

# Mechanical Performance of Carbon Fiber/Polyamide 6: Comparative Study Between Conditioning in Distilled Water with Heating and Saline Solution

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It is particularly important to investigate the mechanical performance of carbon fiber (CF) reinforced polyamide 6 (PA6) composites used for automotive and aerospace applications, where diffused moisture of the environment may potentially weaken the material over time. In this work, CF/PA6 composites were subjected to two different types of conditioning: distilled water at a temperature of 80 °C and saline solution for 12 weeks. The volumetric fraction of CF, PA6 matrix, and the voids of the CF/PA6 composites were determined by acid digestion analysis. At the end of the environmental conditionings, the moisture absorption content and the diffusion coefficient (D) were determined. The mechanical performance of CF/PA6 composites unconditioned and conditioned was evaluated through tensile and interlaminar shear strength (ILSS) tests, and morphological characteristics of the fracture surface after the mechanical tensile test. CF/PA6 composites conditioned in saline solution showed a decrease of 53% (tensile sample) and 72% (ILSS sample) in the diffusion coefficient (D) and insignificant losses of mechanical properties when compared to CF/PA6 composites conditioned in distilled water at 80 °C. This behavior is attributed to the salt molecules blocking the pores and consequently reducing the migration of water into the samples, maintaining the internal integrity of the specimens.

**Keywords:** Polyamide 6, Carbon Fiber, Composites, Moisture, Saline environmental, Mechanical properties.

## 1. Introduction

During their service life, aircraft and automobiles are constantly exposed to a wide range of environmental conditions, such as sudden changes in temperature, precipitation, solar radiation, salt fog, and environmental pollution, in addition to the combination of these factors with mechanical loads. These factors can influence and/or accelerate the degradation of mechanical and physical properties, so it is essential to know the operating environment in which the component will be exposed during its service life, minimizing the need for advanced maintenance and even its replacement<sup>1-3</sup>.

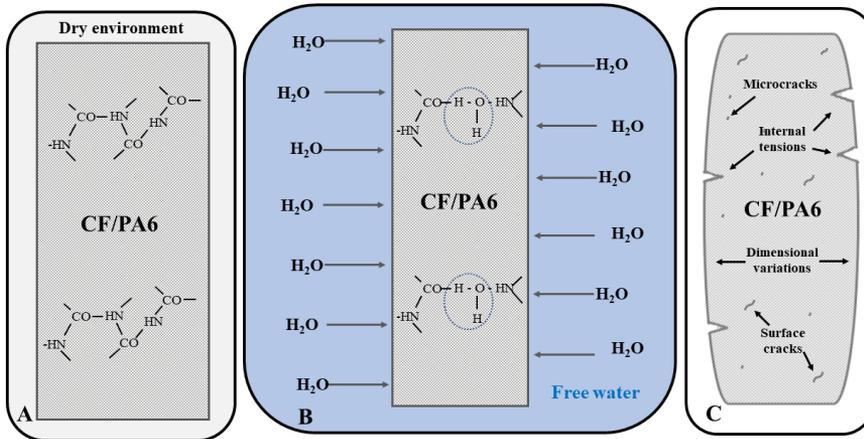
PA6 is a semicrystalline thermoplastic widely applied in the automotive sector, with excellent mechanical, thermal, and chemical properties. However, PA6 is considered a highly hygroscopic material due to the hydrogen bonds between the water molecules and the oxygenated groups (carboxyl and hydroxyl), favoring good moisture absorption; consequently, it can be degraded by hydrolysis<sup>4,5</sup>.

Thus, the behavior of CF/PA6 (Figure 1A) components when exposed to humid environments should be investigated

since moisture can degrade the properties dependent on the matrix and/or the fiber/matrix interface. This occurs because the water can penetrate the polymer matrix by the diffusion process until the equilibrium concentration is reached (Figure 1B), this mechanism being accentuated with the increase in the temperature. In this case, moisture causes the volumetric expansion of the polymer matrix, generating minor dimensional variations and internal stresses, which favor the appearance of damage in the form of surface cracks, micro-cracks in the matrix and/or at the fiber/polymer interface (Figure 1C)<sup>6</sup>.

Conditioning in a saline environment is a standardized method to evaluate the influence of high-salinity environments on materials, often leading to an accelerated corrosion process<sup>7</sup>. The simulated marine environment is used, with controlled salt concentration and temperature. Since it comes to applications in the automotive and aerospace sectors, this test is of great interest, especially when considering the use and flights in coastal and maritime regions. In the marine environment, combined with humidity and temperature differences, swelling of the polymer matrix can occur, which can generate and propagate cracks when cycles of sorption and desorption of water molecules occur.

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**Figure 1.** Influence of humidity on CF/PA6 composites: dry CF/PA6 composites (A), in a wet environment (B), and damage to the CF/PA6 composite from the influence of humidity (C).

In addition, water sorption also leads to the occurrence of corrosive effects on the fibers and the breakdown of chemical interactions between the reinforcement and the matrix, resulting in the weakening of the fiber/polymer matrix interface<sup>8</sup>.

The salt particles present in the marine environment hinder the process of water diffusion into the composite. The diffusion of water molecules from the surface to the interior of the sample occurs mainly through the amorphous phase of the thermoplastic and is facilitated by the presence of microvoids at the fiber-matrix interface. Small salt particles can clog these microvoids, making diffusion difficult, reducing the kinetics of sorption, or making it more difficult for water molecules to enter by capillarity into the material<sup>9</sup>.

In this way, using laboratory scale tests standardized according to technical standards, it is possible to evaluate the moisture content from the mass gain by moisture absorption and the diffusion coefficient. When combined with heating, conditioning in a liquid medium increases the transfer of molecules and consequently increases the rate of moisture diffusion. Furthermore, the effect of temperature and humidity simultaneously often leads to matrix degradation, fiber/matrix debonding, and delamination, which influence the mechanical and morphological properties.

Therefore, the purpose of this work was to evaluate the behavior of CF/PA6 composite exposed to different conditionings, that is, in distilled water at a temperature of 80 °C and saline solution. For this, standardized specimens (CDPs) were evaluated by tensile and interlaminar shear strength (ILSS) mechanical tests, before and after conditioning. The percentage of moisture absorption, the diffusion coefficients, and morphological characteristics also were investigated.

## 2. Methodology

### 2.1. Materials

The raw material used in this study is carbon fiber reinforced polyamide 6 (CF/PA6), 5 plies, 2x2 twill, 415 gsm, 12k, and 39% RC with trade name Toray Cetex® TC910 supplied by Toray® (England).

