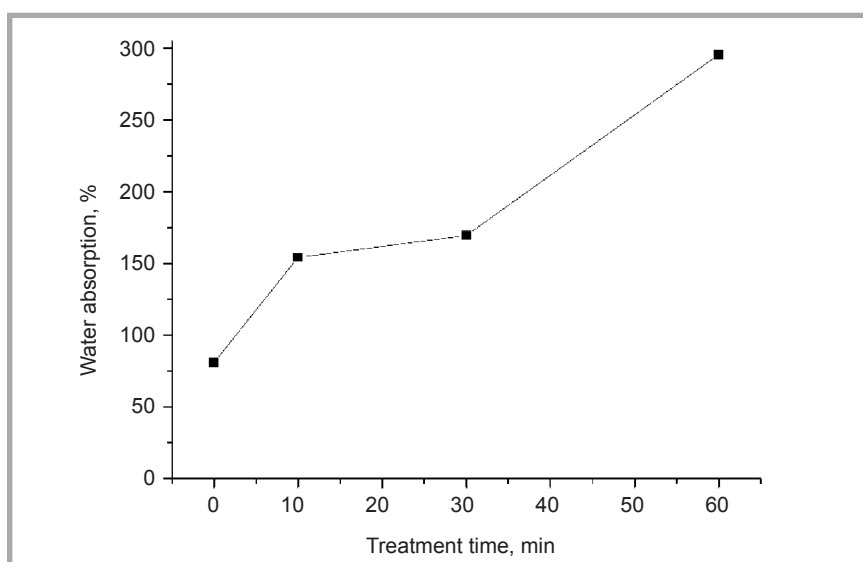


Figure 2. Wettability test chart.

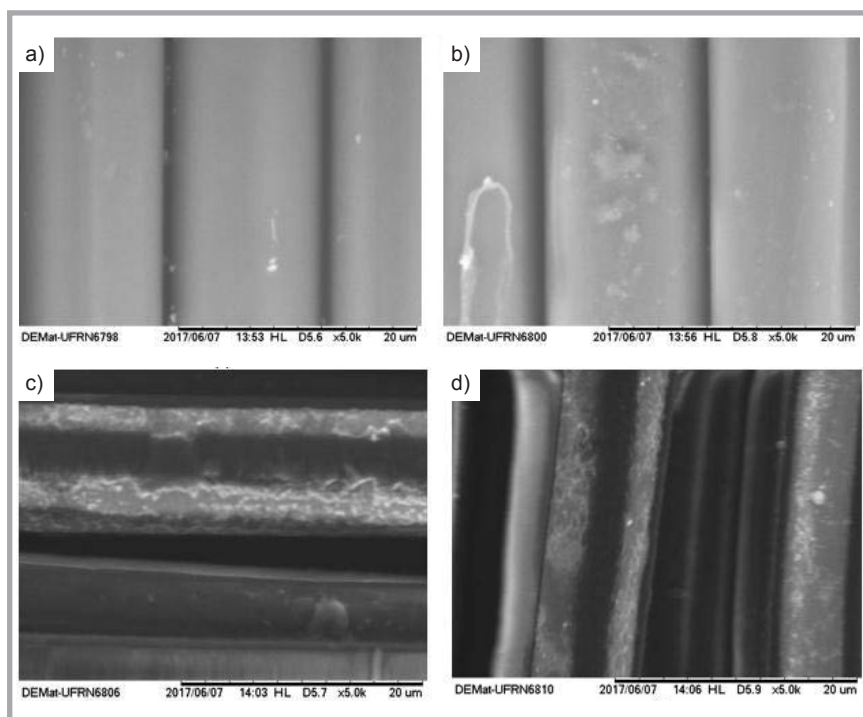


Figure 3. SEM of Kevlar fabric at a magnification of 5000x: a) untreated sample, b) treated for 10 min, c) treated for 30 min, d) treated for 60 min.

30 min and 60 min. Below, we present SEM images and discussions thereof.

Based on **Figure 3.b**, some fibre degradation can be observed with only 10 min of plasma exposure. This is because oxygen plasma is responsible for degrading the material, thus changing the water absorption properties of the fabric and other physical properties of the sample, **Figure 3.a**. This absorption is caused by the formation of small vessels in the fibre, which results in increased fabric water absorption.

In **Figure 3.c**, when comparing to the untreated sample, **Figure 3.a**, we observe a greater fibre degradation. It is further possible to observe that the material had undergone changes in its semi-crystalline structure. For example, the dark regions in the image are those with the most crystalline fibre properties, as they best show the attack on semi-crystalline surfaces that are on the edges where the said changes occurred.

