1 Introduction

Advanced composite materials development has accelerated during the past three decades, triggering the use of composite structures in different applications such as aircrafts and marine vessels, in replacement of traditional materials. Composite materials are preferred because of their low density, high specific strength and stiffness, and corrosion resistance. Even if composite materials do not suffer corrosion, the matrix can absorb humidity, with subsequent degradation of the fiber-matrix interface, which decreases the mechanical properties [1-3]. For this reason composite hulls are commonly protected with a layer of Gel-Coat. Impact damage of composite materials is usually driven by the matrix cracks, which act as onset for delaminations; this failure mode can be affected by the water absorption. This subject has been studied by Imielinska and Guillaumat [4] and Dale, Acha and Carlsson [5], who performed impact tests on specimens exposed to moisture to determine the change in dynamic impact forces and extent of the damage.

Fiber metal laminates (FML) is a class of composite materials developed for aeronautical applications. FML are composed by alternated layers of glass fiber reinforced plastics and aluminum sheets, to form a hybrid with enhanced mechanical properties, specially concerning fatigue resistance with respect to the original comprising materials. This kind of FML is known as Glare and has been originally developed at Delft University of Technology. Other interesting aspect of these materials is that aluminum sheets probably blocks the diffusion of humidity inside the structure, increasing its wear resistance. This is a topic that has been studied by Bothelo, Pardini and Rezende [6], who focused on the determination of damping properties and variation in the elastic and viscous response caused by hygrothermal effects. The objective of the present study is to determine the possibility of using the FML concept to avoid hygrothermal degradation of marine vessels, replacing the gel coat with a thin layer of steel. Another benefit of using a metal sheet to protect the surface of the laminate is that it provides abrasion resistance. The impact response of such FML structure is here investigated. In this work, we introduce the preliminary results of an extended experimental campaign aimed to investigate the performance of the proposed layering configuration. In this paper we present the comparison between the impact properties of virgin and moisture-exposed specimens, to determine the change on their properties and to study the steel-composite interface and the role of hygrothermal effects.

The rest of the paper is organized as follows. In section 2, we present the procedure used to produce the specimens, along with details on the conditioning procedure. In this section we also introduce the techniques used for the estimation of the mechanical properties through dynamic tests, the tribological behavior, and the hygrothermal behavior. In section 3 we present and discuss the results about the moisture absorption, the low velocity impact behavior, the influence of the water absorption on the mechanical properties, the tribological tests, and the heat deflection behavior. Conclusions and final remarks are summarized in section 4.
2.1 Material

Glass fiber reinforced plastic (GFRP) and GFRP protected with steel (GFRP+Steel) specimens were prepared in autoclave with 12 layers of E-Glass/Epoxy balanced woven prepreg with specific weight of 600 g/m$^2$. In the case of the GFRP+Steel specimens, one layer of steel 0.1 mm thick was applied on the external surfaces. The laminates were positioned between two plates, which acted as mold, and closed inside a vacuum bag, thus subjected to the pressure and temperature cycle needed to allow the polymerization of the epoxy resin. The final in-plane dimensions of each panel were approximately 450 by 500 mm. The final thickness of the pansls is 6 +/- 0.2 mm and 6.3 +/- 0.2 mm for the GFRT and the GFRP+Steel, respectively.

12 rectangular specimens, 150 mm long and 100 mm wide according to the recommendations of ASTM D7136 code for low velocity impact tests on composite materials [7], were cut from the panels. In addition, 2 rectangular specimens 500 mm long and 20 mm wide were cut from each panel. These were used for the non-destructive vibration tests to study the damping behavior. The remaining pieces of the panel were used to measure the friction coefficient and wear resistance through tribology tests, and the vitreous transition temperature (Tg) through DSC and DMA tests.

Half of the impact specimens (namely, 6 150x100 mm GFRP+Steel specimens and 6 150x100 GFRP specimens) were subjected to hot-water conditioning, as explained in the following paragraph. In the case of the vibration specimens, all (4) specimens were subjected to the hygrothermal conditioning while measures were done on the same specimens before and after the exposure. The coupons that were not subjected to hygrothermal conditioning were anyway subjected to the same thermal treatment, but without exposition to water. This was made to avoid possible differences between the two groups of specimens, which could have been arisen due to exposition of the resin to high temperature if only moist-conditioned laminates had been subjected to such exposition.