### 2.2. Determination of volumetric fraction by acid digestion method

Acid digestion was performed according to ASTM D3171<sup>10</sup> and aimed to determine the volumetric fraction of CF, PA6 matrix, and void percentage in the CF/PA6 composite. This method degrades the polymer matrix in a hot digestion medium without attacking the fibers.

Firstly, samples of CF/PA6 composites (15 mm × 15 mm × 2.5 mm) were dried in a furnace at 80 °C for 24 h. Then, the samples were weighed and immersed in 60 mL of a solution of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (NEON, PA - Brazil) and heated to 150 °C using a hot plate (Corning®, PC-420D) for acid digestion of the polymer matrix occur. After a period of 3 h, the beaker containing the acid solution was transferred to an ice bath, and was added 20 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) 30% (v/v) (Anidrol, 110 vol (30%), Brazil) were added to complete the acid digestion process, causing the CF to float on the solution (Figure 2). The test was carried out in triplicate.

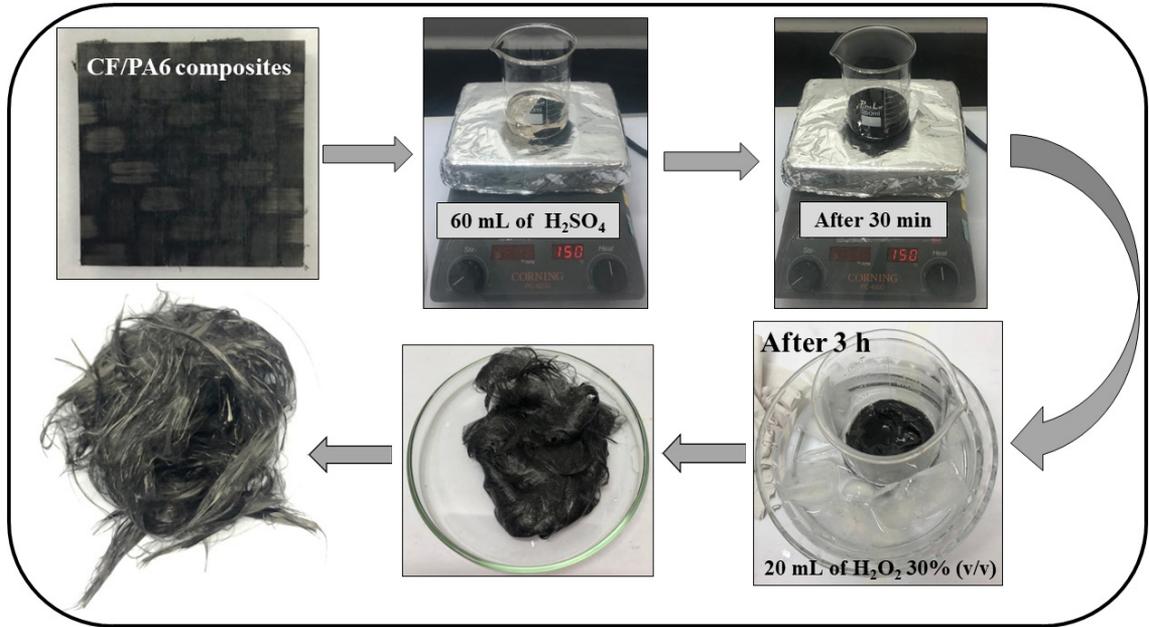
The residue, the CF, was washed three times with distilled water. Then, the CF was dried in a furnace at 105 °C for 24 h and cooled in a desiccator for 1 h. Finally, the CF mass was obtained, and the percentage volume of CF ( $V_r$ ), matrix ( $V_m$ ), and void volume ( $V_v$ ) were determined using Equations 1, 2, and 3, respectively.

$$V_r = \left( \frac{m_f}{m_i} \right) \times \frac{\rho_c}{\rho_r} \times 100 \quad \text{Eq. 1}$$

$$V_m = \left( \frac{m_i - m_f}{m_i} \right) \times \frac{\rho_c}{\rho_m} \times 100 \quad \text{Eq. 2}$$

$$V_v = 100 - (V_r - V_m) \quad \text{Eq. 3}$$

Where  $m_i$  and  $m_f$  are the initial and final mass (g) of the CF/PA6 composites and the CFs, respectively;  $\rho_c$  is the density of composites (CF/PA6: 1.45 g/cm<sup>3</sup>),  $\rho_r$  is the density of the CF (CF: 1.76 g/cm<sup>3</sup>), and  $\rho_m$  is the density of PA6 (1.13 g/cm<sup>3</sup>)<sup>11</sup>.



**Figure 2.** Schematic of the methodology used in the acid digestion process of CF/PA6 composites.

### 2.3. Environmental conditioning tests

Two different types of conditioning were used: distilled water at 80 °C, and saline solution for 12 weeks.

#### 2.3.1. Conditioning test in distilled water at a temperature of 80 °C

The water immersion procedure was based on ASTM D5229/D5229M-20<sup>12</sup> and aimed to evaluate the influence of moisture on mechanical properties. The control of mass gain was performed weekly in samples with different dimensions, such as eight tensile strength specimens (250 mm × 25 mm × 2.2 mm) and seven ILSS specimens (24 mm × 6.25 mm × 3.5 mm). After the environmental conditioning tests, the samples were evaluated by the tensile test and ILSS.

Before starting the hygrothermal conditioning, the samples of CF/PA6 composites were dried in a vacuum furnace (Sheldon Manufacturing, Inc – SVAC1E) at 60 °C for 48 h to eliminate the moisture present in the material. Then, the initial mass ( $M_i$ ) was obtained from dry samples using an analytical balance (AS 60/220.R2, Radwag®) to determine the initial mass ( $M_i$ ).