In **Figure 3.d**, we see an even more degraded fibre, as a result of the longer

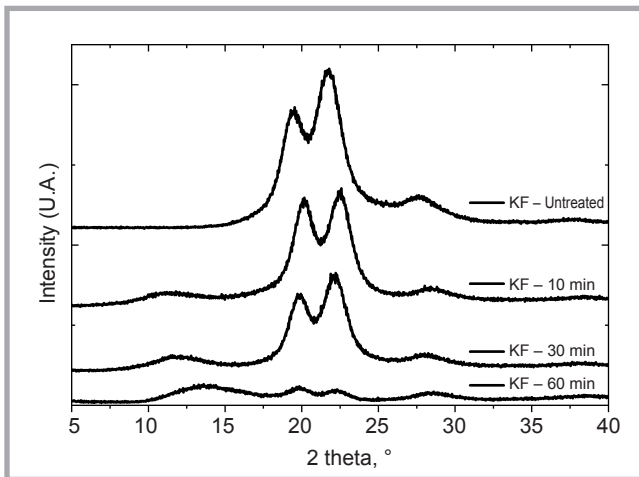


Figure 4. X-Ray Diffraction (XRD) of Kevlar fabric.

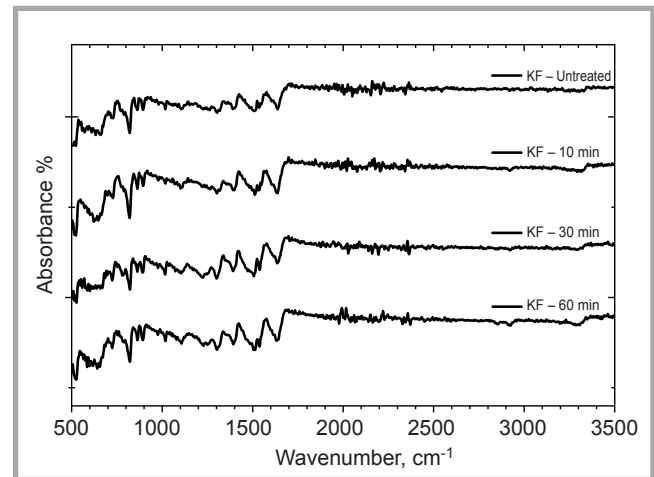


Figure 5. Spectroscopy in the Kevlar-fibre infrared region.

exposure to O₂ plasma, which evidences that the fibre had undergone a greater change in its semi-crystalline region, while there was a decrease in the crystalline region on the edges of the fibre, thus causing an increase in water absorption.

Through an overall comparison of images obtained (see **Figure 3**), we can better observe the effect of oxygen plasma on Kevlar fibre, making it possible to note the physical transformations of samples. It can also be observed that those which were exposed to treatment for longer periods of time were more rigid due to the increase in the semi-crystalline region in the fibre. Although we cannot accurately state so, this may be attributed to the time of exposure of the fibre to X-Ray Diffraction (XRD_ oxygen plasma treatment).

The internal structure of para-aramid (Kevlar 49) fibre before and after treatment with O₂ plasma was studied based

on the X-Ray Diffraction method, aiming at obtaining information on changes occurring in the crystalline and amorphous regions of the material as a consequence of exposure to plasma.

Figure 4 shows diffractograms obtained for the Kevlar fabric for untreated material and material treated for 10, 30 and 60 minutes, respectively.

We can conclude that the material in its initial state, without any treatment, has semi-crystalline peaks, and it was expected that as the treatment time increased, the intensity of the peaks would decrease. In the diffractogram, we can observe two “peaks” corresponding to reflections (110) and (200), which can be related to the planes of a single unit cell orthorhombic or pseudo-orthorhombic lattice. Another peak of lower intensity was observed in the diffractogram obtained, with the reflection corresponding to plane (004) [20-22].

Moreover, we observe that these “peaks” do not present great variation regarding their positioning, although there is a significant difference in the intensity thereof as a result of the treatment with O₂ plasma, which causes the material to be more amorphous. The intensity of the reflections in the treated material, when compared to that of the untreated material, decreases for all treated samples, with greater significance in the 60-minute treatment. This variation indicates that plasma treatment produces a decrease in Kevlar fibre crystallinity.