2.2 Specimen conditioning

Before immersion in water, the sides of the specimens were sealed with a thin layer of high temperature resistant adhesive silicone sealer. Water absorption was measured by means of gravimetric technique. Specimens were kept inside water at 80°C and each ~24 hours the specimens were pulled out of the water, their surface was dried using a paper tissue and then weighed before re-immersion in water.

A Fickian linear absorption was hypothesized [8-13] and a diffusion coefficient was calculated for each family of specimens using the following equation:

$$\frac{M(t)}{M_\infty} = \frac{2}{s} \sqrt{Dt}$$

Where $M(t)$ is the mass at a given time $t$, $M_\infty$ is the saturation mass, $D$ is the diffusion coefficient, $t$ is the immersion time in seconds and $s$ is the thickness of the specimens in mm.

2.3 Low velocity impact tests

Low velocity impact tests were carried out on the specimens by means of a drop-weight machine [14].

The impactor mass was kept constant at 1.25 kg in all tests. A piezoelectric load cell was attached to the lower side of the impactor, in central position. The hemispheric head of the cell (whose diameter was 12.7 mm) was the only part of the impactor which hit the laminate during the test. In this way a reliable measure of the contact force as a function of time was obtained. After rebound (no specimen underwent perforation) the impactor was stopped manually in order to prevent from repeated impacts with the target.

As suggested in the ASTM D7136 code [7], the force signal provided by the load cell has been numerically integrated twice to compute the impactor velocity and displacement as functions of time, according to the following expressions:

$$v(t) = v_i + g t - \int_0^t \frac{F(\tau)}{m} d\tau$$

$$s(t) = s_i + \int_0^t v(\tau) d\tau$$

where $v(t)$ and $s(t)$ are the impactor velocity and position, respectively, at time $t$, $v_i$ and $s_i$ are the impactor velocity and position at the contact onset ($t = 0$), $g$ is gravity acceleration, $m$ is the impactor
mass, $F(t)$ is the measured contact force at time $t$. The output of a laser device, placed approximately 30 mm above the specimen impacted surface, provided the initial conditions for integration. Contact force and impactor velocity being known, the absorbed energy as a function of time has been determined as [7]:

$$E_a(t) = m\left(\frac{v^2}{2} - v(t)^2\right) + m g s(t)$$

The meaning of the symbols remains the same as before. In particular, the value of $E_a$ at the end of contact (when the impactor rebounds from the target) was examined.

Both the force and the laser signal were acquired at a sampling frequency of 100 kHz, without any filtering device. The only filtering was therefore the intrinsic one of the measurement chain.

During impact tests, the specimens were placed on a fixture designed according to ASTM D7136. The laminate to be impacted was supported by a steel plate with a rectangular opening 125 mm long and 75 mm wide. Three pins ensured that the specimen was exactly centered with respect to that opening and that the load cell head hit it in its central point.

As recommended by ASTM D7136, four lever clamps with rubber tips held the specimen in the correct position during impact, preventing loss of contact with the support plate.

Impact tests were performed at two different drop heights: 1 m and 2 m, corresponding to a theoretical kinetic energy of 12.3 J and 24.5 J. Due to friction along the drop-weight tower rails and air drag on the impactor, the actual kinetic energy at the beginning of contact with the laminates ranged from 8.8 J to 10.5 J (in the case of 1 m drop height) and from 18.5 J and 22.4 J (in the case of 2 m drop height). All of the 8 possible combinations of the test parameters (that are presence or absence of the external steel sheets, previous environmental conditioning or not, drop height) were tested, with 3 specimens for each test case, a total of 24 tests are thus presented herein.

2.4 Dynamical mechanical properties

The flexural dynamic modulus and the damping properties were investigated by free vibration analysis according to ISO 6721 [15]. The measure consists on exciting a cantilever beam by an impulsive load and to record the free bending vibrations of the beam. For each laminate type, two rectangular specimens, 500 mm long and 20 mm wide, were tested. The vibration of the samples was detected by means of a laser displacement sensor (therefore not increasing the inertial mass of the system), and recorded at a sampling rate of 1500 Hz.