Afterward, the CF/PA6 composites were immersed in a thermostated bath (Nova Instruments®) containing deionized water at a controlled temperature of 80 °C ( $\pm 2$  °C). The samples were weighed weekly for 12 weeks. This conditioning test in distilled water had a duration of 12 weeks. From the mass of the samples, the moisture content absorbed by the material over the time of immersion in water was obtained according to Equation 4, where:  $M_a$  is the mass of the material after water absorption, and  $M_i$  is the initial mass of the dry composite.

$$M, \% \text{moisture} = \left( \frac{M_a - M_i}{M_i} \right) \times 100 \quad \text{Eq. 4}$$

#### 2.3.2. Conditioning test in saline solution

The saline conditioning was prepared according to ASTM D1141<sup>13</sup>, which simulates the chemical composition of ocean water lacking heavy metals. This conditioning test was intended to determine the influence of salinity present in marine environments on CF/PA6 composites. The mass of the samples was obtained using an analytical balance (AS 60/220.R2, Radwag®) to determine the initial dry mass of samples ( $M_i$ ). Then, the samples were conditioned in an environment containing the standardized saline solution for 12 weeks. The mass of samples was obtained weekly for 12 weeks. From the sample mass, the moisture content absorbed by the material over the time of immersion in saline solution was obtained according to Equation 5, where:  $M_{ss}$  is the mass of the material after water absorption in a saline environment and  $M_i$  is the initial mass of the dry composite.

$$M, \% \text{moisture in saline solution} = \left( \frac{M_{ss} - M_i}{M_i} \right) \times 100 \quad \text{Eq. 5}$$

### 2.4. Fourier-transformed infrared spectroscopy (FT-IR)

FT-IR measurements of CF/PA6 composites before and after the conditioning tests were carried out in a PerkinElmer spectrometer (model 2000) using universal attenuated total reflectance (UATR), an average of 20 scans with 2 cm<sup>-1</sup> resolution, in the range from 4000 to 500 cm<sup>-1</sup>.

## 2.5. Mechanical properties tests

The tensile test was performed on composites before and after conditioning tests in distilled water at 80 °C and saline solution in standardized specimens (250 mm × 25 mm × 2.3 mm), according to ASTM D3039<sup>14</sup>. The tensile test was carried out in an MTS equipment (model Criterion 45), with a 50 kN load cell, at room temperature and a speed of 2 mm/min. Six specimens from each group were tested (without conditioning, after conditioning in distilled water at 80 °C, and after in saline solution).

The interlaminar short beam (ILSS) test was performed to evaluate CF interfacial adhesion mechanisms with the PA6 matrix before and after conditioning tests. The samples (24 mm × 6.35 mm × 4.0 mm) were performed with a 100 kN load cell on an Instron (model 5982) and a testing speed of 1 mm/min, according to ASTM D2344<sup>15</sup>. For this purpose, seven specimens were tested for each case studied. The interlaminar shear strength ( $\tau_{max}$ ) was calculated by dividing the recorded peak reaction force (P) by the area of the cross-section ( $b \times h$ ), as shown in Equation 6.

$$\tau_{max} = 0.75 \frac{P}{(b \times h)} \quad \text{Eq. 6}$$

Before the mechanical tests, the specimens remained in a desiccator with air circulation (Dry box, Arsec, DCV3200) for 24 h at 60 °C.

The results were statistically analyzed using one-way analysis of variance (ANOVA) and Tukey's multiple comparisons test on GraphPad Prism 6 (GraphPad Prism 6 Software Inc., USA)

## 2.6. Fractographic analysis

Surfaces of fractured specimens after tensile tests were inspected with an FEI Company® microscope (Inspect S50), with detectors of secondary electrons mode (SE), an accelerating voltage of 20 kV, and magnification of 250 and 5,000 x. The samples were placed in stubs with carbon tape and coated with a thin layer of gold for 120 seconds using a sputtering Quorum (Q150RS Plus).

## 3. Results and Discussion

Table 1 presents the values of the volumetric fractions of CF, PA6 matrix, and the void content obtained by the acid digestion. The average values determined in the present study agree with the literature<sup>11</sup>. This literature shows volumetric fractions of CF and PA6 of 50% ( $\pm 10\%$ ) and 50% ( $\pm 10\%$ ), respectively, for the same laminate used in the present study.

The quantification of moisture absorption during the conditioning tests by CF/PA6 composites was characterized by diffusion kinetics. Furthermore, due to the low void content of CF/PA6 composites, which is  $0.3 \pm 0.2\%$  as shown in Table 1, it is assumed that the entry of water into the composite concerns only the matrix, since the CFs are considered non-absorbent. Therefore, any moisture absorbed by the composites is due to the polymer matrix, PA6, which is regarded as a highly hygroscopic material<sup>16,17</sup>.

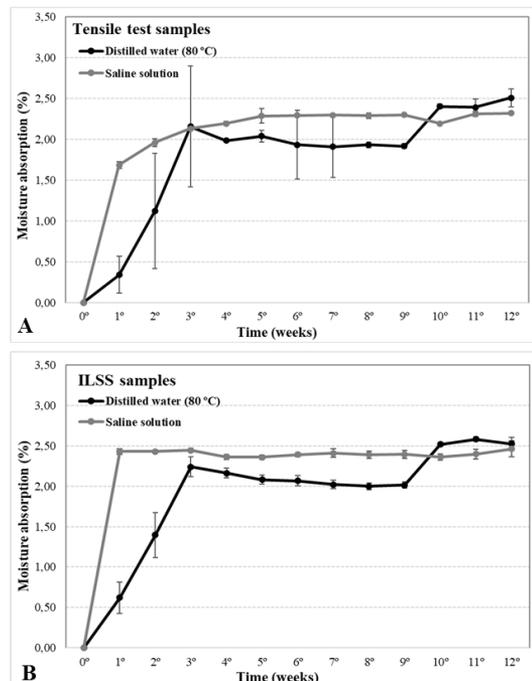
Lei et al.<sup>18</sup> showed that the sorption behavior is extremely affected by the presence of CF, as the PA6 matrix absorbs more

water than the CF/PA6 composites due to the barrier effect of CF. However, according to these authors, the PA6 matrix and the CF/PA6 composites have different water absorption behavior at different temperatures. High temperature can result in progressively increased matrix loss due to hydrolysis, so the maximum moisture content of the PA6 matrix decreases with increasing temperature. On the contrary, it occurred with the CF/PA6 composites, in which the temperature had an effect during the hydrothermal aging and contributed to an increase in the maximum moisture content of the CF/PA6 composites. This fact is due to the PA6 degradation involving swelling, microcracks, and voids, which increased the free spaces for water to penetrate and the composite to absorb.

Figure 3 shows the graph of moisture absorption versus time of conditioning in distilled water and saline solution for different specimens: tensile test (Figure 3A) and ILSS (Figure 3B). It is possible to observe that in both conditioning means, the samples showed a similar behavior throughout the conditioning period, in which the specimens absorbed water quickly and linearly in the first weeks (3<sup>rd</sup>-4<sup>th</sup> weeks) due to the phenomenon known as pseudo-balance<sup>19,20</sup>, and after moisture absorption stabilized until the 9<sup>th</sup> week.

