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Effect of hostile environments in the fatigue behaviour of carbon/epoxy laminates

Masters Dissertation in Mechanical Engineering
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Effect of hostile environments in the fatigue behaviour of carbon/epoxy laminates

Submitted in Partial Fulfilment of the Requirements for the Degree of Master in Mechanical Engineering in the speciality of Production and Project

Efeito de ambientes hostis no comportamento à fadiga de laminados carbono/epóxido

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“Wherever you go, go with all your heart”

Confucius

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Abstract

The main objective of this dissertation is to study the fatigue response of carbon/epoxy laminates, after being immersed during different periods of time in artificial sea water and natural sea water, in this case from *Figueira da Foz*, Portugal.

After being immersed for 35 days and 60 days in both waters, the specimens were weighed in order to quantify the amount of water absorbed. Then the fatigue tests, consisting in tensile fatigue, were performed. In order to enable these tests, special preparations were made on the specimen, namely its geometry and the way it is placed in the machine. Regarding geometry, four different types (rectangular, dog bone shape, dog bone shape with hole, rectangular with hole) were tested, and the most conclusive results were obtained with a rectangular geometry drilled at the centre. To place the specimens in the machine it was glued metal plates at each end of the specimens with an instant glue, in order to avoid indentation of the specimens and possible slippage between them and the grips.

After removing from the respective sea waters and weighing it was noted that the percentage of water absorption does not reach 1%. Natural seawater presented significant degrading effects, causing a decrease in fatigue resistance. Natural sea water has a more pronounced degrading effect than artificial water. Finally, it was still observed, in the S-N curves presented, that there is a large dispersion of points which was reflected in the low values of the correlation coefficients.

Keywords Carbon/epoxy laminates, Composite fatigue; Tensile/compression loads, Degradation by sea water, S-N curves

Resumo

A presente dissertação apresenta como principal objetivo efetuar o estudo da resposta à fadiga de laminados de carbono/epóxido, após imersos durante diferentes períodos de tempo em água do mar artificial e água do mar natural, neste caso da Figueira da Foz, Portugal.

Após imersos durante 35 dias e 60 dias em ambas as águas, os provetes foram pesados de modo a se poder quantificar a quantidade de água absorvida. De seguida realizaram-se os ensaios de fadiga, consistindo em fadiga por tração. Para possibilitar estes ensaios efetuaram-se preparações especiais no provete, nomeadamente a sua geometria e a maneira como são colocados na máquina. Em relação à geometria testaram-se quatro tipos diferentes (retangular, osso de cão, osso de cão com furo, retangular com furo), tendo-se obtido os resultados mais conclusivos com uma geometria retangular furada no centro. Para colocar os provetes na máquina colou-se, com uma cola instantânea, chapas metálicas em cada uma das extremidades dos provetes, isto de modo a evitar a indentação dos provetes e possíveis escorregamentos entre os provetes e as amarras.

Após retirar das respetivas águas do mar e de se pesarem notou-se que a percentagem de absorção de água não chega a 1%. A água do mar natural apresentou efeitos degradantes significativos, provocando um decréscimo na resistência à fadiga; a água do mar natural apresenta um efeito degradante mais acentuado que a água artificial. Por fim, ainda se notou, nas curvas S-N apresentadas, que existe uma grande dispersão de pontos o que se refletiu nos baixos valores dos coeficientes de correlação.

Palavras-chave: Laminados carbono/epóxido, Fadiga de compósitos, Carregamentos de tração/compressão, Degradação por água do mar, Curvas S-N.

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SYMBOLOGY AND ACRONYMS

Symbology

$\sigma_{a,local}$ – Local stress amplitude

$\sigma_{a,net}$ – Net stress amplitude

$\sigma_{a,nom}$ – Nominal stress amplitude

$\sigma_{max,net}$ – Maximum net stress

σ_{max} – Maximum stress

σ_m – Mean stress

σ_{min} – Minimum stress

σ_a – Stress amplitude

σ_R – Tensile strength

A_{net} – Net area

A_{nom} – Nominal area

d – Diameter

K_t – Elastic stress concentration factor

K_f – Fatigue stress concentration factor

m_D – Mass of the dried specimen

m_W – Mass of the specimen after immersion

N_f – Number of cycles until failure

P_a – Load amplitude

P_{max} – Maximum load

P_m – Mean load

P_{min} – Minimum load

q – Notch sensitivity factor

R – Stress Ratio

t – Thickness

w – Width

Acronyms

ASTM – American Society for Testing and Materials

CFRP – Carbon fibre reinforced polymer composite

DEM – Department of mechanical engineering

FCTUC – Faculty of Sciences and Technology, University of Coimbra

FRC – Fibre-Reinforced Composite

FRP – Fibre reinforced polymer composite

ISEC – Coimbra Institute of Engineering

OM – Optic microscopy

1. INTRODUCTION

Throughout history, composites have been used and discovered without having any kind of knowledge of it. When pharaohs ruled Egypt, it was used clay bricks reinforced with hay, by the time of the romans it was discovered the cement and somewhere in history it was developed the first pieces of paper (which, nowadays, continues to suffer variations in its production in a more chemical way), these are some examples of simple composite materials, but which were never considered as composites until some few years ago. In more modern times, with better technologies and knowledge about materials, there have been a big breakthrough in this type of material, being now possible to mix properties of metals, ceramics and polymers with each other's, or even different kinds of metals, ceramics and polymers. With what was discussed previously it is possible to have in mind that in a nearby future (15 to 20 years) composites will represent the majority of all types of material used in every industry.

Since composites have been appearing more for day to day it is important to have in mind their performance at different environments and when submitted to different kinds of loads. Despite everything that has been described so far, before having in consideration switching metals, polymers or ceramics to a composite, it is important to evaluate how composites deal with both static and cyclic loads, as well as with the type of load (tension, compression, bending, torsion, etc.). The environment where the composite will be placed represents another important factor to have in mind, because of the degree of degradation that might be provoked by the environmental agents, such as acids, salt, fuels, and oils.

In costal zones and maritime environments there is a major concern due to the salt concentration in the air which is extremely crucial to the life of certain materials (such as metals), being corrosion one of the main causes of failure. On the other hand, one of the most problematic kinds of loadings are the cyclic loads, so it becomes a case of fatigue, but combined with environmental degradation. With what was said before, this dissertation becomes a study of some of the most problematic situations that affect the structural integrity of most components in maritime and coastal zones.

1.1. Objectives

The main purpose of this study is to evaluate the effects of a hostile environment in the fatigue life of carbon/epoxy composite laminates.

The hostile environment to be considered is sea water. The results obtained by immersion in natural sea water and artificial sea water will be compared with the control sample ones. The composite material will be under water for periods of 35 and 60 days. The effects of sea water in structural integrity of the material which is being studied constitutes the main objective.

The fatigue tests will be performed in notched rectangular cross-section samples subjected to constant-amplitude tension-compression loads. With these tests it will be possible to achieve another objective of this dissertation, which is to obtain the S-N curves (applied stress versus number of cycles to failure) under different environmental conditions and exposure times. With all the data collected, it becomes possible to study the effect of both sea waters in the fatigue life of the composite material, being this study based on the comparison of the S-N curves of the control samples with those of the degraded ones.

1.2. Dissertation structure

The present dissertation is organised into five chapters. A brief description is provided below:

- This chapter, entitled “INTRODUCTION”, introduces the topics to be developed along this study, as well as its main objectives;
- Chapter two, entitled “STATE OF THE ART REVIEW”, presents a summary of previous research conducted in this field. It is divided into five parts: composite material, constitution of composite material, failure mechanisms, degradation of composite material and fatigue tests;
- Chapter three, entitled “MATERIALS AND METHODS”, addresses all materials and methods used to perform the experimental tests;
- Chapter 4, entitled “RESULTS AND DISCUSSION”, presents and discusses the main results obtained using the methods and materials described in the previous chapter;

- Chapter five, the last one, entitled “CONCLUSIONS AND PROPOSALS FOR FUTURE PROJECTS”, lists the main conclusions and culminates with some proposals for future and new studies.

2. STATE OF THE ART REVIEW

In this chapter it will be discussed the base ideas behind this dissertation, which will be divided into five main categories: composite materials, their constitution (also discussing about FRP, Fibre Reinforced Polymer composite, and carbon fibres), composites failure mechanisms, degradation of composites (discussing about the effects of sea water and immersion time at sea water) and, finally, the fatigue phenomenon.

2.1. Composite materials

A composite material, in a more general way, can be described as a combination/mixture of two or more constituents which are plainly distinct in terms of shape and chemical composition, and in their essence, they are insoluble in each other(s). This combination allows to obtain a final product with better properties than those of the base constituents.

Composite materials have always been part of people's life, as it can be seen in Figure 2.1, they appeared initially as paper and straw bricks. The first composite materials were identified as something that can be found in nature, wood (cellulose fibres + lignin), and on the human body, the bones (mineral substance + collagen protein). As it was seen composites can be of a natural origin, but they can also be of a non-natural origin. In these last types of composites enters the engineering composites.

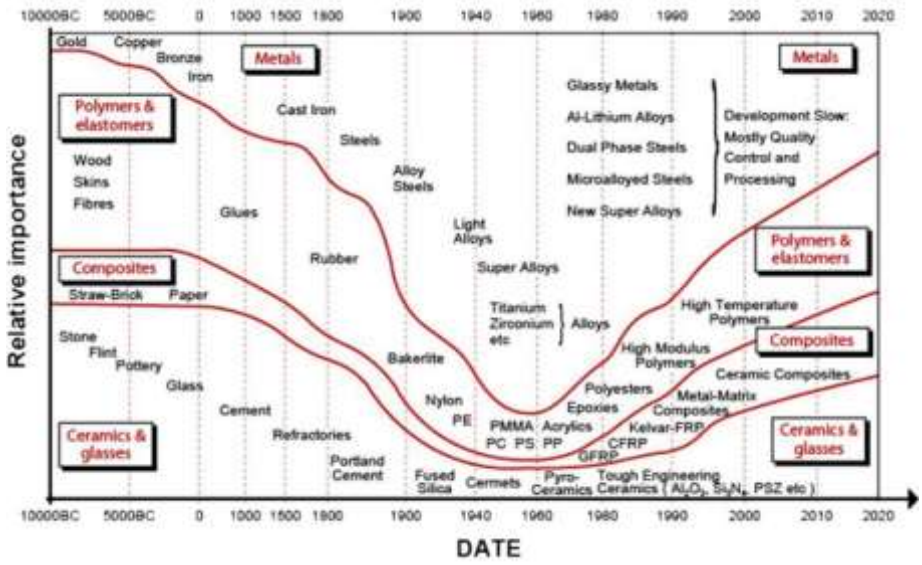

Figure 2.1: Chart representing the evolution of the relative importance of materials along time [1].

The engineering composite materials started to appear in the automotive sport (Formula 1) nearly 40 years ago with the introduction of a chassis totally made of carbon/epoxy composite, as it can be seen from Figure 2.2. These new chassis are now implemented in all the Formula 1 cars substituting aluminium (which was the most typical metal used), becoming the cars lighter and safer. Safer because the composite used in the chassis are specially made to resist the most aggressive loads that may occur during a race, which are the situations when a vehicle crashes against a barrier or another vehicle.

Figure 2.2: Carbon/epoxy chassis of a McLaren MP4-1 formula 1 car [2].

Composite materials have also reached the aviation company, as it can be shown in Figure 2.3. Since the 1970's the percentage of composite material used in planes has been increasing in an exponential way. Nowadays, almost 50% of the materials used in the

manufacturing of commercial and non-commercial aircrafts are composite materials. One of the main reasons is the excellent ratio of resistance to weight of the composite materials.

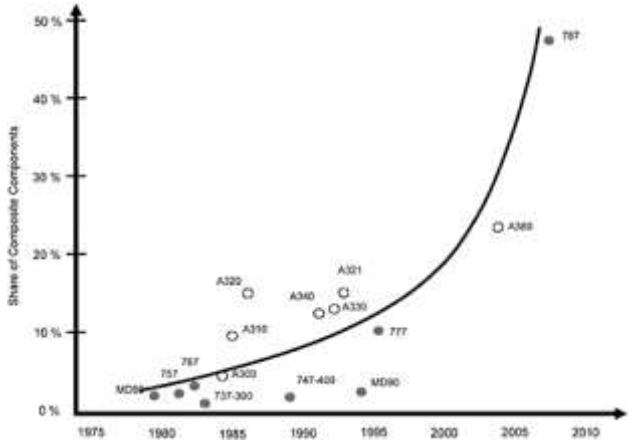

Figure 2.3: Chart with the usage of composite in aircrafts along time [3].

As the composite material is obtained by the combination of different types of materials it shows some advantages such as: better performance for a given weight, better control of mechanical properties in different directions, excellent ratio of tension to weight, good resistance to corrosion (and corrosive environments) and chemical attacks, and finally it is possible to produce complex shapes. Unfortunately, this kind of materials are extremely difficult to repair, they can be very expensive and some of them may need some special heat treatments which involve more production costs [4, 5]. However, and although most of the times the composite materials are more expensive than traditional metals, the ratio price/improvement of the mechanical properties justifies the use of such materials.