The signal was analyzed with a Matlab code written by the authors. The program is based on the algorithm Short Time Fourier Transform, which allows the determination of the vibration frequency and amplitude over time. In addition, the Hanning window together with the zero-padding technique were applied to reduce the leakage of the spectrum and increase the frequency resolution ($\Delta f = 0.01$ Hz).

To evaluate the damping ratio ($\zeta$) the logarithmic decrement method was used, instead of the bandwidth method suggested by the normative. This allowed an improvement on the precision of the data, since the bandwidth method gives imprecise results when testing at very low damping ratios, as only a few points are available in the magnitude curve near a poorly damped resonance when the frequency-response function is determined experimentally. To verify that no additional damping was added to the system, which could be caused by the friction of the plate with the clamp (Coulomb’s damping), the freely decaying amplitude was analyzed. Figure 1 provides an example of this; here the semi-logarithmic plot of the amplitude versus time of the first vibration mode is shown for the same specimen in tight and slack joint conditions, and the related damping ratio through time. The presence of a weak joint is easy recognizable because the amplitude tends to decay linearly instead of exponentially, due to the added damping caused by the friction. The consequence of a slack joint would be an apparently higher damping ratio with respect to the intrinsic material propriety.
FIGURE 1. Effect of the quality of the joint on the damping result. Semi-logarithmic plot of the amplitude (a) and plot of the damping ratio (b) versus time.

The flexural storage modulus $E'$ was obtained by using the dynamic equation of the Euler-Bernoulli beam:

$$E' = (2\pi f_n)^2 \left( \frac{L}{\beta_n} \right)^4 \frac{12 \rho}{h^2}$$

Where $L$, $h$, $\rho$, are the free length, the thickness and the density of the specimen; $\beta_n/L$ is the $n$-eigenvalue and $f_n$ is the natural frequency of the $n$-mode, which is evaluated through the following equation:

$$f_n = f_{dn} \frac{1}{\sqrt{1 - \xi_n^2}}$$

Where $\xi_n$ and $f_{dn}$ are, respectively, the damping ratio and the damped frequency of the $n$-mode, evaluated as described above.

The following relation relates the loss factor $\tan \delta$ to the damping ratio:

$$\tan \delta = 2 \xi$$

The loss modulus $E''$ was calculated with the following equation:

$$\tan \delta = \frac{E''}{E'}$$

2.5 Tribological behavior

The tribological behavior in unlubricated sliding conditions of both GFRP and GFRP+Steel specimens was investigated by a slider-on-cylinder tribometer (block-on-ring contact geometry, see Fig. 2), described with more details in [16]. The dimensions of the specimens were 5x6x60 mm, the counter-material used for the rotating cylinder (40 mm in diameter) was Steel (AISI 316L). Dry sliding tests were carried out under normal loads of 15, 30 and 45 N, at a sliding speed of 0.6 m/s, over a distance of 1000 m.

The maximum wear scar depth was measured at the end of each test by stylus profilometry (pickup curvature radius: 5 µm)

2.6 Heat deflection behavior

The change of the glass transition temperature ($T_g$) induced on the GFRP material by the water absorption was monitored by means of DMA measurements on specimens in dry and saturated conditions. These were carried out in three point bending configuration, with a heating rate of 3°C/min up to 160°C and 1 Hz oscillation frequency. The $T_g$ is coincident with the temperature in which $\tan \delta$ reaches its maximum value.
3 Results and discussion

3.1 Moisture absorption

In this section we introduce the results about the water absorption evaluated as described in section 2. The average weight evolution for both types of specimens is shown in figure 3. As it can be seen, absorption slowed down, reaching saturation after the ~850 hour immersion period (at about 1.3% of weight increase). The regression line obtained and used to calculate the diffusion coefficients is shown in figure 4, where data for specimens with and without metal sheet are plotted using the result of $2/s \sqrt{t}$ on the abscissas and $M(t)/M_\infty$ on the ordinates. The slope of the linear regression is thus $\sqrt{D}$ and the diffusion coefficients $D$ obtained are equal to $2.543 \times 10^{-6}$ mm$^2$/sec for the unprotected GFRP specimens and $1.681 \times 10^{-7}$ mm$^2$/sec for the GFRP+Steel; the standard deviation of $D$ is found to be $6.112 \times 10^{-8}$ and $1.100 \times 10^{-7}$ in each case. Notably, the noise to signal ratio increases substantially for the GFRP+Steel specimens, this is because in some cases some moisture was absorbed by the specimens due to a leakage in the Steel layer.