**Table 1.** Volumetric fractions of CF, PA6 matrix, and CF/PA6 composites void content.

Volumetric content	(%)
Carbon fiber ( $V_f$ )	$51.3 \pm 0.3$
PA6 ( $V_m$ )	$48.4 \pm 0.5$
Voids ( $V_v$ )	$0.28 \pm 0.2$



**Figure 3.** Moisture absorption during the conditioning in distilled water (80 °C) and saline solution as a function of time for different shapes of specimens: tensile test (A), and ILSS (B).

Botelho and Rezende<sup>21</sup> observed a similar moisture absorption result, when carrying out the conditioning test in distilled water of CF/PA66 composites for ten weeks and verified a moisture absorption of approximately 2%.

After the equilibrium period, water tends to remain in the composite as free water; with the passage of conditioning time, it slowly penetrates the polymer matrix by the concentration gradient, known as the diffusion coefficient (D). Furthermore, the hydrogen bonds are well established between the water molecules, the amide group in polymer chains, and the CF. Thus, the formation of the microstructure of hydrogen bonds limits the increase of water-rich regions, inhibiting more moisture absorption by the polymer matrix, even after the samples reach the saturated state. This fact occurs due to the diffusion process, in which water molecules are transported from areas of high moisture concentration to regions of lower moisture concentration due to the random movement of water molecules<sup>18</sup>.

Due to the continuous exposure to moisture, the absorption process becomes slower, which can be attributed to the beginning of the relaxation process of polymeric chains and the filling of voids existing in the composites. In other words, it is the period in which water penetrates the polymeric chain, increasing the free volume of the polymeric matrix, moving the polymeric chains away, and allowing greater mobility of chains. This behavior can be observed from the 3<sup>rd</sup> to the 9<sup>th</sup> week of conditioning (Figure 3) when the samples reached equilibrium and were slowly absorbing more moisture. As a consequence of this process, the increase in the mobility of macromolecular chains may promote plasticization due to the reduction of the van der Waals forces in the composite<sup>22,23</sup>. Thus, it is essential to know the diffusion coefficient since the moisture absorbed by the polymeric composites can cause significant changes in the physico-chemical characteristics of the matrix. This behavior can reduce the mechanical strength and stiffness of the material due to the plasticization effect of the matrix, making the material more ductile, leading to the weakening of the fiber/matrix interface and, consequently, detaching the fiber/matrix interface and degrading the laminate structure<sup>24</sup>.

After the 9<sup>th</sup> week of conditioning (Figure 3), the specimens showed a constant increase in moisture absorption values until the end of the conditioning test in distilled water (80 °C) and saline solution. This behavior may be because water had a more significant deleterious effect and influenced the scission of the chains and the breakage of the van der Waals interaction at the interface, favoring greater moisture absorption. Furthermore, as PA6 is very hygroscopic, this second phase of moisture absorption may have resulted from the hydrolysis process, resulting in the beginning of permanent degradation of the matrix and interface. Consequently, it may influence the reduction of mechanical properties. This phenomenon is less accentuated for the samples conditioned in saline conditions, probably due to the effect of the salt present in the saline solution blocking the pores on the composite surface

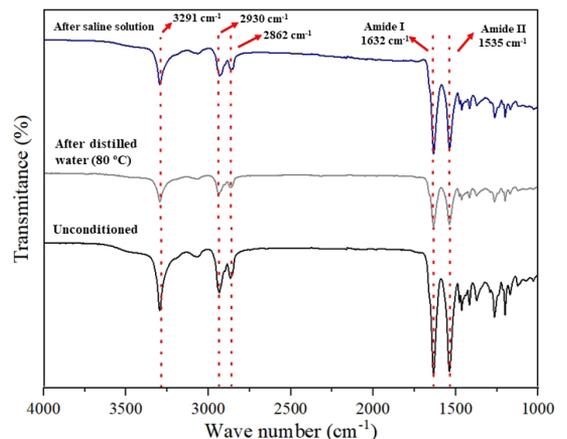
Figure 4 shows the FT-IR spectra of the CF/PA6 composites before and after conditioning in distilled water (80 °C) and saline solution for 12 weeks. The analysis of these spectra shows structural changes in the

polymer matrix that were influenced by moisture through the increase or decrease in the intensity of the bands or their displacement. These changes may indicate possible alterations in the hydrogen bonds between the carbonyl and N-H groups through the determination of the vibrational modes of the amide group.

It is possible to observe that both spectra are quite similar. However, in the spectra of the CF/PA6 composites after the conditioning tests, it is possible to verify a reduction in the intensity of the bands of the amide group I at 1632 cm<sup>-1</sup>, referring to the contributions of the C-O stretching and the vibrations of deformation of C-N; and of the group amide II at 1535 cm<sup>-1</sup> referring to the N-H plane, C-N elongation, and C-C elongation vibrations. The bands at 3291 cm<sup>-1</sup>, 2930 cm<sup>-1</sup>, and 2862 cm<sup>-1</sup> were attributed to hydrogen-bonded N-H stretching, asymmetric CH<sub>2</sub> stretching, and symmetrical CH<sub>2</sub> stretching modes, respectively<sup>25,26</sup>. According to Ma et al.<sup>26</sup>, the changes in intensity and shift of the amide I band (1632 cm<sup>-1</sup>) and the elongation at (3291 cm<sup>-1</sup>) correspond to an increase in hydrogen bonding to the carbonyl group and a weakening of the average hydrogen bond strength to the group N-H, respectively.

Spectra with similar behavior was observed by Ma et al.<sup>26</sup>, who studied the effect of hot water on CF/PA6 composites. According to the authors, the reduction in amide band intensities after conditioning suggests that the amide was dissociated, indicating that the matrix hydrolysis occurred after long-term conditioning. Lim et al.<sup>27</sup> studied the FT-IR spectra of the PA66 after conditioning in a liquid medium and verified that the interactions of water with the PA66 matrix occurred in the amide groups. Moreover, based on the frequency change of amide I and hydrogen-bonded NOH bands, moisture sorption reduced the average hydrogen bonding for the NOH groups. At the same time, an increase was observed for the COO groups.

During the period of conditioning in distilled water at 80 °C and saline solution, all the samples presented absorption of moisture values very close. At the end of the 12-week conditioning tests, the moisture absorption value was close to 2.5%.



**Figure 4.** FT-IR spectra of CF/PA6 composites before and after conditioning tests in distilled water (80 °C) and saline solution for 12 weeks.