2.2. Constitution of composite material

Composite materials are divided into two main constituents: the matrix, and the reinforcement. These constituents are, in general, dependent on each other. In a generic way the matrix can be seen as the external component which protects against the environment and makes the internal part to stick together, being the external part the reinforcement. The reinforcement, normally identified as fibres, is responsible for the mechanical properties of the composite material.

2.2.1. Matrix

In a mechanical point of view the main characteristics provided by the matrix are the resistance to longitudinal compression, transversal traction, and resistance to inter-laminar shear. However, usually, it presents lower stiffness and higher ductility than the reinforcement. Besides those facts, in the case of fibre reinforced composites, the matrix assures the correct pilling of the layers, also acting as a mechanism of load transfer between the fibres.

Depending on the application for which the composite is needed there are three different types of matrixes: metallic, ceramic and polymeric. The most used is the polymeric ones as the thermosets or thermoplastic in the form of resins. Even though the thermoplastics can be melted and reused in general, the more used are the thermosets due to their properties such as higher resistance, better dimensional stability, possibility to process them at lower temperatures and pressure, and finally because they are simpler to process [6].

2.2.1.1. Polymer matrix composites

This type of matrix is quite used in most types of industry, without any kind of restrain, because these composites present several qualities, namely [5]:

- lightweight: resins are polymeric materials, therefore their density is much lower than metals and ceramics, which has a positive impact on the weight of the final product;
- chemical resistance: due to their chemical composition (mixture of resins with fibres) the composites present a good resistance against degradation from chemicals, such as acids;
- high durability against any kind of weather;
- high flexibility in terms of production: when compared with other structural materials, the composites present a huge advantage because in the manufacturing of complex shapes the moulds are easily adaptable to the technologic process in use;
- high mechanical resistance: due to several possible combinations that can be applied between the resin and the reinforcement, these kinds of composites present excellent mechanical resistance and mechanical properties.

2.2.2. Reinforcement (Fibres)

The reinforcement in a general way can be seen as the internal part of any kind of composite material and represents the most important part of this type of material. This is due to the fact that this component is strongly responsible for the mechanical properties of the composite created. These properties depend on several factors which are function of the application of the composite, like the orientation, concentration, distribution, and size and shape of the constituents. The reinforcement can be metallic, ceramic, or natural fibre [6].

Since there are different types of reinforcement, composites can be divided into two main groups. As it can be seen in Figure 2.4, these main groups are identified as particle and fibre reinforcements.

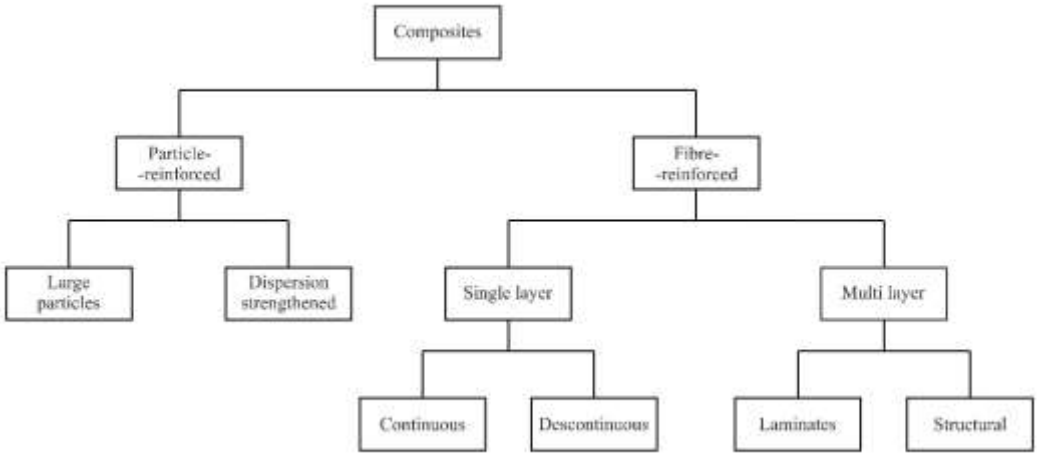

Figure 2.4: Representative scheme with the different classes of composite material, adapted from [6, 7].

The particle-reinforced composites depend on the dispersion and size of the particles. All the improvements given by this type of reinforcement are going to be always under the ones gained by fibre reinforcements. The main gains are in the level of stiffness, and, the level of strength and toughness. Another important property is the wear resistance. It is clearly higher with particles than with fibres (an example of this are the road surfaces). Also, with the introduction of electric conductor particles in the matrix, these constituents can provide a better conductivity to the composite. All these properties will depend on the size of the particles (their diameter), the volume occupied by each of them, and the space between them. The major advantages of these composites are their forming ability, low cost of production, and simplicity of manufacture.

The fibre-reinforced composites (FRC) show more diversity in their nature depending on the application. The final properties achieved with this type of composite will depend on the length, orientation, number of layers, shape and nature of the fibres used. In Figure 2.5, it is presented the types of fibres which can be encountered in composites.

It is possible to divide the FRC into three main categories according to their continuity/discontinuity, orientation, and number of layers. About the first category it is important to make a reference to the fact that continuous fibres present a better efficiency in what concerns the purpose of the reinforcement role in a composite. On the other hand, discontinuous fibres present two major advantages regarding the costs (which are lower) and manufacturing (easier to produce). The orientation of the fibres is mostly dictated based on the information about the application and loads which the composite will be subjected to. This occurs due to the fact that composite materials are anisotropic materials, meaning this that the mechanical properties of the composite will vary with the direction of the fibres. There are three main types of orientation mostly used: unidirectional, multidirectional and random direction. The number of layers is particularly important in a structural point of view. The FRC can be separated in laminates and sandwich panels. There are different ways to design the laminates. The composite laminates are formed by pressing multiple layers, with a certain orientation(s), within the matrix, using for example the autoclave processing. The sandwich panels are a structure made of three layers: a low-density core, and a thin skin-layer bonded to each side, which can be from composite materials.

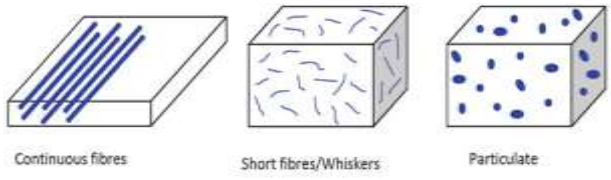

Figure 2.5: Types of fibres which can be found in composites [8].

2.2.2.1. Fibres

This study is based upon carbon fibres, but there are two other kinds of fibres which are also very used, like glass fibres and Kevlar fibres. Fibre glass is the most popular fibre used in industry because of its combination of excellent mechanical (and non-mechanical) properties with a low price. This type of fibre can be bought in different shapes, since a simple thread shape to the shape of a blanket (combinations of threads with different orientations). The Kevlar fibres are mostly found in the war industry in the production of

bullet proof vests and high strengthen cables and threads. The Kevlar fibres present excellent mechanical properties (such as high mechanical resistance and high Young's modulus) and low density. The carbon fibres present the best mechanical properties of all the fibres discussed in this section, except for the impact resistance which is the worst of them all. However, its cost is higher than the other ones. In Figure 2.6, it is presented the steps of the process to obtain carbon fibres through polyacrylonitrile (PAN) fibres.

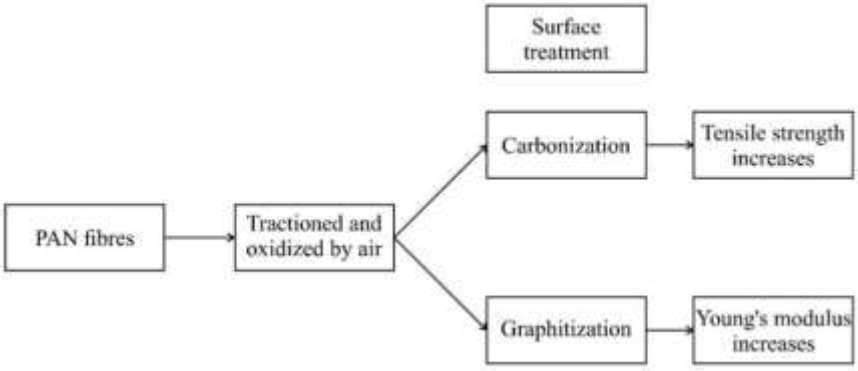

Figure 2.6: Carbon fibers process of obtaining via PAN fibers, adapted from [5].

To have a better idea of the difference between the various mechanical properties of these types of fibres, a summary is shown in Figure 2.7. In this it is possible to observe a set of graphics comparing the resistance to compressive loads, traction loads, Young's modulus and impact resistance for all the fibres.

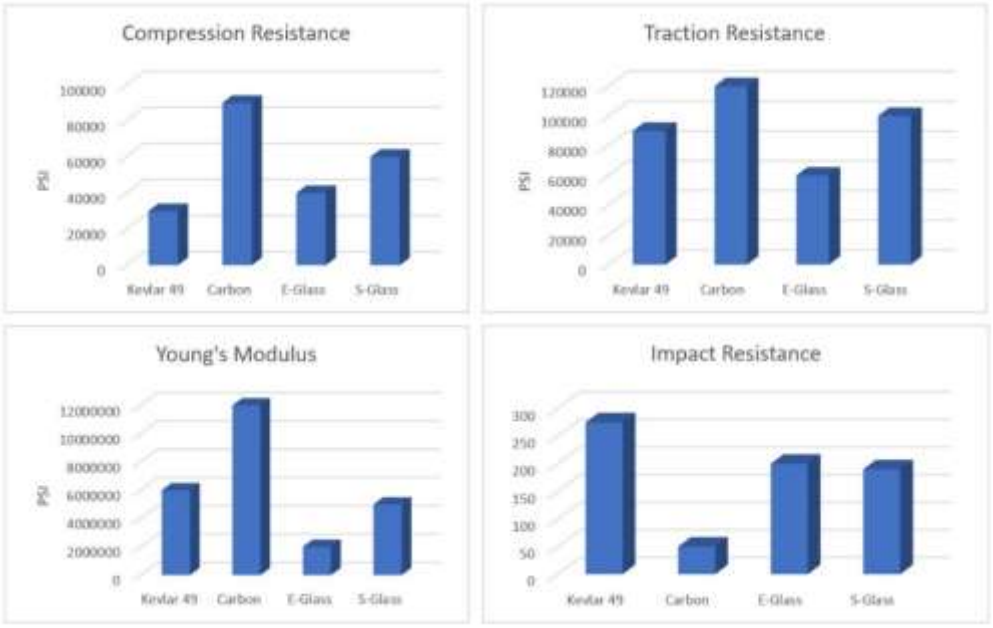

Figure 2.7: Comparison of the mechanical properties of Kevlar 49, Carbon, E-Glass and S-Glass, adapted from [5].

2.3. Failure mechanisms

The principal failure mechanisms of composite materials are:

- Matrix cracking;
- Fibres failure;
- Delamination;
- Debonding fibre/matrix.

Normally the first one that appears is the matrix cracking. The total failure of a composite is given by the total fibre failure which it is only possible after the matrix cracks, because without the matrix, the fibres will be exposed to the environment becoming easier for them to break/failure. It is difficult to define a proper order between all of the failure mechanisms described previously, being the failure of the matrix the one which is likely to happen first. This is because these mechanisms will depend on the properties of the material, as well as on the conditions/environments to which they are subjected.

Since the main focus is the fatigue behaviour of a composite material, it is known that cyclic loads applied into the material induce variations at the load itself, namely can vary from tension to compression and vice-versa. These variations first provoke cracking of the matrix, because this constituent is at the front line of attack of the applied loads, and also due to the fact that fibres have the main mechanical properties of the composite such as mechanical resistance (being this resistance bigger for carbon fibres than for polymers). This

kind of failure will affect the performance of the composite mainly because it will allow that particles from the surrounding environment enter in contact with the fibres, degrading them quickly, according with [9].

The debonding between the constituents is promoted by a weak fibre/matrix bond strength. This lack of strength can be achieved when the applied loads reach high values, thus provoking that the maximum elastic deformation is attained.

Delamination it is mainly noticed in composites composed by several layers, because this mode of failure is based on the fact that a crack which is formed at the matrix is passed to the next layer until the last one gives in. So, delamination only can occur after the cracking of the matrix, therefore it can be said that one mode of failure relates to the other. Delamination normally occurs between layers with different fibre orientations. As it can be seen in Figure 2.8, there are three types of failure by delamination: crack opening, sliding shear, and scissoring shear.

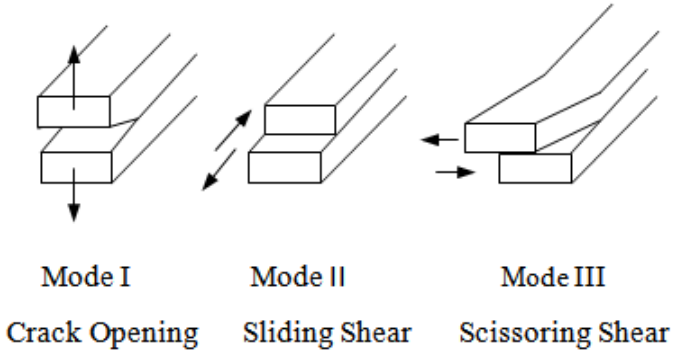

Figure 2.8: Types of failure by delamination [10].