Spectroscopy in the infrared region (FTIR)

To investigate the chemical compositions of Kevlar fabric before and after treatment with oxygen plasma, FTIR spectra of untreated Kevlar fabric and fabric treated at different treatment times (10, 30 and 60 minutes) were recorded. The corresponding curves are shown in the figure below.

The comparison of normalised FTIR spectra shows that the intensities of the main peaks vary as the test times increase, although they do not show significant differences in positioning. Two changes arising from plasma treatment can be seen in the chart: the first in the C=O bond, which corresponds to approximately 1638 cm⁻¹, and the second in amide-II interactions, which corresponds to the lowest energy bonds compared to C-C and C-H. We believe that new functional groups were formed in the material near the said bonds. However, based on the FTIR, it was not possible to detect what functional groups they are, because this type of evaluation does not analyse the surface of the material, but the overall fibre volume.

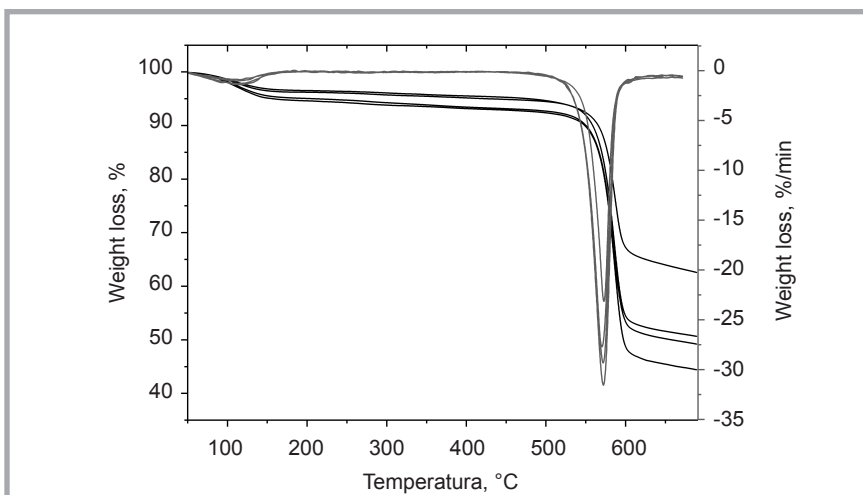


Figure 6. Thermogravimetric curve chart.

N-H stretching bands of 3312 cm⁻¹ (amide A), C=O stretching of 1638 cm⁻¹ (amide I), N-H flexion/C-N interaction stretching of 1538 cm⁻¹ and 1513 cm⁻¹ (amide II), C-N stretching of 1305 cm⁻¹ (amide III), and the symmetrical deformation of the NO₂ group at 1300-1255 cm⁻¹ are characteristics of Kevlar, and can be considered as internal standards of the material [23, 24].

Thermogravimetric analysis (TGA)

Quantitative and qualitative analysis was performed through the mass change related to temperature and time. See **Figure 6**.

Based on **Figure 6**, samples treated with plasma showed no structural changes, as the endothermic peak for all samples, including untreated ones, occurs at the same point (approximately 570 °C). However, the TGA analysis chart shows that samples treated with plasma present a decrease in mass loss after the degradation thereof.

Conclusions

After finalisation of this study, which aimed to investigate the treatment of Kevlar-49 fabric with O₂ plasma, with time intervals of 10, 30 and 60 minutes, using a constant pressure of 4 mBar, we concluded that:

- O₂ plasma treatment influences the chemistry and morphology of fibres, bringing an improvement in the wettability of the fabric due to the increased surface roughness, given that oxygen is a highly reactive gas that when it collides with the surface promotes the tearing of atoms, resulting in the erosion or incorporation thereof and the forming of microporosities;
- The treatment was effective in improving absorption, as all treated samples obtained a higher water absorption compared to untreated ones, making the material more hydrophilic;
- In the wettability test, the 60-minute sample showed the best water absorption result compared to the others, thus being considered the optimal parameter for future works;
- Treatment with O₂ plasma converts the initially semi-crystalline material into an amorphous one. This variation shows that the treatment is suitable for decreasing the crystallinity of Kevlar fibre;
- We believe that new functional groups were formed near some of the bonds mentioned throughout this work as a result of treatment with plasma. However, it was not possible to detect what these functional groups are, because the technique used does not analyse the surface of the material, but the overall fibre volume;
- The treatment did not present any changes regarding thermal properties of the material, as the endothermic peak for all samples, including untreated ones, occurs at the same point (approximately 570 °C).

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