![Figure 3 - Weight increase over time for the six specimens of each type. The line is only to guide the eye.](image3.png)

![Figure 4 - Fraction of the saturation concentration in terms of the square root of the exposure time divided by half of the specimen thickness. The slope of the tendency line is equal to the square root of the diffusion coefficient.](image4.png)

3.2 Low velocity impact behavior

The envelope of internal delaminations induced by impact was clearly visible on the specimens due to the translucent appearance of glass fiber composites. Generally, the laminates subjected to a 1 m drop height impact showed a very small (a few millimeters), roughly circular, faintly opaque zone around the impact point, indicating that this energy level was probably slightly larger than the minimum required for delamination onset. A number of matrix cracks, both in the warp and in the weft direction of the fabric, were also visible.
on the back (unimpacted) side. In the laminates that underwent a 2 m drop height test, a wider delamination was evident in the form of a completely opaque circular area, with the outermost ply slightly protruding from the back face. The number and extent of matrix cracks also was definitely larger. In the case of specimens with external steel layers, thin marks could also be noticed on the back side steel sheet, showing a similar pattern to the one of matrix cracks, probably attributable to local yielding of metal. No evident qualitative difference was noticed between the specimens previously subjected to hot-moist conditioning and the others.

Prior to commenting on quantitative results obtained by the analysis of impact tests, it is necessary to consider that, although the drop height of the impactor was kept precisely constant at the required values, the same could not be done for its actual velocity as a consequence of energy loss due to friction. Indeed, the impactor velocity at the beginning of contact ranged from 3.76 m/s to 4.10 m/s for 1 m drop height impacts and from 5.45 m/s to 5.98 m/s in the case of 2 m drop height. Thus, the possibility that results have been biased by such difference must be taken into account.

It is known that scaling rules can be established for impact problems as long as no material damage occurs. Such rules must therefore be applied with caution when failures are induced, especially in the prediction of damage extent [18-20]. One can expect, however, that errors introduced by the application of scaling rules to impact events causing damage become smaller as the severity of damage decreases.

In the case of the present study, this can be appreciated by the diagrams in figure 5 and figure 6, respectively showing the maximum contact force and the maximum impactor displacement of all impact tests plotted against the measured impactor velocity at the beginning of the contact with the specimens. It can be seen that a linear relationship holds between these two parameters with fairly good approximation (slightly larger contact forces and smaller displacements are observed in laminates with steel layers due to their higher flexural stiffness). This can be justified by means of simple analytical impact models [18]. As will be shown later, in the present test conditions the laminate dynamic response to impact is dominated by the first vibration mode, higher modes giving much smaller contribution. A one-degree-of-freedom model can therefore be reliably applied, in which the overall stiffness of the specimen is reproduced by a spring, while the impactor is modeled by a mass. According to such model, the maximum contact force is directly proportional to impact velocity, which is in good agreement with the data in figure 5 and figure 6.

This proves that, due to the limited damage extent as well as to typical low velocity impact test conditions, scaling rules may be applied with satisfactory results to the present tests. For the aims of the present study, a scaling rule has been used to correct for the difference in impactor velocity, according to the following formulas:

\[
F_{\text{max}}^* = F_{\text{max}} \frac{V_{i\text{ref}}}{V_i} \\
S_{\text{max}}^* = S_{\text{max}} \frac{V_{i\text{ref}}}{V_i}
\]

where \(F_{\text{max}}\) and \(S_{\text{max}}\) are the measured values of maximum contact force and maximum impactor displacement, respectively, \(F_{\text{max}}^*\) and \(S_{\text{max}}^*\) are the corresponding scaled values, \(V_i\) is the measured impact velocity and \(V_{i\text{ref}}\) is a reference value for velocity which has been set to 4.00 m/s for 1 m drop height tests and to 5.60 m/s for 2 m drop height tests. Since the absorbed energy \(E_a\) is proportional to the area enclosed by the force-displacement curve, the following scaling rule has been adopted for this parameter:

\[
E_{a\text{f}}^* = E_{a\text{f}} \left( \frac{V_{i\text{ref}}}{V_i} \right)^2
\]

Where \(E_{a\text{f}}\) indicates the computed final value of \(E_a\) (at the end of impact) and \(E_{a\text{f}}^*\) is its scaled counterpart. Again, it must be noted that this approach cannot be given a sound theoretical foundation, because energy absorption is mostly due to material damage, which should not be present for a scaling rule to be applicable. Based on the previous arguments and on the result shown in figure 5 and figure 6, the error introduced with scaling is supposed to be small and has been considered acceptable.