Finally, it only remains the failure of the fibres itself. This is the most problematic failure of all, because the fibres are the constituents which give all the resistance to the composite. Therefore, when this happens, the composite collapses as a consequence of the applied loads, becoming impossible to repair or reutilise it. This situation is mostly provoked at the interface between the matrix and the fibres due to the increase of shear tensions there [6][9].

2.4. Degradation of composite material

As it was showed previously, with the passing of the years, composite materials have been increasingly used in a wide range of industries, since small utensils used in a daily base to aerospace components. So, it can be seen that composite structures can be exposed

to various environments during their service-life. This exposition can cause a degradation in the structural integrity of the composite. Therefore, it becomes crucial to evaluate the effect of the environment in the degradation of the composite, as well as to study the variations of its mechanical properties. In this section, it is discussed the effects in the properties of carbon/epoxy composites when immersed in sea water. As composite materials are widely used in the naval industry, evaluate the effect of the sea water on the mechanical properties of this kind of materials is very important. The salt concentration, UV and moisture are factors which can contribute to a faster degradation of the material. Apart from these factors, it is important to have in mind that time (of immersion) and temperature (of the water) have a major effect at the main properties of the composite materials, due to the increase of the degradation rate via contact with the water and via the increase of temperature. These factors will be addressed along this sub-chapter.

2.4.1. Influence of water

The absorption of water molecules, or in a simpler way, the water uptake of polymeric based composites has major degradation effects on both physical and chemical ways, which will have a negative impact at the mechanical behaviour of the composite.

At the physical point of view, the two main consequences are the plasticization phenomenon and swelling effects. The plasticization of the matrix will induce modifications along the polymeric structure of the matrix, which can result in a breakage of the weaker bond between the polymeric chains. This phenomenon brings, as consequences, the decrease of the glass transition temperature due to the interruption of the van der Waals bonds between the polymers chains and the decrease of the moduli and failure stress. With the penetration of water into the polymeric matrix, it will suffer a swelling effect, which will provoke volume variations of the matrix (induced by deformations in the chain of the polymer). With these variations, in volume, the composite can present interfacial cracks and, eventually, start to fail due to matrix/fibre debonding [11].

Considering now the chemical degradation, a process denominated as hydrolysis is generated by a reaction between water compounds and the polymer from the matrix. In other words, it can be said that by adding water for a certain amount of time to a polymeric matrix, their bonds will start to breakdown, allowing water to penetrate further into the fibres, provoking volume variations of the matrix, known as swelling effect [12][13]. So, it

is expected to observe a change in mechanical properties of composites materials after submerged in water.

As it is known, sea water is one of the biggest natural corrosion agents in the world. It has a special corrosive effect on metals, in general, making them to gradually lose their properties until a point where it is impossible to save them. Polymers present in their nature a high corrosion resistance property but are not completely safe from the effects of sea water, such as the weakening of mechanical properties. The composite at study is a polymeric matrix-based composite which presents some corrosion resistance, but just until a certain point. Because the fibres provide the major strength of the composite, with their degradation, it can be expected to see a major decrease of their service life when operating in a corrosive environment [14]. After a certain time, it will be possible to observe and evaluated the corrosive effects of the salt in the composite material.

Visco et al. [15] and Assaad and Hassam [16] have studied the effects of sea water at room temperature for specific immersion periods of time. The first one studied the effect along a total time of 10 months in which at every 2 months some specimens were taken out from the water and tested. Three-point bending, and torsion static tests were performed in order to evaluate the flexural modulus, maximum flexural strength and shear modulus of two composites, constituted by different resins, defined as orthophthalic polyester resin and isophthalic polyester resin. It was possible to conclude that with the increase of the immersion time, the values of the flexural modulus, maximum flexural strength, and shear modulus decrease.

The latter study [16] was based on the variations observed in the load capacity, axial displacement and radial strain of CFRP-wrapped columns. These specimens were immersed for periods of 7, 30 and 90 days. With the increase of the immersion time, all properties studied showed a reduction of their values.

Therefore, in sum, with the increase of immersion time is expected that the mechanical resistance of CFRP decreases.

2.5. Tensile fatigue tests

In the final part of this chapter, it will be discussed the second main theme of this dissertation, the fatigue phenomenon. About this topic, it will be presented some of the basis behind the phenomenon, the different loading scenarios that can be encountered, and

the main parameters which have a determinant influence on the fatigue resistance. After that, it is presented a brief description of some fatigue life prediction models based on S-N curves. Finally, it will be discussed the fatigue behaviour of composite materials.

2.5.1. Fatigue phenomenon

The definition provided by ASTM states that: "Fatigue is a permanent, progressive and localized structural alteration process which occurs in a material that is subjected to conditions producers of tensions or dynamic extensions in one or several points, and which may culminate in cracks or in a full fracture, after a sufficient number of load variations.".

This phenomenon, as schematized in Figure 2.9, can be divided into three main periods: crack initiation, crack propagation, and final fracture. The first period can be subdivided into two main phases, i.e. crack nucleation and microscopic crack growth. The second period is constituted by the macroscopic propagation. The last period consists of final fracture, when the remaining cross-section of the mechanical component is too weak to carry out the imposed loading.

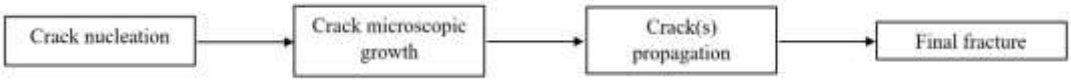

Figure 2.9: Steps of the fatigue phenomenon, adapted from [17].

As it has been discussed previously, the last phase of a complete fatigue test is the final fracture of the specimen. The first fatigue models, for example those proposed by Wohler, relate the number of cycles to failure with the applied stress amplitude. These relations are termed S-N curves. In this approach, the final number of cycles results in the sum of both the number of cycles of initiation and the number of cycles of crack propagation.

2.5.1.1. Fatigue stress cycles

Fatigue is usually associated with the application of dynamic loads, which implies variations over time. Due to these variations in time, the concept of fatigue stress cycles has appeared. This concept was then applied to describe the variation of applied stress with time, or with the number of loading cycles.

Depending on the type of the applied stress amplitude, there are two main groups of fatigue stress cycles, which are as follows:

- Constant-amplitude stress cycles, that can be divided into: alternating (Figure 2.10.(a)), repeated (Figure 2.10.(b)) and pulsating cycles;
- Variable-amplitude stress cycles, that can be divided into: blocks (Figure 2.10.(c)) and random (Figure 2.10.(d)).

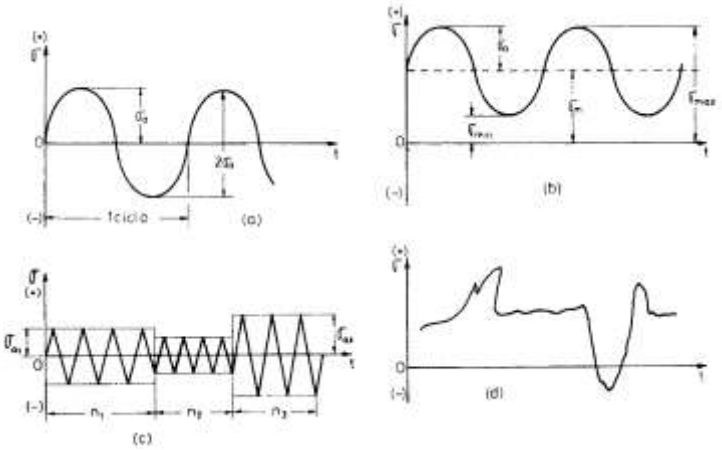

Figure 2.10: Types of fatigue stress cycles ((a) alternating; (b) repeated; (c) blocks; (d) random) [17].

In this dissertation it will be performed tension-compression fatigue tests with constant-amplitude stress values. This means that the stress amplitude is constant over time. The stress amplitude, σ_a, is given by equation (2.1).

$$\sigma_a = \sigma_{máx} - \sigma_m \tag{2.1}$$

where $\sigma_{máx}$ represents the maximum applied stress and σ_m the mean stress. The mean stress is given by equation (2.2).

$$\sigma_m = \frac{\sigma_{máx} + \sigma_{mín}}{2} \tag{2.2}$$

where $\sigma_{mín}$ represents the minimum applied stress. With equation (2.2) it is possible to rewrite equation (2.1) as follows,

$$\sigma_a = \frac{\sigma_{máx} - \sigma_{mín}}{2} \tag{2.3}$$

Based on the above-mentioned equations, it is clear that alternating, repeated and pulsating cycles differ from each other at the mean, maximum and minimum stresses, in the following way:

- Alternating cycle: it has mean zero stress with maximum stress of tension and minimum stress of compression;

- Repeated cycle: it has non-zero mean stress, so the maximum and minimum stresses can be both tension or compression.
- Pulsating cycle: it occurs in a particular case, when the minimum stress is zero.

Mean stress is a main parameter in fatigue tests. It is, usually, quantified by the stress ratio, R. This ratio is obtained by the following relation:

$$R = \frac{\sigma_{mín}}{\sigma_{máx}} \tag{2.4}$$

Knowing the value of R, it becomes easier to know in which cycle the test inserts in by the following way:

- $R = -1$: alternating cycle.
- $R = 0$: pulsating.

2.5.2. S-N Curves

S-N curves are one of the most used methods to analyse the data of fatigue tests performed under constant-amplitude. This S-N nomenclature comes from the literature, i.e. are curves of applied stress versus the number of cycles of failure.

To have a final and definitive curve it is tested a set of identical specimens submitted to different loads. After that, it is registered the number of cycles that each one of the specimens underwent until its total failure. In general, in high-cycle fatigue regime, if the specimen reaches cycles at the range of 10^7 to 10^8, the test is stopped and marked as finished, even without the failure of the specimen. With all these points, it is possible to obtain the S-N curve. When, in the majority of the specimens tested, the number of cycles to failure passes the value of 10^4, there is a linear relation, in a log-log scale, between these two variables. The S-N curve (see Figure 2.11) can be written in the form:

$$\log(\sigma_a) = \log(C') - c * \log(N_f) \tag{2.5}$$

or,

$$\sigma_a * N_f^c = C' \tag{2.6}$$

where, c and C' are the material and test conditions constants.

For tension/compression tests, in smooth specimens, the nominal tension is obtained by the quotient between the applied load and the minimum area of cross-section of the specimen.

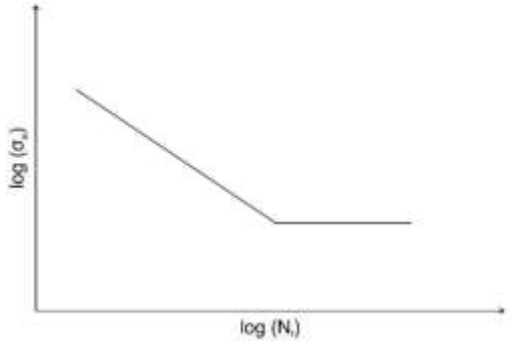

Figure 2.11: Example of a S-N curve [17].

As it can be seen in Figure 2.11, it is common to observe, in high-cycle fatigue regime, that the lower the tension, the bigger the number of cycles to failure. Besides, there are some materials whose S-N curve becomes a straight line when the applied stress reaches a specific value. For applied stresses under this limit, the material can, probably, present an infinite life. This stress limit is called endurance limit. But, this does not occur for all materials. In other cases, S-N curves show a constant decreasing line without a straight part. For these materials, the fatigue stress limit can be defined for a specific life, for example 10^8 cycles.

2.5.3. Fatigue behaviour parameters

In order to obtain better results from the fatigue tests it is important to know some characteristics about the specimens. Fatigue is a very complex phenomenon affected by a wide range of parameters.

These parameters are as follows: surface finishing, size and geometry of the specimens, stress concentration, environmental effects, temperature, mean stress, residual stress and surface finishing.

Specimens that present a good surface finishing detain lesser chances of presenting superficial defects capable of provoking stress concentrations which will difficult the crack initiation. Therefore, specimens highly polished and with low rugosity will present higher fatigue resistance, becoming necessary to apply a bigger number of stress cycles to enable crack nucleation. Besides, improved surface finishing, superficial treatments and coatings can provide surfaces with higher toughness, making more difficult the crack initiation, which will increase the fatigue resistance of the material.

As can be read in references [17][18], it has been performed experimental research to study the effects of the size of specimens on fatigue resistance. The conclusions were that with the increase of size, the fatigue resistance decreases, and that the major factor which better characterizes a specimen size is its cross-sectional area. In a common-sense point of view, the machines have limited dimensions, therefore it is not always possible to realize tests on large specimens. Finally, when comparing a smaller specimen with a bigger one, it is possible to argue that with the increase of volume, the probability to find defects increases, reducing the fatigue resistance.

As already mentioned before, the mean stress has a considerable impact on the type of cycle. Besides that, the mean stress also affects the fatigue resistance, as it can be seen in Figure 2.12. The S-N curves suffer some variations when the mean stress is different from zero. With a more detailed observation, it is possible to realize, for the same number of cycles, that with the increase of the value of R (which implies that the mean stress also increases) the amplitude of the stress fatigue limit of the material decreases (the stress amplitude follows the same behaviour, and the maximum stress increases). Thus, with the increase of the mean stress, the fatigue resistance decreases.

