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# THE DEGRADATION OF MECHANICAL CHARACTERISTICS AND MORPHOLOGY IN GFRP COMPOSITE UNDER REAL MARITIME CONDITIONS FOR MARINE STRUCTURE APPLICATION

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The composite elements have proven their significance across all technological domains, particularly in the creation of materials for use in construction engineering, like GRP Rebars. Specifically, glass fibers are utilized as reinforcement in polymeric composites across several sectors. Engineers create composite materials to address concerns related to mechanical characteristics, erosion conduct, instantaneous breaking, and heat resistance. The present article reveals the effects of degradation conditions like seawater and distilled water on the utilization of composite elements in building construction. The article explains the effects of these marine environments on the damage of unsaturated polyester/glass composites. The concept of composite materials in diverse applications may provide a new avenue in contemporary engineering, and research was conducted to determine the energy absorption capacity under impact. We tested glass/unsaturated polyester composites for two months in both salt water and distilled water. The technique of resin transfer molding was used to produce the samples with a $40\%$ glass fiber mass ratio $M_f$. The Charpy impact test was performed on composite specimens, and the results showed that the glass/polyester composite in distilled water after $1$ month and $2$ months has the highest absorption of energy compared with the samples of composite degrading in seawater, but it is not a big difference, so it is pretty close. Furthermore, (SEM) was utilized to illustrate the distinct failures in fracture surfaces. It was found that the glass/unsaturated polyester composite after aging in marine conditions failed by fiber fracture and fracture through the matrix.

Keywords: impact strength, GFRP, mechanical properties, seawater, distilled water.

## 1. Introduction

Glass Fiber reinforced polymer composite materials are used in many marine and water transport industries [1-4], construction of bridges [5] and GFRP rebars [6-9], It replaces ordinary steel bars with bars made of composite materials, which have corrosion-resistant properties in various aquatic environments and are cheaper in import and manufacturing costs, and the first choice in various applications. It has good mechanical properties and high hardness so used in offshore structures. In this case, composite materials are subjected to mechanical loads and harsh environmental conditions which lead to damage and corrosion over time.

However, a decrease in mechanical proprieties of polymeric composites occurs upon exposure to moisture in distille-water and seawater environments due to the plasticization, hydrolysis of polymer resin and the effect of salts in the water on its properties [10-14]. Researches focused on impacting the functionality of fiber glass reinforced polymers (FRP) when subjected to extremes of heat [15], because the most important factor in the progression and hastening of the deterioration of composite materials' mechanical properties is the rise and fall of temperature. More recently, the integration of fiber-reinforced polymer laminates is recognized as an expanded material for the bridge structures owing to its higher strength rating [5, 16, 17]. Therefore, rebars made of composite materials are used as an alternative to steel due to their excellent

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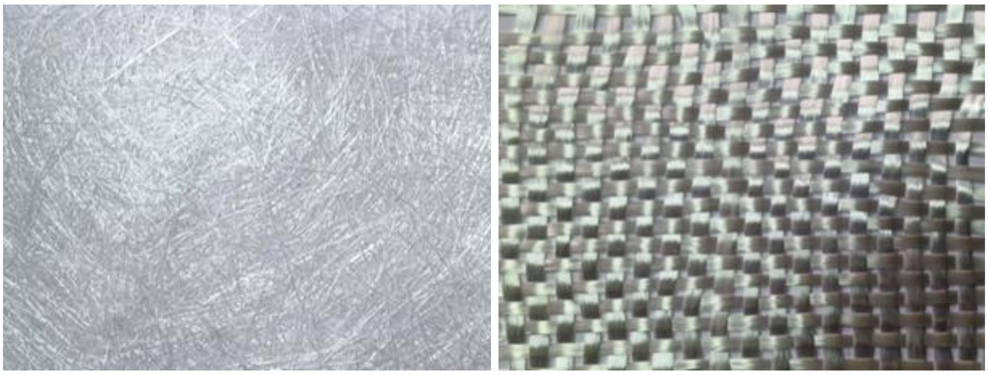
properties, or they are used as an addition to steel and are called hybrid bars, or repairing steel bridges as they give additions to the properties of steel and give more durability and resistance over time. [18-20] studied the decrease in the mechanical properties of basalt fiber reinforced polymers (BFRP) rebars embedding inside the supersulphated phosphogysum-slag cement (SSC) concrete after the exposure in seawater; the maritime environment diminishes dynamic tensile strength and failure strain, while exerting a negligible influence on the elastic modulus [18] .

Therefore, from the literature, it is evident that the FRP composite has been widely used for the beams in construction marine, so, the goal of the current study is to investigate the structural strength, focusing on the ability to maintain mechanical properties, energy absorption capacities under impact of the specimens and damage characteristics of GFRP composites reinforced with E glass, after exposed to accelerate environmental aging. Hence, the main objectives of this study are to investigate the impact strength capacity and morphology structure of mixed non-woven/woven glass fiber reinforced with unsaturated polyester resin, prepared with Vacuum Assisted Resin Transfer Molding and to analyses the Impact strength, failure modes, and crack pattern of fiber glass reinforced with unsaturated polyester under the influence of seawater and distilled water. Additionally, the study will consider various factors, such as the time of immersion in solutions and type of the condition.