Moisture absorption behavior by CF/PA6 composites can be investigated by determining the water diffusion coefficient (D). The diffusion of moisture through composites is one of the main environmental factors of their deterioration and loss of service life. The moisture diffusion coefficient was obtained from the angular coefficient of the line in the graph of Figure 5 ( $M_T/M_\infty$  versus  $(t)^{0.5}$ ). These lines in the graphs were constructed considering the entire conditioning period, that is, all points on the curve. This procedure was adopted to have an average D value involving all the behavior observed in the conditionings, that is, the first increase until the 4<sup>th</sup> week (more accentuated), the stabilized region (4<sup>th</sup> – 9<sup>th</sup> weeks), and the last increase (9<sup>th</sup> – 12<sup>th</sup> weeks). Where  $M_T$  is the mass gain as a function of time, and  $M_\infty$  is the equilibrium mass gain, as shown in Equation 7. Where  $b$  is the thickness of the sample exposed to moisture on all sides, D can be determined by Equation 8.

$$\frac{M_T}{M_\infty} = \frac{4}{b} \left( \frac{D}{\pi} \right)^{0.5} t^{0.5} \quad \text{Eq. 7}$$

$$D = \frac{b^2 (\text{coeficiente angular})^2 \pi}{4^2} \quad \text{Eq. 8}$$

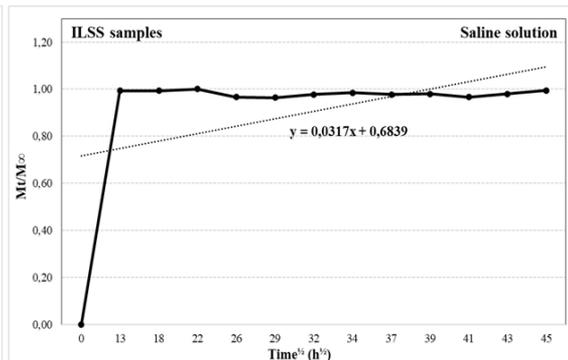
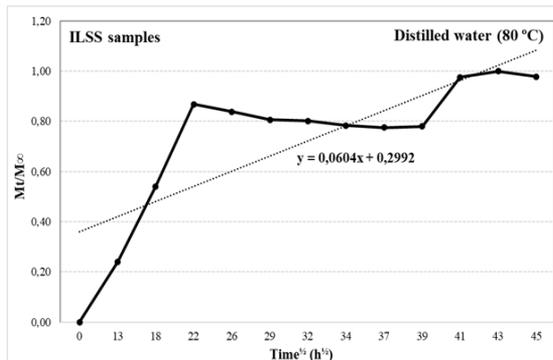
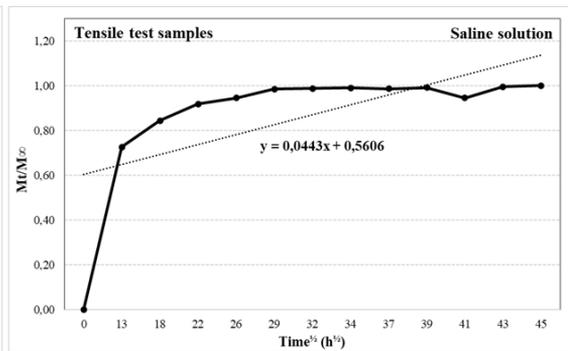
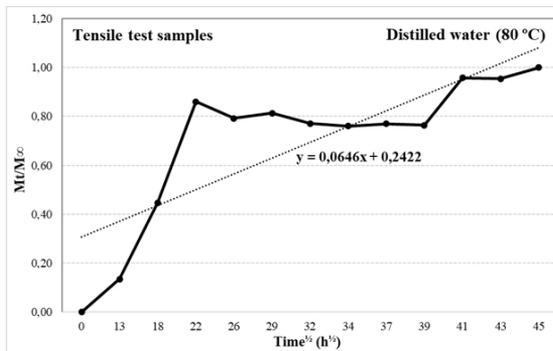
Table 2 presents the D values of the tensile and ILSS samples after conditioning in distilled water at 80 °C and saline solution. First, it is observed that the D values vary according to the specimen size. This occurs because moisture absorption occurs mainly through the cross-section of the specimens, especially for those exposed to distilled water at 80 °C. Thus, longer or thicker specimens favor moisture absorption.

Table 2 also shows that the D values of samples conditioned in saline solution were lower than those of samples submitted in distilled water at 80 °C. This behavior was expected since the presence of salts in marine environments can obstruct the pores of the polymeric matrix, since the large salt molecules can restrict the water diffusion process, delaying the diffusion process in the matrix of composite materials and, consequently, reducing the sorption kinetics or making it more difficult for water molecules to enter by capillarity into the material<sup>28</sup>.

Furthermore, the temperature may have influenced the higher absorption of moisture. The increase in temperature influences the absorption of water, as it can induce the formation of micro cracks and microvoids, facilitating the action of capillarity. Thus, causing an increase in the flow of moisture through the interfacial region and its absorption in the material. Additionally, thermal cycles can increase water absorption, as the differences between the coefficients of thermal expansion, between the fibers and the matrix, induce residual stresses, which lead to the detachment of the fiber/matrix interface.

**Table 2.** Diffusion coefficient (D) for the CF/PA6 composites before and after conditioning tests in distilled water (80 °C) and saline solution for 12 weeks.

Samples	Diffusion coefficient (D) ( $10^{-7}$ cm <sup>2</sup> /min)	
	Distilled water (80 °C)	Saline Solution
Tensile	6.6	3.1
ILSS	5.9	1.6



**Figure 5.**  $M_T/M_\infty$  graph versus root of time (hours) to obtain the diffusion coefficient.

Sang et al.<sup>29</sup> studied the influence of temperature (20 °C, 40 °C, and 60 °C) on hydrothermal conditioning in CF/PA6 composites. The authors showed that the values of the diffusion coefficient of the composites were higher with increasing conditioning temperature, which may have been caused mainly by accelerated diffusion rates of water molecules at higher temperatures. Ma et al.<sup>26</sup> also observed an increase in diffusion coefficient values with increasing conditioning temperature in liquid medium from 80 °C to 98 °C in CF/PA6 composites.

The hydrothermal aging of polymeric composites, combined with humidity and heat, causes harmful effects on the mechanical performance of these materials, reducing the service life of a designed structure and favoring premature and catastrophic failure modes. Alam et al.<sup>30</sup> studied the effects of environmental aging on wind turbine blades based on thermoplastic composites. According to the authors, these studies are critical, as it is possible to design the part considering the humidity and temperature factors, resulting in a more realistic result.