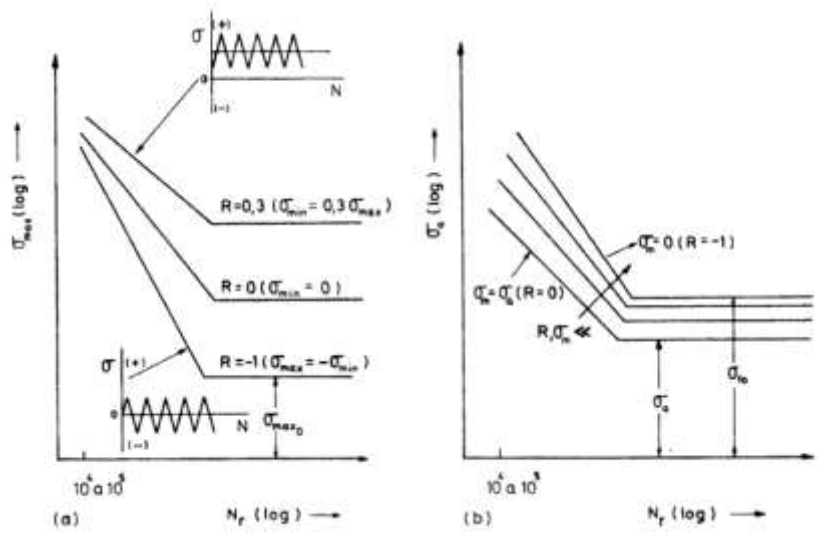

Figure 2.12: Effect of the mean stress at the fatigue resistance [17].

The existence of holes, grooves, fillets or others geometric discontinuities changes the local stress state and introduces zones of stress concentration. These zones have a detrimental influence on fatigue life, since the fatigue resistance decreases dramatically. To properly evaluate this difference, two S-N curves - one obtained using smooth specimens and another using grooved specimens - are compared in Figure 2.13. The difference between

a specimen with and without zones of stress concentration is clearly noticeable. The stress variations in these zones can be evaluated by the value of the stress concentration elastic factor, K_t, since this factor describes the ratio between the maximum stress at the discontinuity zone and the nominal stress. Under fatigue loading, the stress concentration is usually accounted for using the fatigue stress concentration factor, K_f. This factor can be expressed by the ratio of the fatigue stress limit of a smooth specimen to the fatigue stress limit of a notched specimen (these variables are represented by σ_{f0} and σ_{fe}, respectively, in Figure 13). This factor can be related to the elastic stress concentration factor from the following equation,

$$K_f = 1 + q * (K_t - 1) \tag{2.7}$$

The coefficient *q* represents the stress sensitivity factor and helps to evaluate the sensitivity to any notch that can be found at the specimen at study.

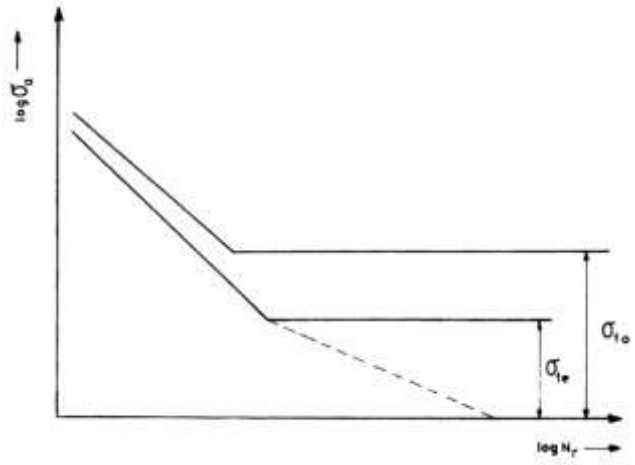

Figure 2.13: Comparison between a specimen without any defect and one with a groove, adapted from [17].

The environment in which the material is placed is highly crucial for evaluating the fatigue life. As it was described before, one of the most critical environments is sea water due to the fact that it combines the degradation by water/humidity and the degradation by salt, which induces the process of corrosion. With both types of degradation, the material loses its mechanical properties and resistance; so, the bigger the time of exposure, the greater the loss of properties and resistance. Therefore, fatigue resistance is likely to decrease.

2.5.4. Fatigue in composites

Normally, the crack initiation occurs at the surface in zones where the stress concentrations are bigger or in zones with defects, but in composite materials it starts to

appear at voids that the matrix might have or even in discontinuity zones between the fibre and the matrix, which are the zones with more probability to appear as defect zones. According to [19], the stress concentration due to holes, grooves or other imperfections induces a significant reduction of the tensile strength of a composite. But, on the other side, it will increase the fatigue resistance, because the damage at these zones will not provoke any kind of damage to the fibres, instead the crack will propagate along aside the fibres inside a certain laminate or the crack will propagate between laminates.

As already discussed in the previous sections, frequency and mean stress are important variables on fatigue behaviour. Composites are more sensitive than metals to the latter variable. Because of the compressive loads, the fibres present big difficulties to support this kind of loads. Compression loads will make the fibres to suffer from buckling which consequently will make easier the separation between the fibres and the matrix [19].

Turning the focus to the frequency effects, it has been observed that a decrease in the frequency results in a decrease in the fatigue resistance of a composite. This effect, of the frequency, can be explained by the change of the failure mechanisms, temperature effect and type of wave. When the failure is controlled by the matrix, the effect of the frequency is more significant than when is controlled by the fibres. This change can be associated with the temperature variation, because during a process of fatigue the composite's temperature increases with the increase of the applied load and frequency. Supposedly it could be concluded that for the reduction of frequency the fatigue resistance decreases due to a process of weakening (and later cracking) of the matrix under low temperatures. Another hypothesis is related to the time which the load is maintained near its maximum value. Since this time increases as the frequency decreases, it can be developed some damage due to creep [19].

In 2.3 was presented the main reasons of failure of composite materials. Combining that with the fatigue phenomenon, there are two modes of failure which are likely to occur during a fatigue test: (i) the matrix cracking is delayed until the fibres present enough stiffness to endure the amount of strain shifted to the matrix; and (ii) the delamination can occur due to the fatigue loading applied. All the failure modes are presented in Figure 2.14 in the format of a S-N curve.

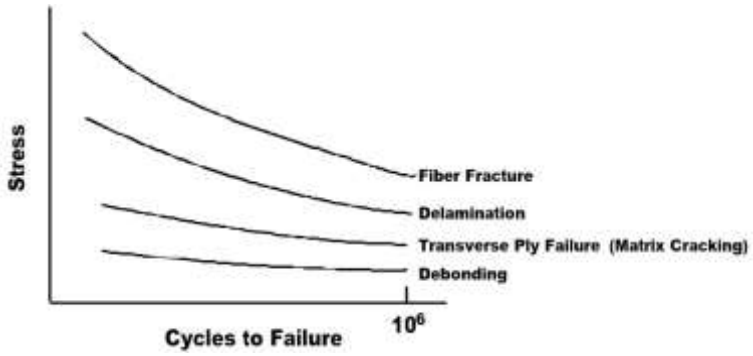

Figure 2.14: Effect of the various ways of failure of composites in their fatigue life [9].

During the crack propagation, the fracture of the matrix and the fibres can be accompanied by shear cracks. Both can be caused by tensile splitting, fibre rupture ahead of crack with no matrix crack, and vice-versa. The formation of these types of cracks can be helpful to fatigue life because they have the ability to absorb fracture energy by increasing the fracture path and have the tendency to attenuate the fatigue crack. Shear cracks can occur ahead of the fatigue crack due to differential Poisson's strain between fibre and matrix. When the failure strain of the fibre is small compared to that of the matrix, the fibres can fail ahead of the crack. For the case of ductile fibres, in a brittle matrix, the matrix can fail leaving the fibres intact. On the other hand, in multi-ply laminates, the fibre angles and ply boundaries can have a significant impact on fatigue crack propagation. This, generally, can progress with little interference in the direction parallel to the fibres, thus the transverse plies in a cross-ply composite will fail first under both static and fatigue loading. The cracks in the transverse plies can also be detained at the interlaminar boundaries to produce crack blunting and shear cracking [9].

Moreover, it can be said that the fatigue life of composites is highly affected by the following factors:

- Fibre property: to have a bigger fatigue strength, it is important that the composite presents a combination of both high strength and stiffness, as already referred to in Section 2.2.2;
- Matrix property: as it was seen before, the stronger and resistant the material of the matrix is, the more load it can be subjected to.
- Orientation: As it can be seen in Figure 2.15, on-axis loading results at the best fatigue strength. However, by orientating the fibres at a slight off-axis loading, longitudinal splitting can be induced resulting in a reduced crack growth rate and, therefore, an increase in fatigue life in

the high-cycle fatigue regime. This effect can also be seen for larger off-axis orientations although the overall fatigue strength decreases.

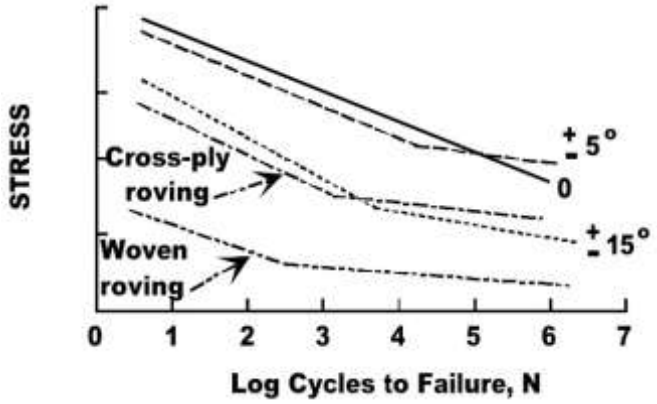

Figure 2.15: Effect of the fibres orientation at the fatigue life of a composite [9].

- Fibre fraction: From Figure 2.16, it can be concluded that with the increase of fibre percentage in the composite material, the fatigue strength also increases.

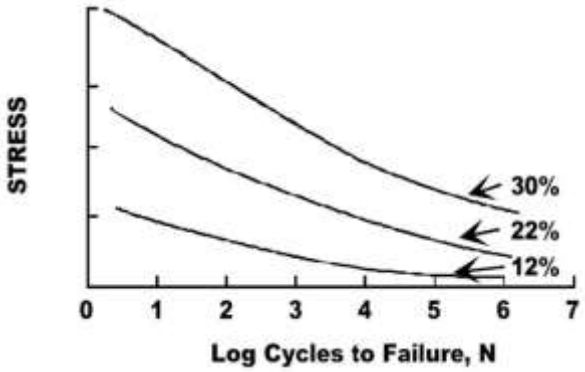

Figure 2.16: Effect of the fibre fraction at the fatigue life of a composite [9].

3. MATERIALS AND METHODS

In this chapter it will be described the basic information about the material being used, such as: the way it was manufactured, dimensions and orientations of the final specimens obtained. About the methods it will be discussed the environmental agents, and how they were obtained, and the different tests performed: tensile and fatigue tests. In each one of them it will be described the procedures, the preparations made, and the machines used, as well as the defined parameters. Finally, it will be described the methodologies followed in the observation of the fracture surfaces of the specimens by OM.

3.1. Material

Composite laminates were prepared, according with the recommendations of the manufacturer, from high strength unidirectional carbon pre-preg "TEXIPREG HS 160 REM" and using the autoclave/vacuum-bag moulding process. The procedure used on the production was: make the hermetic bag and apply 0.05 MPa vacuum; heat up till 125 ºC at 3 to 5 ºC/min rate; apply a pressure of 0.5 MPa when a temperature of 120 or 125 ºC is reached, then maintaining pressure and temperature over 60 min; cool down to room temperature maintaining pressure; and, finally, get the part out from the mould. The volume fraction of carbon fibre is 40%. The plates were manufactured in a useful size of 300×300×1.8 [mm^3]. The final plate presents a thickness of 1.8 mm which results on a stack of 12 layers with the following orientations: [0;45;90;-45;0;90]s.

Before starting the degradation, the tensile, and fatigue tests, it was necessary to cut several specimens in order to start with the main study of this dissertation. These specimens had the size of 100×10×1.8 [mm^3].

3.2. Methods

In this sub-chapter, it is described how both waters were obtained, as well how the tensile, fatigue and OM tests were performed, and it will also be discussed all the parameters involved for each one of those tests.

3.2.1. Environmental Agents

As it was discussed before, the specimens will be submerged in sea water for the periods of 35 days and 60 days. Besides the fact of having two different immersion times, there is also the effect of two different sea waters: natural sea water and artificial sea water. With this information, i.e. different immersion times and different sea waters, it will be possible to observe the different effects provoked by a natural source (approximation of a real-life case) and an artificial source on the performance of the material being studied.

For each time and water, there will be used a total of 24 specimens (this number will be explained at 3.2.3 when discussing about the fatigue tests). Each specimen will be weighted before and after the immersion, with the purpose of observe the water absorption, and if it will have a significant impact on fatigue results.

3.2.1.1. Artificial Water

With the help of professor Ana Piedade, it was possible to produce an approximation of sea water. Following the standard ASTM D1141 [20] it was produced a water with a weight/volume ratio of NaCl of 2.45% combined with a pH of 8.2.

As it can be seen in standard ASTM D1141 [20], to produce a substitute for the ocean water, there is a lot of compounds needed in certain quantities to better approach real water. Since there are compounds which are needed in concentrations less than 0.2 g/L, these compounds were not considered in the present study. The artificial water was produced with the combination of $NaCl+MgCl_2+Na_2SO_4+CaCl_2+KCl$ with the concentrations (in g/L) of 24.53+5.20+4.09+1.16+0.695, respectively.