Thanks to scaling, possible bias induced by different actual impact velocity can be significantly reduced. In the following discussion, average values and standard deviations of the parameters under consideration refer to single test values.
These data are collected in Table 1 for each of the 8 test cases considered. The most evident difference between unconditioned and conditioned laminates can be observed on the energy absorption. After a 1 m drop height impact, specimens without external steel layers showed a definite increase in absorbed energy as a consequence of conditioning. As reported in Table 1, such increase is much larger than the standard deviation. On the other hand, the difference in energy absorption after a 2 m drop height impact is less pronounced and almost comparable to the dispersion of results. As one can expect, laminates protected by the steel sheets showed the same energy absorption, regardless of environmental conditioning, when subjected to a 1 m drop height impact. At the highest impact energy level, however, the energy absorbed by conditioned specimens seems to be slightly smaller than the one absorbed by unconditioned specimens, but with a considerable dispersion of experimental data.

Other test parameters (maximum contact force and maximum impactor displacement during impact) exhibit little or negligible differences between the specimens that were previously immersed in water and the ones that were not. Average values of maximum displacement were systematically, slightly larger after conditioning (sometimes the difference is comparable to standard deviations). Peak contact force seems to be slightly lower in conditioned specimens without steel layers. On the other hand, in laminates with steel layers undergoing a 2 m drop height impact the reverse was observed, but with much higher standard deviations.

Detailed examination of the specimens dynamic response to impact also indicated that hot-moist conditioning did not induce any evident change in that sense. Figure 7 presents the contact force history recorded during 1 m drop height impact tests of two specimens without steel layers, one of which was previously conditioned. Figure 8 shows the corresponding force-displacement curves for the same specimens. Analogously, Figure 9 and Figure 10 contain the force-time and force-displacement diagrams for two laminates that underwent a 2 m drop height impact, only one of the two specimens being subjected to environmental conditioning.

In both cases no qualitative difference can be recognized between unconditioned and conditioned laminates. The shape of the curves is almost identical. The quantitative difference visible in Figure 7 and Figure 8 can be attributed to the dissimilar impact velocities. Indeed, force and displacement values in the plots were not scaled. For this reason, as far as possible, two pairs of specimens with actual impact velocities close to each other were selected for comparison. In the case of Figure 7 and Figure 8, however, the difference in impact velocity was not negligible. This explains different values of peak load and displacement, while the contact duration (see Figure 7) and the slope of the force-displacement plot in the loading phase of contact (see Figure 8) are identical, meaning that the specimen stiffness was the same. Figure 9 and Figure 10 also indicate that hot-moist conditioning did not induce any evident change in material stiffness.

The lower contact force values exhibited by the conditioned specimen in the unloading phase of contact (as can be seen in Figure 8) are responsible for the larger energy absorption, in the case of 1 m drop height impact, that has been commented on earlier.

The impact behavior of laminates with steel layers did not show any significant difference between unconditioned and conditioned specimens. For this reason the relevant plots are not presented here, because they would have been very similar to the ones in Figures 7 through 10.

Figure 5. Peak contact force as a function of impact velocity. Empty symbols: GFRP. Full symbols: GFRP+Steel.
Figure 6. Maximum impactor displacement as a function of impact velocity. Empty symbols: GFRP. Full symbols: GFRP+Steel.

Figure 7. Contact force history of laminates without steel layers, subjected to 1 m drop height impact. Thin curve: unconditioned specimen (impact velocity 3.86 m/s). Thick curve: conditioned specimen (impact velocity 4.00 m/s).

Figure 8. Load-displacement curves of laminates without steel layers, subjected to 1 m drop height impact. Thin curve: unconditioned specimen (impact velocity 3.86 m/s). Thick curve: conditioned specimen (impact velocity 4.00 m/s).