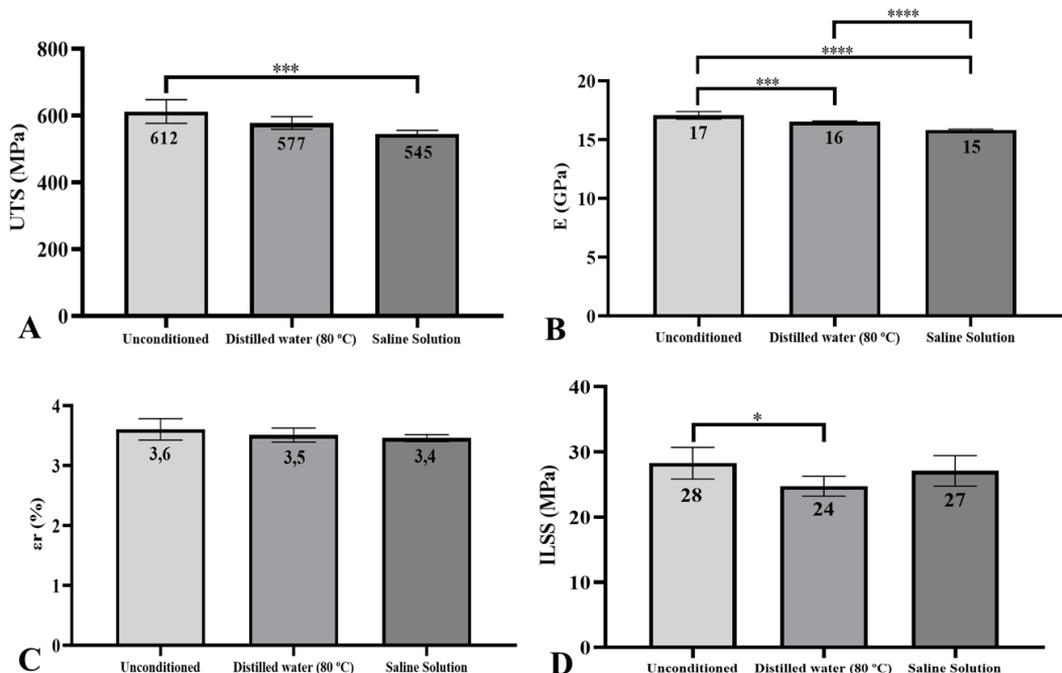
Due to the highly hygroscopic behavior of PA6, that is, due to its polar function and hydrogen bonds, the PA6 matrix can easily absorb water in the environment. So, it is essential to verify its behavior when exposed to humid environments and subjected to mechanical stresses. The moisture is allocated primarily in the amorphous phase of the PA6 matrix, which can induce a plasticizing effect. This effect leads to an increase in bond length and a decrease in van der Waals forces, causing the PA6 matrix to lose strength and stiffness, but gain greater toughness<sup>31</sup>.

Furthermore, according to the literature, changes in the mechanical strength of CF/PA composites are affected by moisture in the material<sup>32,33</sup>.

Kikuchi et al.<sup>34</sup> subjected PA6 and CF/PA6 composites obtained by additive manufacturing in an aqueous media to verify the influence of moistures on the mechanical properties of samples. The authors proved that the equilibrium moisture content is related to the volumetric fraction of the polymer matrix, which is hygroscopic. Therefore, the CF volumetric fraction decreases the maximum water uptake. Thus, due to the barrier effect of CF, the diffusion coefficient of CF/PA6 composites was lower than the neat PA6.

Premature failure in advanced composites can occur due to the fiber's orientation and its volumetric fraction, and due to the polymer matrix nature. However, moisture is one of the leading causes of the degradation of composite materials. As previously discussed, the diffusion of water molecules into the composites can influence the swelling of the sample, due to the plasticization process, breaking the van der Waals bonds between the polymer chains, and affecting the mechanical properties of component material<sup>35</sup>.

So, the mechanical properties of PA6 are sensitive to moisture. The structural instability of the CF/PA6 composites, before and after being submitted to the environmental conditioning tests in distilled water at a temperature of 80 °C and in a saline solution for 12 weeks, was evaluated through the mechanical behavior of ultimate tensile strength (UTS) (Figure 6A), elastic modulus (E) (Figure 6B), deformation at break ( $\epsilon_r$ ) (Figure 6C), and ILSS (Figure 6D).



**Figure 6.** Mechanical behavior of the CF/PA6 composites before and after environmental conditioning in distilled water at 80 °C and in a saline solution: ultimate tensile strength (A), elastic modulus (B), deformation at break (C), and interlaminar shear stress. Results are given as mean  $\pm$  SD (n = 6), significance levels: \*\*\*p < 0.001, \*\*\*\*p < 0.0001, and \*p  $\leq$  0.05.

From the analysis of the average values of the mechanical tests, presented in Figure 6 and Table 3, it is possible to observe a decrease in UTS, E, and  $\epsilon_r$  from tensile properties and ILSS test of CF/PA6 composites after being submitted to environmental conditioning in distilled water and saline solution.

Regarding the tensile strength, a decrease of 5.5% and 10.8% were observed for the CF/PA6 composites submitted to distilled water and saline solution, respectively, when compared to the CF/PA6 unconditioned. The elastic modulus of the CF/PA6 composites subjected to conditioning in distilled and saline solution was reduced by around 2.9% and 7%, respectively, compared to the CF/PA6 unconditioned. The deformation at break decreased by 2.7% and 4.1% after conditioning in distilled water and saline solution compared to the composites unconditioned.

Similar behavior was observed in the study of Botelho and Rezende<sup>21</sup>, who evaluated the influence of high moisture concentration on the mechanical properties of CF/PA66 laminates. The authors also observed a decrease in tensile strength after hygrothermal conditioning for ten weeks. According to the authors, the water diffused through the amorphous regions of the polymer matrix acted as a plasticizer, in addition to influencing the degradation of the polymer/CF interface. The presence of moisture, on the other hand, can swell the polymer and probably alter the level of residual stress, with a reduction of radial compression in the filaments due to differences in the expansion coefficients.