3.2.1.2. Natural Water

This kind of water was taken from a small bay in the city of *Figueira da Foz*, Portugal, near a harbour, because of the corrosive agents that can be found there such as: gasoline, oils and sanitary discharges. With all these agents (or most of them) mixed in the water becomes possible to analyse an even more degradant environment, which comes even closer to a real-life case study.

3.2.2. Tensile tests

This type of test was performed to obtain the main mechanical monotonic properties. In order to perform these tests, it was necessary to have into account the procedures described in ASTM D3039 [21]. At page 6 of this standard, we can find the table presented at Figure 3.1.

Fiber Orientation	Width, mm [in.]	Overall Length, mm [in.]	Thickness, mm [in.]	Tab Length, mm [in.]	Tab Thickness, mm [in.]	Tab Bevel Angle,°
0° unidirectional	15 [0.5]	250 [10.0]	1.0 [0.040]	56 [2.25]	1.5 [0.062]	7 or 90
90° unidirectional	25 [1.0]	175 [7.0]	2.0 [0.080]	25 [1.0]	1.5 [0.062]	90
balanced and symmetric	25 [1.0]	250 [10.0]	2.5 [0.100]	emery cloth	—	—
random-discontinuous	25 [1.0]	250 [10.0]	2.5 [0.100]	emery cloth	—	—

Figure 3.1: Table from ASTM D3039 with the dimensions needed to perform a tensile test, adapted from [21]

Since the composite studied presents a symmetric orientation, it can be seen at the third line of Figure 3.1 that the dimensions needed for this test are 25×250×2.5 mm (width × length × thickness). These dimensions were considered here.

Tests were performed in an INSTRON 5584 servo-mechanical testing machine, with a load cell of 150 kN (see Figure 3.2) at ISEC. Both specimens were placed between the grips respecting the following distances: external gauge length of 50 mm and spec gauge length of 75 mm. It was also used a mechanical INSTRON extensometer to measure the displacement and to obtain the stress-strain curves. Finally, it was defined the velocity of 2 mm/min for each test.

Figure 3.2: INSTRON 5584 servo-hydraulic machine (1- Grapples; 2- Specimen; 3- Mechanical extensometer).

3.2.3. Fatigue tests

These tests were accomplished with the help of a DARTEC servo-hydraulic testing machine, with 100 kN capacity, as can be seen in Figure 3.3. Each specimen was then coupled between the two hydraulic grips which operate under a pressure of, approximately, 45 bar. After assuring that the specimen was correctly placed, the control was passed to the computer in order to define the test conditions, namely frequency, mean load, load amplitude and type of load wave.

Figure 3.3: DARTEC servo-hydraulic and its constituents (control panel and computer, from left to right).

Fatigue tests were organised into five series of tests: (i) control samples; (ii) 35-day immersion in natural sea water; (iii) 35-day immersion in artificial sea water; (iv) 60-day immersion in natural sea water; and (v) 60-day immersion in artificial sea water. For each series, at least 6 specimens were tested.

In this kind of test, it is also very important to define a proper geometry. Initially, it was pretended to perform three-point bending tests, reason why the specimens were cut with a constant rectangular cross-section of 10x1.8 [mm^2] and a length of 100mm. But due to the impossibility of using the equipment needed when the tests were going to start, the idea of performing three-point bending fatigue tests was put aside. Becoming the objective to perform constant-amplitude tension fatigue tests. Since all of the specimens were already cut into the rectangular shape, it was drilled a hole, *a posteriori*, in the centre of the specimen with a diameter *d*, to ensure that the specimens would fail at the proof zone. A dog bone shape geometry - also suitable to avoid the failure at the grips - was tried, with the help of a

milling machine, but it was impossible to ensure the reproducibility of the fillets. All of these changes of geometry will be better explained at chapter 4.

The final step before running the tests consisted of preventing any damage caused by the grips. To accomplish these conditions, the specimens were glued (with instantaneous glue) into four small pieces of metal. To make sure that the glue acted as intended, the faces of the metal pieces which were going to be glued to the composite were sanded to enhance the rugosity of the surface. It made possible to the glue to have better adherence to the metal. This preparation can be seen at Figure 3.4.

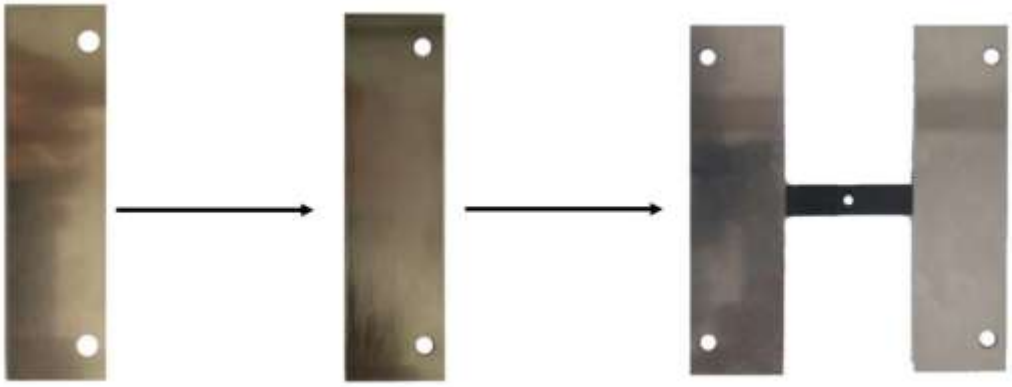

Figure 3.4: Preparation of the specimen for the fatigue tests (form left to right: normal piece of metal, sanded piece of metal).

These tests were performed in load control mode, using sinusoidal waves, and a frequency of 12.5 Hz and $R = 0.1$. The mean load (P_m) and the load amplitude (P_a) are given by the following formulae:

$$P_m = \frac{P_{max} + P_{min}}{2} \tag{3.1}$$

$$P_a = \frac{P_{max} - P_{min}}{2} \tag{3.2}$$

where P_{max} is defined by the user while P_{min} is defined by:

$$P_{min} = R * P_{máx} \tag{3.3}$$

Since R = 0.1, equation (3.3) can be rewritten as follows:

$$P_{min} = 0.1 * P_{máx} \tag{3.4}$$

At Table 3.1 are presented the loads applied in each specimen as well as the dimensions that present more significance to posterior calculations.

Table 3.1: Dimensions of the specimens and applied loads.

Specimen no.	t [mm]	w [mm]	d [mm]	P_m [kN]	P_a [kN]	Specimen no.	t [mm]	w [mm]	d [mm]	P_m [kN]	P_a [kN]
1	1.8	9.81	3	3.421	2.799	**16**	1.8	9.87	3	3.454	2.826
2	1.8	10.01	3	4.026	3.294	**17**	1.8	9.81	3	3.663	2.997
3	1.8	6.94	1.7	2.915	2.385	**18**	1.8	9.75	3	4.125	3.375
4	1.8	9.87	3	3.740	3.060	**19**	1.8	9.84	3	3.685	3.015
5	1.8	9.85	3	3.196	2.615	**20**	1.8	9.78	3	3.652	2.988
6	1.8	9.80	3	3.905	3.195	**21**	1.8	7.62	3	4.191	3.429
7	1.8	9.91	3	3.966	3.245	**22**	1.8	9.75	3	3.878	3.173
8	1.8	9.87	3	4.092	3.348	**23**	1.8	9.74	3	4.345	3.555
9	1.8	9.98	3	3.256	2.664	**24**	1.8	9.72	3	5.675	2.675
10	1.8	9.72	3	3.377	2.763	**25**	1.8	10.03	3	4.037	3.303
11	1.8	9.72	3	4.582	3.749	**26**	1.8	10	3	3.894	3.186
12	1.8	9.71	3	3.372	2.759	**27**	1.8	9.82	3	3.674	3.006
13	1.8	9.85	3	3.196	2.615	**28**	1.8	7.25	1.7	3.768	3.083
14	1.8	9.94	3	4.235	3.465	**29**	1.8	9.79	3	4.142	3.389
15	1.8	9.90	3	4.208	3.443	**30**	1.8	9.72	3	4.345	3.555

3.2.4. Failure micro mechanisms

The final step of the experimental part of this dissertation consisted of in the examination of fracture surfaces of the specimens failed. This study becomes possible to understand where the cracks present more tendency to appear and to identify the main failure mechanisms. To obtain this information, fracture surfaces were observed by optical microscopy.

In this analysis, it was placed several specimens underneath a microscope, which was attached to a digital camera, as it can be seen at Figure 3.5. The microscope in use was a Stemi 2000-c model from Carl Zeiss with an ampliation capacity of 5x combined with both micrometric and macrometric focus capacity. For the specimens analysed, it was used two different magnifications, 0.8 and 2, in order to have more data and a better notion of what happened during the fatigue test. The digital camera it was a POWERSHOT G5 model from CANON with an ampliation capacity of 16x.

This system was connected to a computer which enabled the user to operate with the digital camera and to save the photos taken.

Figure 3.5: Equipment used to perform the OM tests (from left to right: microscope with the camera attached, computer).

4. RESULTS AND DISCUSSION

At the present chapter, it will be discussed all the variations that happened to the material, the modifications made in the geometries of the specimens and the results from both the tensile and fatigue tests. In the fatigue tests, it will be presented all the graphics obtained for each type of water and immersion time, being all of this compared in the end.

4.1. Water Absorption

Once the specimens are submerged in water it is probable that they will absorb some percentage of water, which will induce mass variations. By analysing the mass deviation of each specimen, it becomes possible to determine if this composite is fit, or not, to be placed under solicitations which will englobe water.

So, if the variation of masses becomes relevant, it can be concluded that this is not the best composite to be put under water, or in contact with water. For better comprehension of this variation, it is calculated for each specimen the percentage of water that it is absorbed, with the help of the equation (4.1):

$$Water\ absorption = \left(\frac{m_W - m_D}{m_W}\right) * \ 100\% \tag{4.1}$$

where m_W represents the mass of the specimen after being immersed and m_D represents the mass of the specimen before being immersed.

Using the software MS Excel, it was obtained the percentage of water absorbed for each specimen, which are summarised in Table 4.1 (No. is referred to the specimen number).

As it can be seen at Table 4.1, the water uptake is always less than 1%. However, this does not mean that the water presence does not affect the mechanical properties of the composite materials.

Table 4.1: Masses and weight percentages of the specimens.

No	m_D [g]	m_W [g]	%	No	m_D [g]	m_W [g]	%
1	3.02179	3.03187	0.332	**13**	3.03736	3.05919	0.714
2	3.33644	3.34639	0.297	**14**	3.20715	3.22380	0.516
3	3.03708	3.05350	0.538	**15**	3.07653	3.09616	0.634
4	3.09746	3.11460	0.550	**16**	3.46529	3.48070	0.443
5	3.39858	3.41480	0.475	**17**	3.29129	3.30576	0.438
6	2.97315	2.98477	0.389	**18**	3.24135	3.25800	0.511
7	3.04392	3.06624	0.728	**19**	3.32710	3.34205	0.447
8	3.46739	3.48817	0.596	**20**	3.29817	3.32111	0.691
9	2.87611	2.89072	0.505	**21**	2.89765	2.91931	0.742
10	3.36054	3.37490	0.425	**22**	3.15208	3.16840	0.515
11	2.94404	2.95275	0.295	**23**	3.26290	3.28070	0.543
12	3.33355	3.34995	0.490	**24**	3.19233	3.21218	0.618

4.2. Tensile Tests

As it was discussed previously, the main purpose of these tests was simply to gain more knowledge about the value of the tensile strength, which is an interesting parameter in order to help defining the applied loads in fatigue tests. So, after performing such tests, it was concluded that the tensile strength of the composite at study presents a value about 725 MPa (see Figure 4.1).

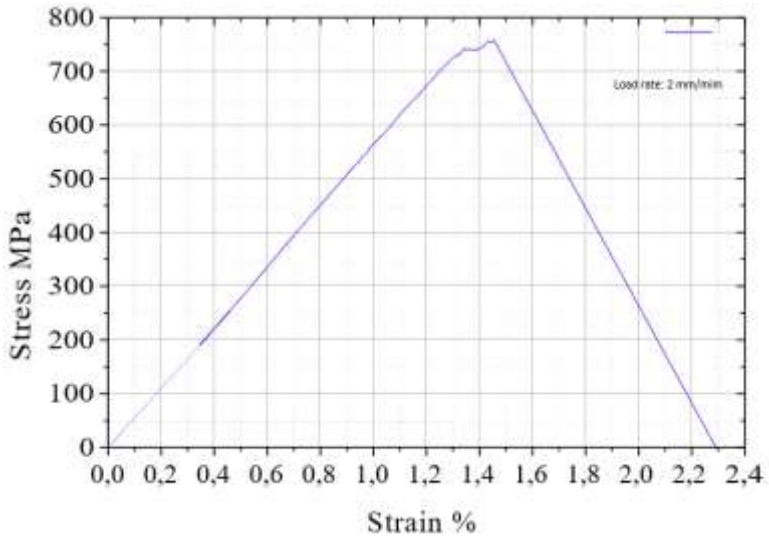

Figure 4.1: Typical curve obtained from the tensile tests performed.