## 2. Experimental

### 2.1. Materials and Preparations of composites

A standard unsaturated polyester resin and woven and non-woven fiberglass (mats & taffeta) Fig.1. and gel coat resin were provided by a local company. We used the method of Infusion molding (VARTM: Vacuum Assisted Resin Transfer Molding) in the fabrication of unsaturated polyester/glass laminates.



**Non-Woven glass fibers** **Woven glass fibers**

Fig.1. Mats (non-woven) and taffeta (woven) glass fabric.

The composite material matrix was constructed from unsaturated polyester resin with the addition of catalyst for accelerating the hardening process. The catalyst was incorporated into the unsaturated polyester, and the mixture was agitated prior to being poured into the mold. Fiber glasses were arranged inside the mold. Four fiberglass's (mats) and four (taffeta) with nominal size $1m^2$ used in each layer plus layer of gel coat, Composite maritime constructions have been safeguarded with a terminal layer of gel coat, which shields them from damage by water. The unsaturated polyester matrices were subsequently poured onto the glass fiber within a mold.

The size of the mold was $1m^2$ . And was swept by the wax and encased in a steel frame for effortless removal and optimal surface treatment for the laminate samples. The sample preparation procedure was demonstrated in Fig.2. The sample was ultimately taken out of the mold and after that subjected to a 24-hour curing period at ambient temperature to guarantee sufficient hardness and dryness for the cutting.

Fig.2. Preparation of fiberglass reinforced unsaturated polyester with infusion molding (VARTM).

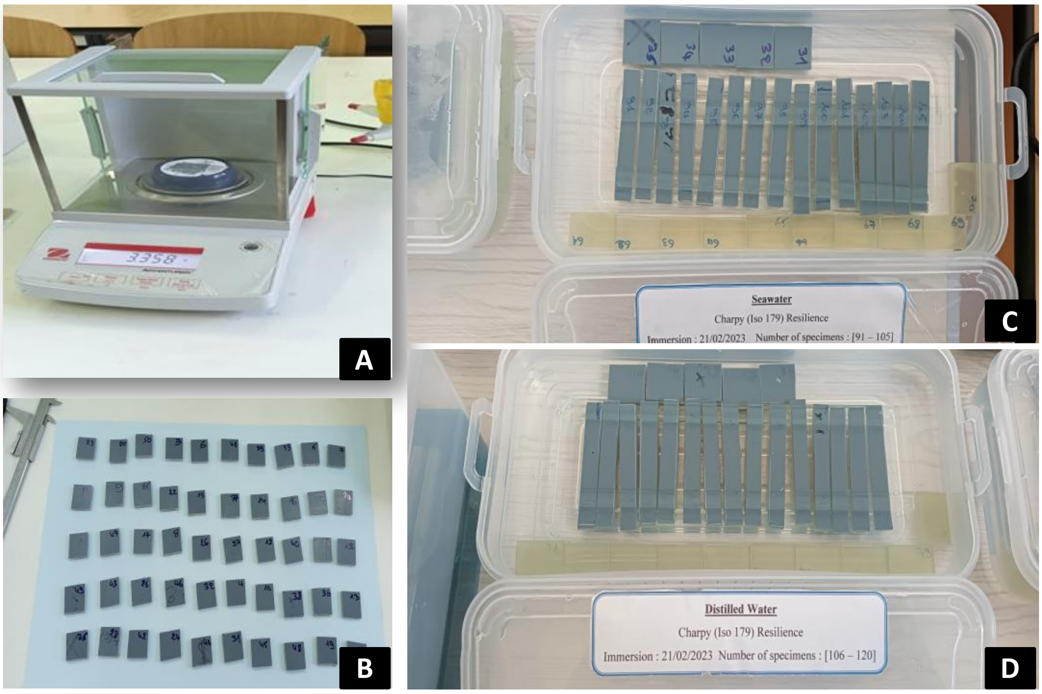



Fig.3. Weight and immersion of the specimens.

## 2.2. Immersion process

The composite laminate samples were immersed in distilled water and seawaters liquids in closed sealed plastic containers was shown in Fig.3.C,D, under conditions of laboratory $(23°C)$ for $2$ month. Samples were extracted weekly over the environment's aging treatment and weighed to analyse the change in weight of the specimens, the absorbing capacity of these materials upon immersion in various solutions has been measured by the amount of weight change compared to the oven-dry value. Five of the samples have been weighed to determine each composite type in the weight increase analysis.