Figure 9. Contact force history of laminates without steel layers, subjected to 2 m drop height impact. Thin curve: unconditioned specimen. Thick curve: conditioned specimen. Impact velocity 5.55 m/s in both cases.
**Figure 10.** Load-displacement curves of laminates without steel layers, subjected to 2 m drop height impact. Thin curve: unconditioned specimen. Thick curve: conditioned specimen. Impact velocity 5.55 m/s in both cases.

**Table 1.** Average scaled values (see article text) and standard deviation of peak contact force, maximum displacement and absorbed energy recorded during low velocity impact tests.

<table>
<thead>
<tr>
<th>Conditioning</th>
<th>Steel layers</th>
<th>Maximum contact force (kN)</th>
<th>Maximum impactor displacement (mm)</th>
<th>Absorbed energy (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No</td>
<td></td>
<td>6.21 ± 0.14</td>
<td>3.05 ± 0.04</td>
<td>2.40 ± 0.11</td>
</tr>
<tr>
<td>Yes</td>
<td></td>
<td>8.37 ± 0.24</td>
<td>4.24 ± 0.11</td>
<td>6.78 ± 0.32</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.39 ± 0.03</td>
<td>2.93 ± 0.01</td>
<td>3.59 ± 0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.54 ± 0.24</td>
<td>4.13 ± 0.09</td>
<td>8.55 ± 0.61</td>
</tr>
<tr>
<td>Yes</td>
<td></td>
<td>6.09 ± 0.05</td>
<td>3.09 ± 0.03</td>
<td>3.02 ± 0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.26 ± 0.04</td>
<td>4.35 ± 0.02</td>
<td>7.00 ± 0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.37 ± 0.04</td>
<td>3.02 ± 0.04</td>
<td>3.60 ± 0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.72 ± 0.12</td>
<td>4.20 ± 0.08</td>
<td>7.93 ± 0.47</td>
</tr>
</tbody>
</table>

**Table 1.** Flexural storage modulus and flexural loss factor before conditioning.

<table>
<thead>
<tr>
<th>Material</th>
<th>Frequency (Hz)</th>
<th>Flexural modulus, ( E' ) (GPa)</th>
<th>Flexural loss factor, ( \tan \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>GFRP</td>
<td>19.69 ±0.01</td>
<td>24.8 ±0.3</td>
<td>0.0124±5E-4</td>
</tr>
<tr>
<td>GFRP+Steel</td>
<td>23.72 ±0.04</td>
<td>32.6 ±0.5</td>
<td>0.015±1E-3</td>
</tr>
</tbody>
</table>

**3.3 Dynamical mechanical propriety**

The vibration tests were performed on two specimens of each type (2 GFRP and 2 GFRP+Steel), in different conditions in terms of moisture (dry, saturated with moisture, and dried), the advantage of working with non-destructive techniques (NDT) is that, by testing always the same specimens while changing the conditioning, there is no inter-specimen variability, and a more precise impact of the conditioning can be quantified.

It was seen that the initial values of the flexural storage modulus and flexural loss factor of the GFRP+Steel specimens were higher by 31% and 21% respectively with respect to the GFRP ones (all values reported in Table 1). The errors reported are the maximum magnitude between the uncertainties due to the instrument precision and the fluctuation of the registered value in a pre-set range of amplitude oscillation. This last type of error prevails in case of damping measurements because of its sensibility to the external factors (e.g. the friction with clamps and air).

The moisture absorption had low effect on the flexural modulus of the GFRP specimens; a negligible change in the value measured was found. The behavior was different for the GFRP+Steel specimens, where water caused some delamination of the steel layer, since the silicone sealer used on the sides did not fully accomplish the protection; and caused a reduction of the modulus. The steel delamination continued when the specimens were left to dry, this led to a further decrease of the value for \( E' \), as it can be seen in figure 11.

Respect the loss factor, the results show an interesting behavior (figure 12); the loss factor of the GFRP specimens underwent a substantial increase of 40% after the saturation with moisture. The effect can be considered reversible since the \( \tan \delta \) returned almost to the original –dry– value after the specimen was dried again, considering the intrinsic error of measurement. The change on the damping properties can be explained by a plasticization of the polymeric resin and by a breakage on the fiber-resin interface [21], the recuperation of the original values suggests that the second factor mentioned did not occur, since the breakage of the interface would have been an irreversible phenomenon. This was further confirmed by the invariability of the flexural modulus (see figure 11). The increase of the loss factor on the water saturated specimens could be related with the increment of energy absorption observed during the impact tests.