4.3. Geometries

In order to have meaningful results, it is fundamental to ensure that the specimen fail at the zone of proof and not at the grips. In Figure 4.2, it is presented all the geometries developed and tested, in a first stage, to overcome the problems associated with the changes of the test type (i.e. tension-compression test and not three-point bending test).

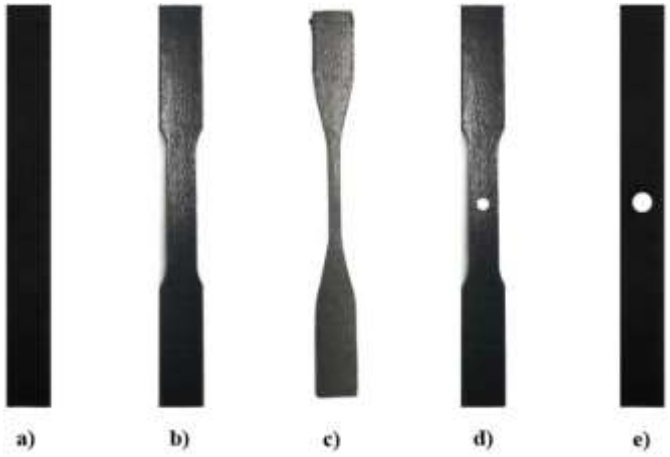

Figure 4.2: Geometries tested.

In another point of view, it can be seen this variation in geometries as an optimization process. Briefly, the major problems presented by the initial specimens were: (i) failure in the grip zone; (ii) high concentration stress zones far from the middle section; (iii) and problems caused by the machining process.

The specimens represented at Figure 4.2.a) presented variations between 1 and 2 mm in width (due to some slips in the saw) and, knowing such a fact, all the calculations were made in order to perform the best test possible. Despite everything, the tests were not conclusive because the specimens failed near the grips, instead of at the middle zone.

In order to prevent what happened previously a new geometry was then tried. As it can be seen in Figure 4.2.b) the new specimens presented a dog bone shape. With this new geometry the load to be applied decreased (due to the width reduction), but the specimens failed at the fillet zone (again near the grips). In some of the specimens with the shape referred to above, it was reduced the fillet zone (by sanding them) and, they became thinner than previously (Figure 4.2.c)). Once more, specimens failed near the grips at the fillet zone.

As it can be seen at Figure 4.2.d) a hole was drilled in the centre of the specimen which resulted in a failure – as intended - at the hole. In order to simplify the process, the

remaining specimens were simply produced in a rectangular shape with a central hole (see Figure 4.2.e)). This last geometry has proved to be the most efficient one. With this geometry, the specimen definitely failed at the hole.

4.4. Fatigue tests

In this section, it will be presented all the information gained by performing the fatigue tests, namely the variations of geometry, the effects produced by the immersion in sea water on fatigue life of laminates of carbon/epoxy composite, and examination of fracture surfaces by OM. It will be also provided a comparison, in terms of fatigue performance, between the results of the control samples and the degraded ones.

The main objective of these tests is to obtain the S-N curves for the different the sea water and immersion time conditions. Every S-N curve were constructed by having on the y-axis the following variables: nominal stress amplitude ($\sigma_{a,nom}$), net stress amplitude ($\sigma_{a,net}$), and local stress amplitude ($\sigma_{a,local}$). While at the x-axis, the variables selected was the number of cycles to failure. These stresses were obtained as follows,

$$\sigma_{a,nom} = \frac{P_a}{A_{nom}} \tag{4.2}$$

where A_{nom} is calculated by the following equation,

$$A_{nom} = t * w \tag{4.3}$$

The net stress amplitude is obtained by,

$$\sigma_{a,net} = \frac{P_a}{A_{net}} \tag{4.4}$$

where the A_{net} is defined by equation (4.5).

$$A_{net} = (w - d) * t \tag{4.5}$$

And, finally, the local stress amplitude is given by,

$$\sigma_{a,local} = \sigma_{a,net} * K_t \tag{4.6}$$

Another fact to have in mind is that the amplitude and mean loads will have a variation from specimen to specimen due to small variations at the geometry (mainly the width of the proof zone) of each one. In order to account for these variations, the following equation of K_t, encountered in reference [22], was used:

$$K_t = 3 - 3.13 * \frac{d}{w} + 3.66 * \left(\frac{d}{w}\right)^2 - 1.53 * \left(\frac{d}{w}\right)^3 \quad (4.7)$$

With this constant, it is possible to calculate the local stress taking into account the hole and with for each specimen.

As exposed at chapter 2, the value of K_f was obtained with equation (2.7), while q was estimated, as a first approach, considering the composite to be a mild steel with more than 200 HB. In Figure 4.3 its presented a graphic to obtain the notch sensitivity factor value, for a certain radius. The specimens tested presented a hole with the radius of 0.85mm and 1.5mm (depending on the specimen). Since the x-axis needs to be multiplied by 25 to obtain the correct value of the radius, it was reached the values of 0.034mm and 0.06mm (for the radius of 0.85mm and 1.5mm, respectively). With these values it was reached the values, of q, of, approximately, 0.82 and 0.90 (for the radius of 0.85mm and 1.5mm, respectively).

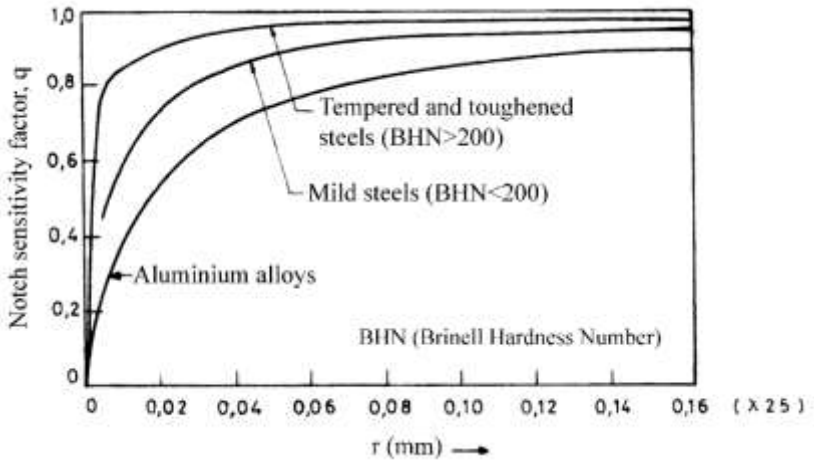

Figure 4.3: Notch sensitivity factor graphic, adapted from [17].

The applied loads of the fatigue tests, in a first stage, were defined on the basis of the tensile strength determined in Section 4.2. In each test was considered ratios of the maximum local stress to the tensile strength (see equation (4.8)) between 90% and 65%, with increments of 5% from each other. This also permits to have a big range of observation in terms of fatigue lives, or in other words, it permits to observe if the specimen failed for a relatively low or a relatively high number of cycles.

$$\text{Ratio} = \frac{\sigma_{\text{max,net}}}{\sigma_R} \quad (4.8)$$

4.4.1. Results

With the help of equations (2.7), (4.2), (4.4), (4.6), (4.7) and Table 3.1, Tables 4.2 to 4.6 were constructed, exposing all the necessary data to construct the S-N curves for each case tested. The data are, therefore, the: nominal stress amplitude, the net stress amplitude, the local stress amplitude, the elastic stress concentration factor, the fatigue stress concentration factor, and the number of cycles to failure. Figures 4.4 to 4.8 plot the main results as well as the corresponding S-N curves determined using the least square method. The arrows represent a run-out test.

Table 4.2: Data for the control specimens.

Specimen No.	$\sigma_{a,nom}$ [MPa]	$\sigma_{a,net}$ [MPa]	K_t	K_f	$\sigma_{a,local}$ [MPa]	N_f
1	236.21	308.56	2.448	2.187	755.22	18267
2	190.92	252.86	2.430	2.173	614.56	374299
3	172.24	247.45	2.344	2.209	579.98	44687
4	193.66	277.38	2.347	2.212	650.91	62318
5	180.77	261.11	2.339	2.205	610.70	138655
6	157.92	228.42	2.338	2.204	533.96	1177063

With the previous table, it is now possible to present the following S-N curves for the control specimens (see Figure 4.4),

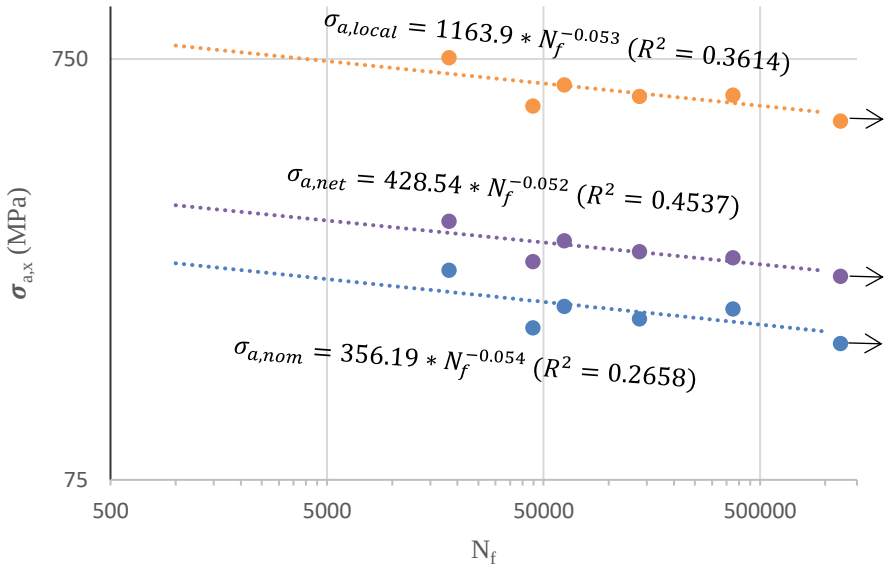

Figure 4.4: Graphic for the control specimens.

For both immersion times at the natural water, it was constructed the following tables,

Table 4.3: Data for the natural sea water specimens immersed for 35 days.

35 days						
Specimen No.	$\sigma_{a,nom}$ **[MPa]**	$\sigma_{a,net}$ **[MPa]**	K_t	K_f	$\sigma_{a,local}$ **[MPa]**	N_f
1	152.89	221.13	2.338	2.204	516.96	231596
2	202.77	293.03	2.338	2.205	685.23	8521
3	192.31	277.78	2.339	2.205	649.68	2337
4	182.82	261.06	2.349	2.215	613.35	10953
5	177	252.86	2.349	2.208	593.98	1065134
6	159.75	228.21	2.349	2.214	536.10	373244

Table 4.4: Data for the natural sea water specimens immersed for 60 days.

60 days						
Specimen No.	$\sigma_{a,nom}$ **[MPa]**	$\sigma_{a,net}$ **[MPa]**	K_t	K_f	$\sigma_{a,local}$ **[MPa]**	N_f
1	203.19	293.90	2.338	2.204	687.02	1849
2	192.29	277.25	2.341	2.206	648.90	11265
3	181.12	261.03	2.341	2.207	611.05	2965
4	170.06	244.87	2.342	2.208	573.42	75449
5	157.83	228.39	2.337	2.203	533.79	135405
6	147.46	212.04	2.343	2.209	496.82	3113244

Reaching now the following graphics (Figure 4.5 and Figure 4.6),

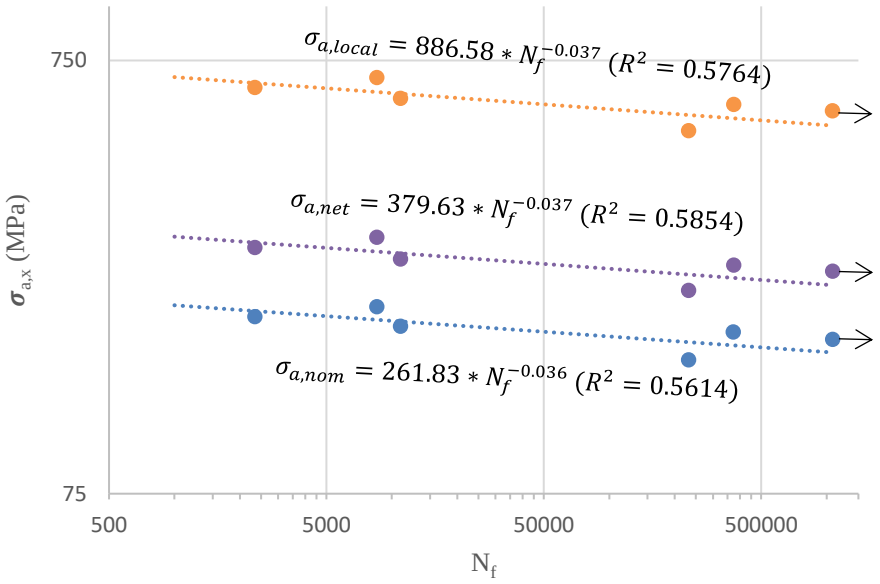

Figure 4.5: Graphic for the 35 days of immersion in natural sea water specimens.