However, moisture can also be favorable for composites, increasing tensile strength. As in the study by Faria et al.<sup>36</sup>, who submitted CF/PPS and fiberglass (FG)/PPS composites to hygrothermal conditioning for eight weeks and observed an increase of 12% and 5%, respectively, in the tensile strength. According to the authors and based on the study carried out by Cândido et al.<sup>37</sup>, the presence of moisture in the composites may have reduced the matrix stiffness and consequently increased its toughness. Furthermore, the presence of moisture may have caused the expansion of the polymer matrix volume and a greater distance between

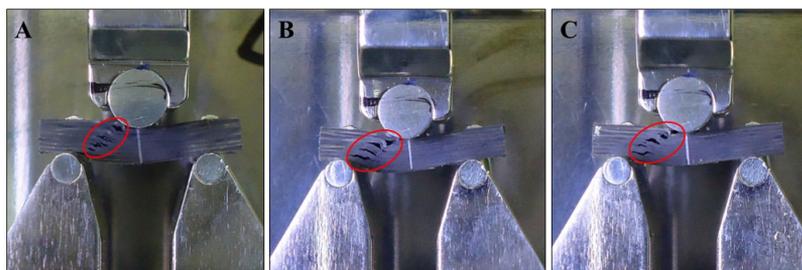
the molecular chains. Thus, the water may have acted as a toughening agent, influencing the mechanical properties of the composites and improving the transfer of stresses in and out of the laminate plane. In this specific case, the conditioning period may have favored the water molecules to form several hydrogen and van der Waals bonds and even bonds of a covalent nature. However, it is known that in specific thermoplastic composites, the diffusion of water in the material can lead to its aging, that is, degradation by hydrolysis resulting in a decrease in its mechanical properties.

Regarding the ILSS results, it was possible to observe a reduction of 12.3% and 4.1% after conditioning in distilled water at 80 °C and in saline solution, respectively, in comparison with the CF/PA6 unconditioned. This reduction in the ILSS values after the conditioning tests may be due to the 12-week period in which the samples were submitted to the humid environment and thus absorbed moisture, resulting in the plasticization process of the polymer matrix. This behavior was more pronounced in the composites that were exposed to distilled water at 80 °C. This fact corroborates the results presented and discussed on the diffusion coefficient (Table 2) since the presence of salt molecules in the water (saline solution) restricted the entry of moisture into the specimens. Consequently, the water tends to be trapped only on the surface of the sample, that is, it did not migrate to the interfacial regions of the samples, and thus did not significantly influence the reduction of ILSS values, as observed in Figure 6 and Table 3.

Figure 7 presents macroscopic images of the ILSS fracture of the CF/PA6 composites before (Figure 7A), after exposure to water at 80 °C (Figure 7B), and after the saline solution (Figure 7C). It is possible to observe a similar fracture behavior in all images, indicating that the presence of conditioning factors, such as humidity, temperature, and the presence of salts did not influence the shear failure mechanism. The images indicate multiple interlaminar fractures, characteristic of the beginning of a delamination process, with fiber rupture, in addition to the elastic behavior of the polymer matrix.

**Table 3.** Results of the tensile test of the CF/PA6 composites before and after the environmental conditioning test in distilled water at 80 °C and saline solution for 12 weeks.

Samples	UTS (MPa)	E (GPa)	$\epsilon_r$ (%)	ILSS (MPa)
<b>CF/PA6 unconditioned</b>	612.0 ± 35.3	17.0 ± 0.3	3.6 ± 0.1	28.2 ± 2.4
<b>CF/PA6 in distilled water (80 °C)</b>	577.8 ± 18.9	16.5 ± 0.1	3.5 ± 0.1	24.7 ± 1.5
<b>CF/PA6 saline solution</b>	545.7 ± 10.1	15.8 ± 0.1	3.5 ± 0.1	27.1 ± 2.3