The GFRP+Steel specimens underwent a much more contained increase of the damping properties.
In these the absorption of moisture was much lower thanks to the protection provided by the steel layers, but some of the change on the damping behavior can be explained by the already mentioned delamination of the steel. This caused also a less stable vibration, which is the reason of the increased error associated with the measurement. Notice also that the damping properties do not return to the initial conditions after drying the GFRP+Steel specimens, as it was observed for the GFRP material.

3.4 Tribological behavior

The friction coefficient was calculated by averaging the rate of tangent to normal forces after the first 200 m. The coefficient obtained for the steel-steel contact resulted higher than that of the steel-polymer contact, as it can be seen in figure 13. This was an expectable result since the polymeric resin acts as a solid lubricant decreasing the friction with the rotating countermaterial. Regarding the results of the maximum wear depth, presented in figure 14, the maximum depth in the case of the GFRP polymer increased substantially from the test done with a load of 30 N with respect to the tests conducted with a load of 15 N. However, the depth remains quite invariant when the load is increased to 45 N, this is probably because the wear reached the glass fibers under the first layer of resin, and the wear rate of the fibers is much smaller that the wear rate of the polymer.

In the case of the specimens protected with the steel layer, the system does not show any wear in testing conditions with a load of 15 and 30 N. Instead, when the load is 45 N, the contact between the specimen and the rotating mandrel develops a quantity of heat capable of melting the polymer underneath the steel and the metal deforms plastically still laying over the GFRP surface; the imprint detected with the profilometry has a maximum depth of 13 µm, however it is not caused by wear, but it is actually an indentation damage on the GFRP.
3.5 Heat deflection behavior

The DMA tests conducted on the GFRP specimen on dry conditions revealed a transition temperature Tg of 114°C, this value was verified with DSC tests. The Tg of the wet specimen (saturated in water at about 1.3% w/w) was measured with the DMA three times. The first measure revealed a Tg of 89°C, corresponding to a decrease of more than 20%. The second scan on the same specimen was performed after the specimen returned to room temperature in nitrogen atmosphere. The specimen was expected to be drier than during the first scan and to recover its original Tg. However, as depicted in figure 15, the tan δ is maximum at a temperature of 104°C. The same specimen was thus dried for three more days in nitrogen atmosphere before testing it a third time, when a Tg value of 112°C was obtained. This result shows that the humidity take-up causes an important reduction on the glass transition temperature, however, this degradation is almost completely reversible. It is thus predictable that water causes no real damage on the interface nor on the polymer, while it only changes the composition decreasing the heat resistance properties. Notably, drying the material can reverse this process. These results are in line with the ones obtained though vibration tests.

![Figure 15](image)

Figure 15 – tan δ versus temperature for dry specimen (full line) and another specimen initially saturated with water (pointed line), partially dried (short dashed line) and completely dried (long dashed line)

4 Conclusions

In this work we presented the preliminary results of an extended study on the possibility of using the FML concept to avoid hygrothermal degradation of marine vessels, replacing the gel coat with a thin layer of steel. GFRP specimens reinforced by outer steel layers were tested and results are compared with virgin GFRP specimens. An increase of the energy absorbed during low velocity impact tests was detected on specimens without outermost steel layers after hot-moist conditioning, but only at the lowest impact energy level (1 m drop height). Other test parameters such as peak contact force and maximum impactor displacement were found to be very similar, if not identical, in conditioned and non-conditioned laminates.

Vibration tests revealed that the steel increases up to 40% the damping properties; a similar change was seen to be caused by saturation with water on GFRP specimens. In all cases a total recovery of the original properties was possible by drying out the specimens. DMA tests were performed to evaluate the change caused by the water on the glass transition temperature, which was seen to decrease to 88°C from an original value of 124°C. Also in this case the reversibility of the process was observed.

The outer steel layers are found to effectively protect the GFRP material from water absorption. However, in some cases, delamination of the steel sheet was observed. This was caused by the local leakage of the sealing on the sides, resulting in some water absorption. This can be improved by providing a better lateral sealing. Tribological tests have shown a dramatic increase of wear resistance provided by the steel, as it was expected.

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