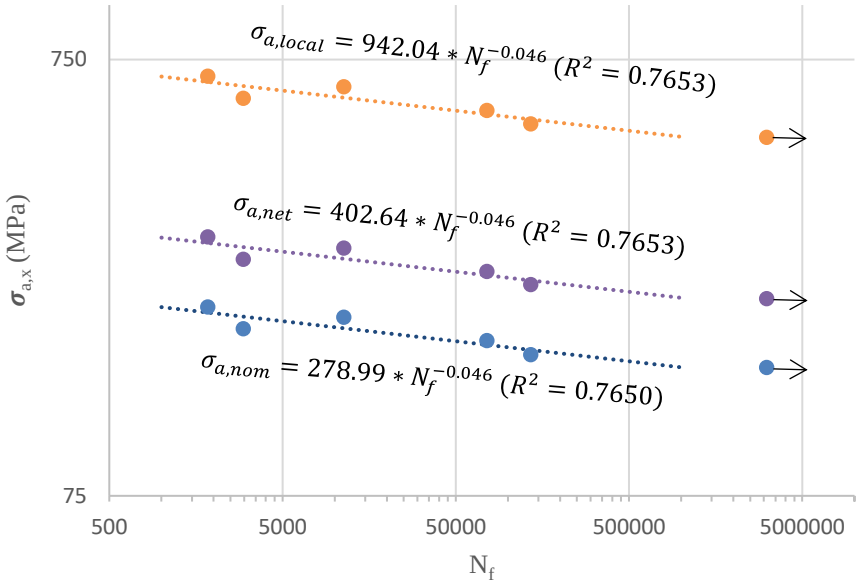

Figure 4.6: Graphic for the 60 days of immersion in natural sea water specimens.

Finally, are presented the tables for the artificial sea water for both immersion times. These are as follows,

Table 4.5: Data for the artificial sea water specimens immersed for 35 days.

35 days						
Specimen No.	$\sigma_{a,nom}$ **[MPa]**	$\sigma_{a,net}$ **[MPa]**	K_t	K_f	$\sigma_{a,local}$ **[MPa]**	N_f
1	188.45	270.74	2.344	2.209	634.57	2282
2	193.18	277.17	2.345	2.211	649.98	3241
3	182.95	261.02	2.350	2.215	613.49	161689
4	169.72	244.49	2.341	2.207	572.44	259469
5	158.51	228.34	2.341	2.207	534.62	42577
6	148.30	212.03	2.348	2.213	497.92	3166016

Table 4.6: Data for the artificial sea water specimens immersed for 60 days.

60 days						
Specimen No.	$\sigma_{a,nom}$ **[MPa]**	$\sigma_{a,net}$ **[MPa]**	K_t	K_f	$\sigma_{a,local}$ **[MPa]**	N_f
1	181.89	260.85	2.345	2.211	611.81	24927
2	169.73	244.83	2.340	2.206	572.94	648411
3	159.07	228.52	2.344	2.209	535.62	3535*
4	193.01	277.29	2.344	2.209	649.91	7396
5	214.25	309.89	2.338	2.204	724.42	0
6	147.46	212.04	2.343	2.209	496.82	3243975

* Invalid test

From these tables, the following graphics were constructed (Figure 4.7 and Figure 4.8),

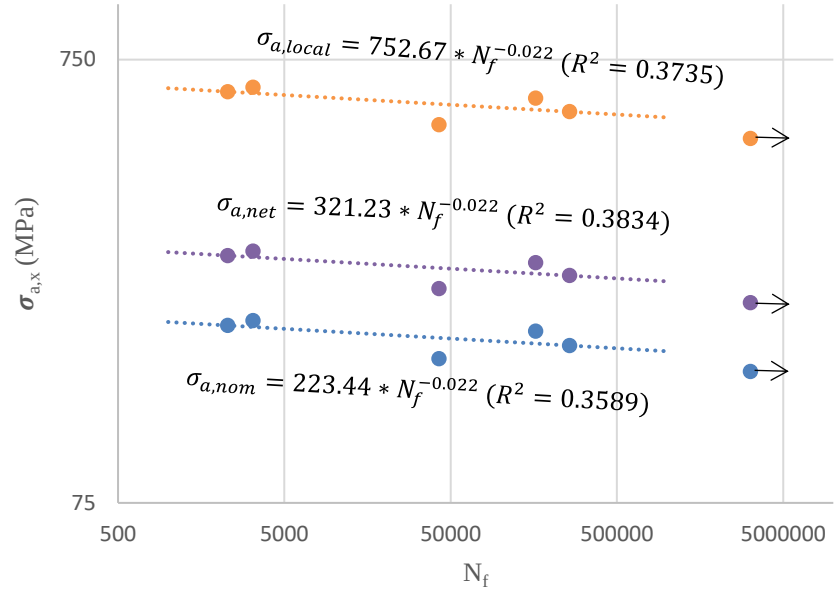

Figure 4.7: Graphic for the 35 days of immersion in artificial sea water specimens.

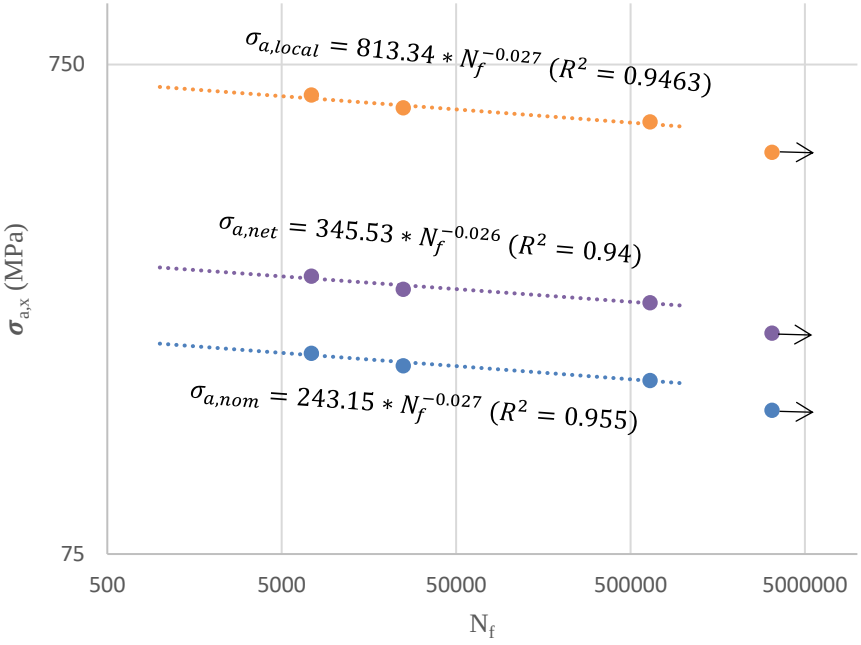

Figure 4.8: Graphic for the 60 days of immersion in artificial sea water specimens.

Due to the effect of the stress concentration caused by the hole, it can be observed (for the same life) that the local stress presents higher values, which was expected since the

hole represents 30% of the width of the specimen. This phenomenon was observed for every trial performed.

Passing onto the correlation coefficients, each type of trial presented different sets of values. The control specimens presented the values of 0.3614, 0.4537 and 0.2658 (local, net and nominal stress amplitudes, respectively), which are acceptable, since there are specimens with lower width than the others tested. The natural sea water presented the values of 0.5614, 0.5854 and 0.5764 (nominal, net and local stresses, respectively), for the 35 days of immersion; and for the 60 days of immersion, it presented (for the nominal, net and local stresses) the following values: 0.7650, 0.7653 and 0.7653 (respectively). The increase of the correlation coefficients can be due to the fact that all the specimens used at the natural sea water tests had the same width. On the other hand, all these values for the control, natural sea water and 35 days of immersion at artificial sea water specimens (as can be seen at Figure 4.7) are rather low because of the low number of tests performed for each case. In this case, it was performed 6 tests for each case.

The specimens immersed for 60 days at artificial sea water present higher values for the correlation coefficients. These S-N curves created defined from only three points (see Figure 4.8) which can explain such a fact.

4.4.2. Comparisons

In this section, it will be presented a series of comparisons between the control and degraded specimens, and between the different types of water.

In these comparisons, S-N curves are plotted only on the basis of the local stress amplitudes. Besides this, the fatigue endurance lines were defined in a theoretical basis assuming a limit of 10^6 cycles.

4.4.2.1. Control VS Natural sea water

From Tables 4.2, 4.3 and 4.4 it was drawn the graphic that can be seen at Figure 4.9 which shows the variation of the local stress amplitude with the number of cycles to failure for the control, 60 days and 35 days immersion at sea water specimens.

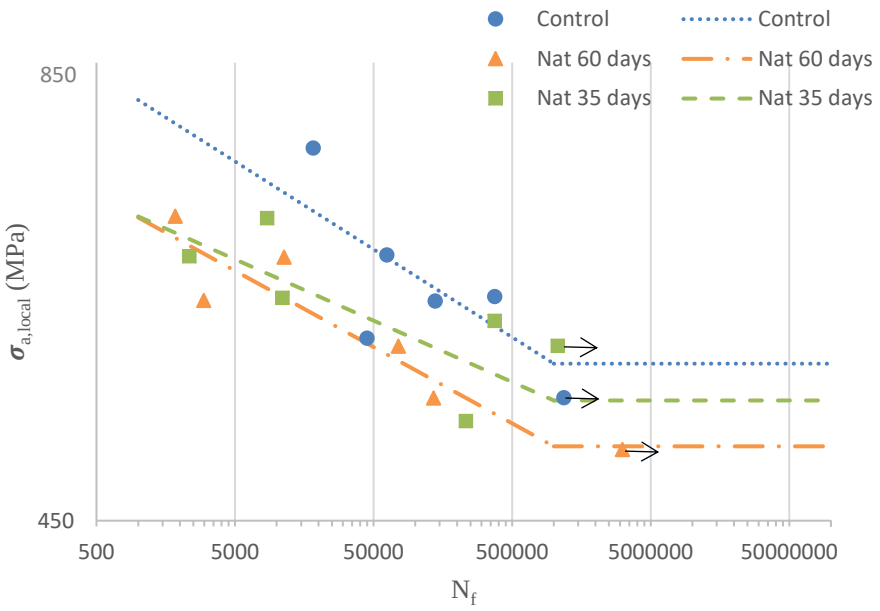

Figure 4.9: Comparison between the control specimens and the ones degraded by the natural sea water.

As it can be seen from Figure 4.9, the effects of natural sea water in the fatigue endurance are noteworthy observed. There is a decrease of 5% for 35 days of immersion and 11% for 60 days. For less than 10^6 cycles, the slope of the curve, for the 35 days of immersion, become less accentuated than the control one. When plotting a line for a certain value of stress it can be seen a major decrease of the number of cycles to failure, but for under 2000 cycles the lines for the immersion times become overlapped, meaning that the specimens will break more or less for the same number of cycles.

In reference [11], it was tested the effect of sea water in carbon/epoxy specimens, for an immersion period of 7500 hours and for different temperatures (including room temperature). In order to evaluate the different scenarios on the composite behaviour, it was performed tensile and interlaminar shear stress tests, both static. With these tests, it was observed a decrease of 20% to 40 % in failure strengths and that interfacial adhesion under shear loading is affected. On the other hand, in [23] was performed a study, for the same material, but for a case of fatigue, being this studied for the cases of three-point and four-point bending tests, considering R=0.1. It was concluded that the water degradation reduced the fatigue performance: dry specimens survived at 80% UFS (Ultimate Flexural Strength) but failed at 90% UFS, while water conditioned coupons survived at 65% UFS but failed at 80% UFS. The outcomes of these studies clearly show that sea water reduces the

mechanical properties of CFRP, namely fatigue performance, which is also observed in Figure 4.9.

4.4.2.2. Control VS Artificial

Now it will be presented the differences between the control specimens and the specimens immersed, at both times of immersion, in the artificial sea water. These differences can be seen at Figure 4.10, which was obtained with the help of Tables 4.2, 4.5 and 4.6.

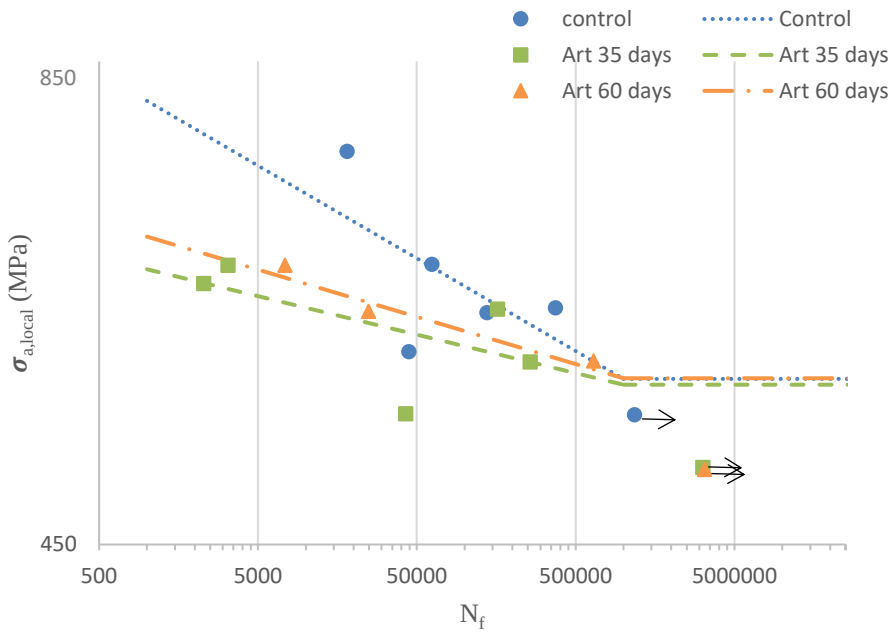

Figure 4.10: Comparison between the control specimens and the ones degraded by the artificial sea water.