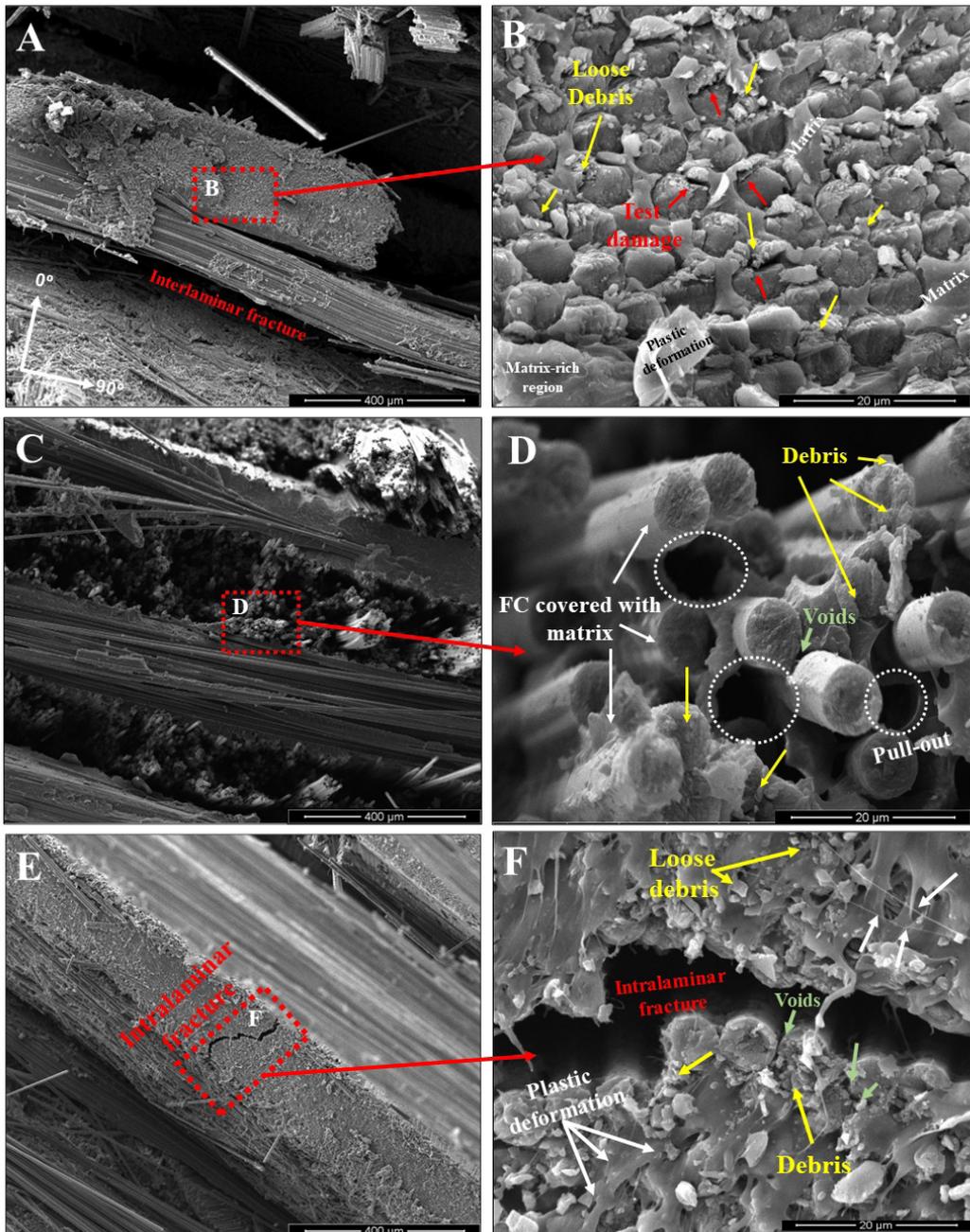


**Figure 7.** Representative fracture images from the ILSS test of CF/PA6 composites: unconditioned (A), after distilled water at 80 °C (B), and after the saline solution (C).

SEM micrographs (Figure 8) of tensile fracture morphologies are applied to analyze the interface between CF and PA6 matrix before (Figure 8A, B) and after the conditioning test in distilled water (80 °C) (Figure 8C, D), and in saline solution (Figure 8E, F), for 12 weeks.

Figure 8A shows CF tows in directions 0° and 90° and the presence of interlaminar fracture, originating during the tensile test. This figure also shows the excellent adhesion between the CF and PA6 matrix, which resulted in a good interface between the CF and PA6 matrix. This aspect is due to the physico-chemical compatibility between both components

and the good consolidation of laminate. Figure 8B shows a detailed image of the top of CF tows with fiber breakage (indicated by red arrows). The strength of the CF/PA6 composite was high and resulted in a translaminar fracture (fiber failure), which resulted in a transversal fracture of the CF. This fracture surface also shows the presence of debris (highlighted with yellow arrows) across the analyzed surface, generated by grinding the fracture surfaces against each other during post-failure loading. This figure shows in major detail that the PA6 matrix is strongly adhered to the CFs, with the presence of rich regions in the matrix and plastic deformations.



**Figure 8.** SEM of the fracture surface of CF/PA6 composites tested in tensile: unconditioned, 500x (A) and 5,000x (B); after conditioning test in distilled water (80 °C), 250x (C) and 5,000x (D); and after saline solution, 250x (E) and 5,000x (F).

Humidity and temperature can considerably influence the fracture morphology, as they contribute to reducing the interaction forces between the CF and the matrix, promoting damage mechanisms that are controlled by the interface performance of the interface.

Figure 8C, D shows the fracture surface of the CF/PA6 composite after conditioning in distilled water at 80 °C, for 12 weeks. Figure 8D shows the presence of pull-out locations (indicated in orange color), due to the weakening of the interface in these regions, which may have been affected by the presence of moisture. On the other hand, regions with good CF/matrix interface also are observed, even after the conditioning period, indicating that the interface was not completely compromised.

Figure 8E, F corresponds to the fracture surface of CF/PA6 composites after conditioning in saline solution. This image shows good consolidation of the laminate even after conditioning and a flat fracture surface. This type of fracture is typical of brittle material and shows that the integrity of the composite has been preserved. The observed behavior can be attributed to the conditioning in saline solution, which attacks preferentially the external face of the specimens. This fact indicates that the salts present in the solution may have obstructed the diffusion of water into the sample; that is, the moisture that diffused into the sample was trapped and only a part permeated through the free volume of the composite<sup>38,39</sup>.

In Figure 8E, it is possible to observe the presence of an intralaminar fracture. Figure 8F shows the 5000x magnification of the intralaminar fracture region. It is possible to observe the presence of plastic deformation along the extent of the fracture surface with the presence of fibril formation (white arrows). That is, with the presence of voids that nucleate at the interface between the matrix and the CF (highlighted with green arrows), probably during the tensile test. These fracture aspects explain the characteristic behavior of higher fracture toughness of thermoplastics, as fracture energy is mainly absorbed through void coalescence, ductility, and fibrillation<sup>40</sup>.

In both morphologies of the fracture surface of the composites exposed to conditioning tests, regions with a decrease in the interfacial interaction between the CF and the PA6 matrix were observed. This fact may be due to the reduction of van der Waals forces, and the plasticization of the matrix may have occurred due to the absorption of moisture present in the environment of conditionings, as discussed above, resulting in a decrease in mechanical strength (as observed in Table 3 and Figure 6). Furthermore, according to Sang et al.<sup>29</sup>, as the conditioning period in a humid environment increases, so does the number of voids between the fiber and the matrix (highlighted in green in Figure 8D, F) increases also. According to the authors, these interface interruptions are caused by the absorption of moisture that weakens the transfer of tension from the polymer matrix to the fibers, consequently reducing the tensile strength.

## 4. Conclusions

This study shows that the conditioning of the CF/PA6 composite in distilled water at 80 °C and in saline solution can decrease the mechanical properties due to the combined effects, such as moisture, temperature, and saline environmental

effects during the exposure period. The influence of these factors, mainly humidity, may have resulted in the plasticization process of the polymer matrix, reducing the mechanical behavior. Diffusion coefficients showed lower values for the CF/PA6 composites submitted to conditioning in saline solution.

Both conditionings during 12 weeks showed similar values of moisture absorption. However, after the 9<sup>th</sup> week of conditioning, a constant increase in moisture absorption was observed, indicating that the water has a more significant deleterious effect. This process was probably favored by the hygroscopic characteristic of PA6. A small reduction in the UTS, E,  $\epsilon_r$ , and ILSS values was observed, probably due to the drying of the samples before the mechanical tests, indicating that part of the absorbed water occurred through a reversible process.

Fractographic analyses showed a good interaction between CF and the PA6 matrix in the unconditioned composites. The samples conditioned in distilled water at 80 °C showed the presence of pull-out and debris, due to the weakening of the CF/PA6 interface. The samples conditioned in a saline environment showed that the main attack occurred on the external face of the specimen, with the presence of plastic deformations, formation of fibrils, and preserved interface. This behavior is attributed to the salts present in the medium that blocked the diffusion of moisture in the sample, preserving its structure and its mechanical properties.

Therefore, the present study showed important and interesting results that could help the various industrial sectors that use FC/PA6 composites in the manufacture of various components.

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