From Figure 4.10, it is possible to observe a decrease of the mechanical properties of the composite with immersion time. Nevertheless, the results are somewhat controversial. Surprisingly, the S-N for 60-day immersion time results in higher fatigue lives than that of the 35-day immersion time. It is suggested to repeat these two series in the future. On the other hand, the fatigue endurance for both immersion times only presents a variation of 1% with regard to the control tests. This value seems to indicate that artificial sea water has sort of a stabilizing effect for longs lives. Despite the conclusions that have been presented, the case for 60 days of immersion unfortunately do not present enough points to guarantee that the S-N curve obtained is the best one, therefore it is only presented for comparison purposes and to observe how the data obtained would be displayed.

Returning to the literature, it was found that in [24] was performed tensile fatigue tests (with $R = 0.2$ and a frequency of 1 Hz) in a carbon fybre-vynil ester composite to evaluate the effects of sea water, at a temperature of 40ºC, for an immersion of 6 months. It was concluded that the fatigue life shortened dramatically, up to 85%, when cyclic loading was applied under immersed conditions, leading to a very significant loss of mechanical strength under cyclic loading due to sea water exposure. In [25] was concluded that open-hole laminates of carbon/epoxy composites when subjected to compression-compression fatigue tests, after being degraded for 27 days at a temperature of 75ºC, presented a decrease above 15% in the compressive fatigue life. Finally, in [14] it can be found that by performing a three-point bending static test at carbon/epoxy, after being degraded between 1 to 3 months in an artificial sea water with a weight/volume ratio of NaCl of 3.4% - 3.5% at a temperature of 50ºC, it was concluded that the mechanical properties were significantly reduced after short term immersion due to the edge effects, while the damage of the fibre/polymer interface became more significant to laminate degradation after longer-term immersion.

So, as it can be seen from the literature, it is expected to observe a notorious decrease of the fatigue life. This fact is only partially confirmed in the figure presented above. Therefore, it is suggested to perform additional tests to clarify this matter.

4.4.2.3. Control VS Artificial

Figure 4.11 compares the S-N curves, for both types of water, considering an immersion period of 35 days.

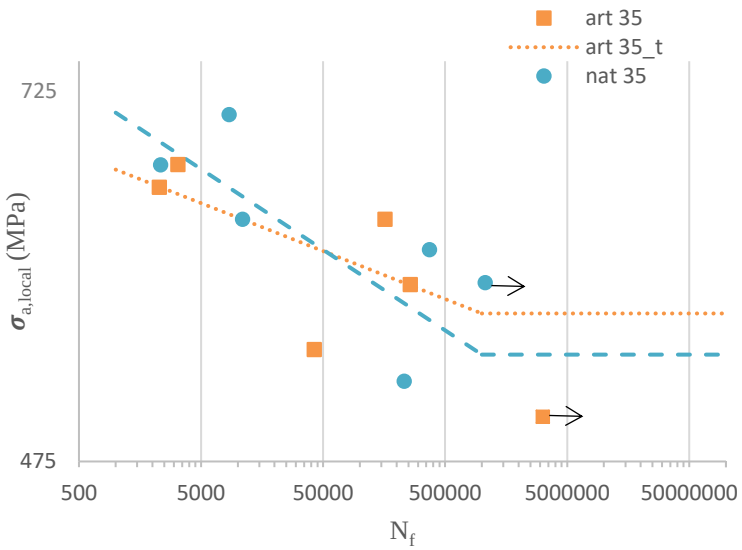

Figure 4.11: Comparison between the effects of the natural sea water and the artificial sea water.

As it can be observed at Figure 4.11, there is a considerable different between the slopes, being the natural water the most accentuated of both. This behaviour can represent which of the sea waters presents a more degrading effect, and therefore which one of them will have a more significant impact at the decrease of the mechanical properties. On the other hand, the artificial sea water presents a smoother transition along both axis, which can be translated as a low effect of the artificial water at the mechanical properties of the specimens.

When comparing the fatigue endurance of these waters, they present a difference of about 4%, being the natural sea water the one which presents the smaller value of both.

For 60 days of immersion, as previously discussed, the case of the artificial water does not present enough points to guarantee that a proper S-N curve will be obtained, therefore no definitive conclusions are drawn at this stage.

4.4.3. Project curves

Putting these results into a more engineering point of view, it will be presented at Figure 4.12 the project curves for these sets of specimens (control and natural sea water for the immersion time of 60 days). These curves were obtained using local stresses, a survival probability of 90%, and a two-sided confidence band of 80%. All of this goes accord the standard from IIW [25].

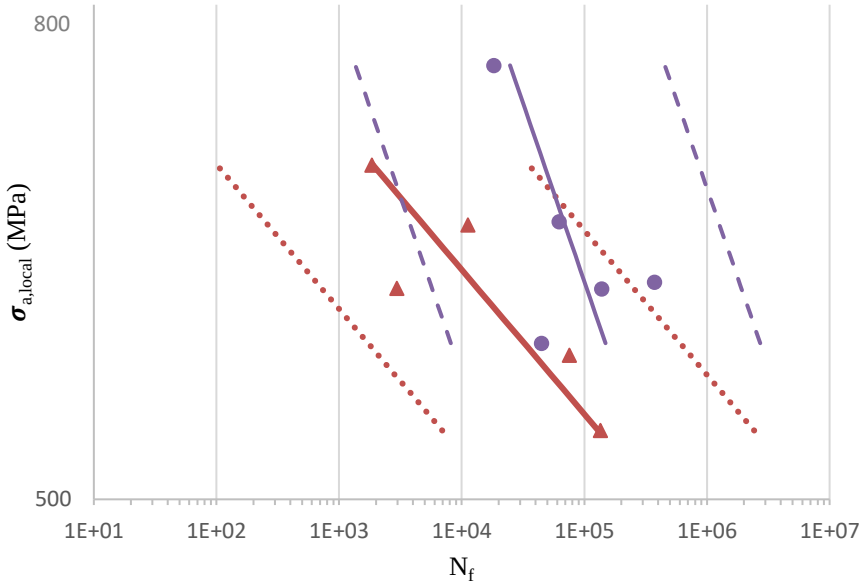

Figure 4.12: Projects curves.

As it can be seen from Figure 4.12, the confidence bands present a relative distance from the curve at study which can be explained by the small number of tests performed for each case and the fatigue scatter associated with composite materials. The cases represented show a rather similar behaviour, which means that both follow the same distribution of points.

With the increase of stress, the effects of the environment become more noticeable, which can be seen by the increase in distance between the lines. It is also observable that the effects of the environment increase with the decrease of the number of cycles.

4.5. Failure micro mechanisms analysis

As discussed previously, the OM tests will show an amplified image of the zone where the crack presented more tendency to initiate and propagate. Analysing Figure 4.13, it can be seen that the drilled zone is where the specimen failed, as expected. In a more detailed analysis, it is possible to say that the failure of the CFRP in use shows a total failure of the matrix in a tangent zone to the hole. With this failure, the fibres started to fail in the most vulnerable zone, continuing to propagate the crack. Some of the fibres just failed in a position relatively distant to the hole, passing the idea that the specimen was ripped apart in half. These conclusions are in line with those reported in references [26, 27]. The principal modes of failure of the composites, matrix cracking, fibre failure and delamination, are identified in Figure 4.13.

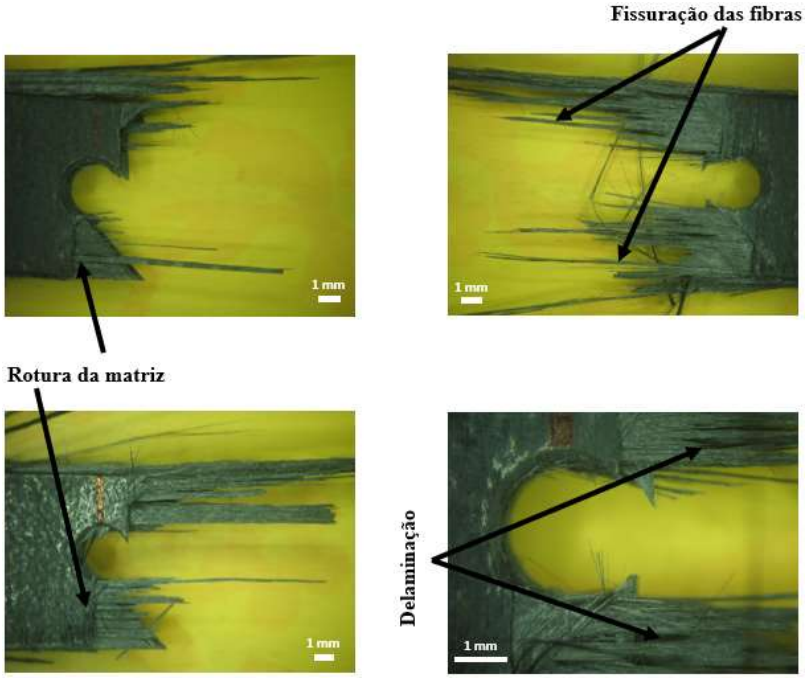

Figure 4.13: Modes of failure observe by the OM tests.

In Figure 4.14 are some examples of different types of failure. Basically, the crack propagated in a certain direction, that in some layers the zone tangent to the hole continued with a good amount of intact fibre near it. Since the crack is more probable to follow the weakest path, there might have been some porosity (or other microstructural defects) during the manufacturing of the original plaque. These conclusions are in accordance with [28,29].

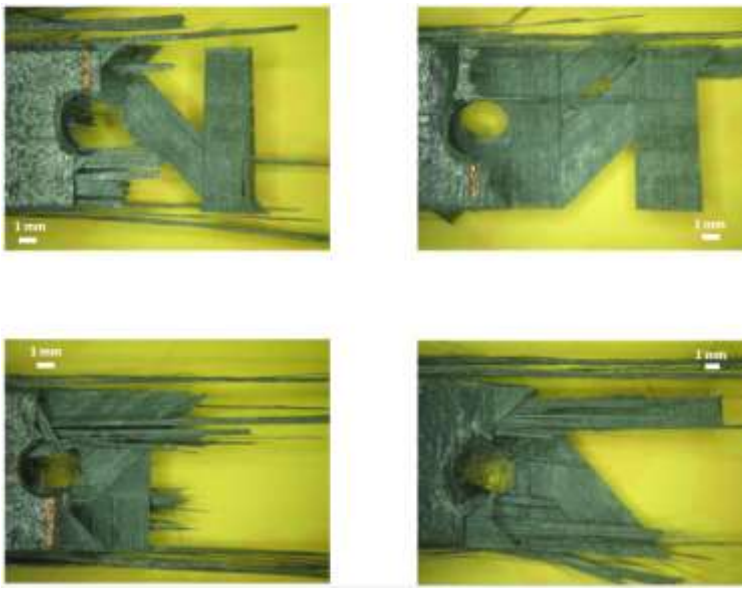

Figure 4.14: Examples of different types of failure.

5. CONCLUSIONS AND PROPOSALS FOR FUTURE PROJECTS

Finally, its presented the last chapter of this dissertation. Here, it will be presented a summary of the main conclusions and will be suggested additional work to address unsolved questions.

5.1. Conclusions

The main objective of this dissertation was the evaluation of the effects of sea water on the fatigue life of carbon/epoxy specimens. The following conclusions can be drawn:

I. The mass variation due to the water absorption of the specimens did not presented any kind of significance, since the variation of masses was always under 1%;

II. When drawing the S-N curves, it was noted that carbon/epoxy presented a rather big dispersion of points. This behaviour can also be observed when analysing the correlation coefficients presented at figures 4.4 to 4.8; the maximum value obtained was 0.7653 (considering only the local stress).

III. The natural sea water presented rather significant losses at the fatigue endurance, more specifically 5% and 11% (35 and 60 days of immersion, respectively).

IV. By the slopes, it was noticeable that the natural sea water presented a higher level of degradation than the artificial water.

V. Some of the specimens showed signs that they failed due to fibre failure, which normally occurs after the matrix cracking.

5.2. Future projects/applications

To finalize this dissertation, it will be presented some ideas to continue the study of the effect of sea water on fatigue behaviour carbon/epoxy laminates.

I. To have a better notion of the effects of artificial sea water, more tests should be performed for each series, in order to have more information;
II. Increasing the immersion time, up to 12 months or more, it will help to have a better view of the degradation effect of sea in the composite at study;
III. Instead of cyclic tensile tests, it could be interesting to perform other type of tests, namely cyclic three-point or four-point bending tests, and to compare the results with those obtained in the present work;
IV. To better understand how carbon/epoxy laminates behave in real life, it would be interesting to perform tests with increasingly complexity, namely variable-amplitude loading, random loading, and multiaxial loading histories;
V. Since composites can be fabricated with different cross-sections, it would also be interesting to the study the effect of sea water on fatigue behaviour considering alternative geometries, including solid and hollow rectangular and circular sections;
VI. Evaluate the effect of sea water at the matrix and fibres of the carbon/epoxy laminates by scanning electron microscopy.

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