### 2.3. Absorption testing

The absorption in weight percentage $(w)$ was calculated from Eq.(2.1):

$$w(\%) = \frac{w_t - w_0}{w_t} \times 100 . \tag{2.1}$$

Where $w_t$ and $w_0$ denotes weight of wet composite at time $t$ and the weight of dry specimen, respectively , the process was shown in Fig.3.A,B, were weighed All coupons dry and measured with a precision of $\pm 0.1\ mm$ . And categorized into three classes based on the type of maritime environments (dry, seawater, distilled water)

### 2.4. Charpy testing

Five specimens of composite were fabricated for each condition marine, Standard ISO 179 Charpy notched specimens [21], $78\ mm \times 10\ mm \times 5{,}5\ mm$ was cut from the composite plate and tested with energy $50$ Joule. Using a cutting machine, the specimens were meticulously cut and refined from the composite to the precise dimensions. The notches were created with a radius of curvature using a motorized notch vis in the center, in accordance with the norm. The Charpy impact examinations were performed with a universal testing equipment Zwick-Roell Fig.4A, and the Fig.4.B,C shows the specimens before and after breaking.

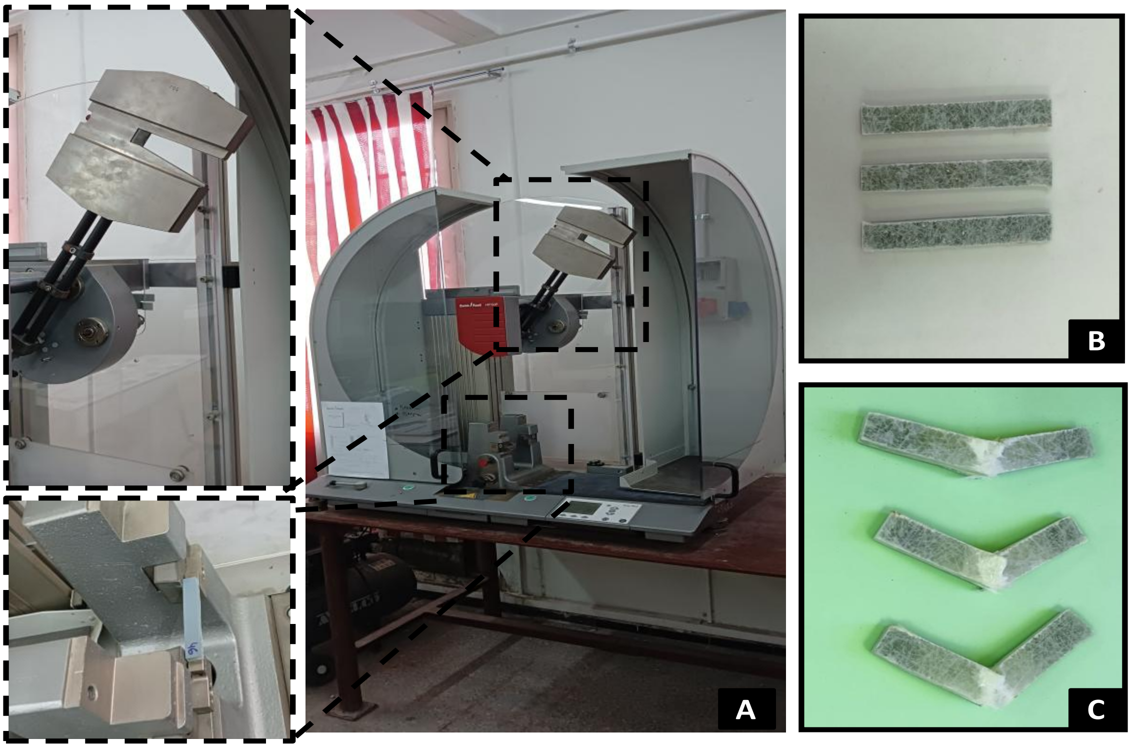



Fig.4. Charpy impact teste machine and specimens of charpy impact.

## 3. Result and discussion

### 3.1. Absorption properties

Figure 5 illustrates the weight gain of the composite as a function of immersion duration in two different aqueous environments: seawater and distilled water. The weight gain, expressed as a percentage, increases progressively with time for both media, indicating the absorption by this material. In early stages, especially in the first *14* days, a fast uptake is seen, which might be ascribed to capillary action and surface diffusion into micro-voids and fiber-matrix interfaces. We also saw that salt water was absorbed more slowly than distilled water. These findings support earlier studies [10], which indicated that the glass/unsaturated polyester increased and rose in weight by a lesser amount when exposed to salt water compared to when exposed to distilled water. This is due to the presence of salts in seawater and the entry and positioning of these salts in the voids of the composite materials, which leads to a decrease in the percentage of absorbed water, unlike distilled water, which does not contain salts and is therefore easily absorbed by the composite material in larger amounts. During ageing, the cavities in the composite fill with liquids, either saltwater or distilled water, depending on the case. The rate of diffusion and the quantities absorbed depend on the nature of the ageing liquid. Salt water diffuses less easily into the composite than distilled water because of its higher density and composition (salts). Salts slow down diffusion. Subsequently, the absorption rate then decreases and eventually reaches a plateau when balance is close. However, the glass/ unsaturated polyester composite submerged in distilled water exhibits a little higher weight gain compared to seawater, especially after *35* days. The variation may be attributed to the lower ionic concentration in distilled water and the absence of large amounts of salts, which may enhance the diffusion gradient and make water absorption faster. Conversely, the presence of salts in seawater probably causes molecular effects and might lower the rate of water diffusion because of interactions with the composite matrix or partial pore blockage.

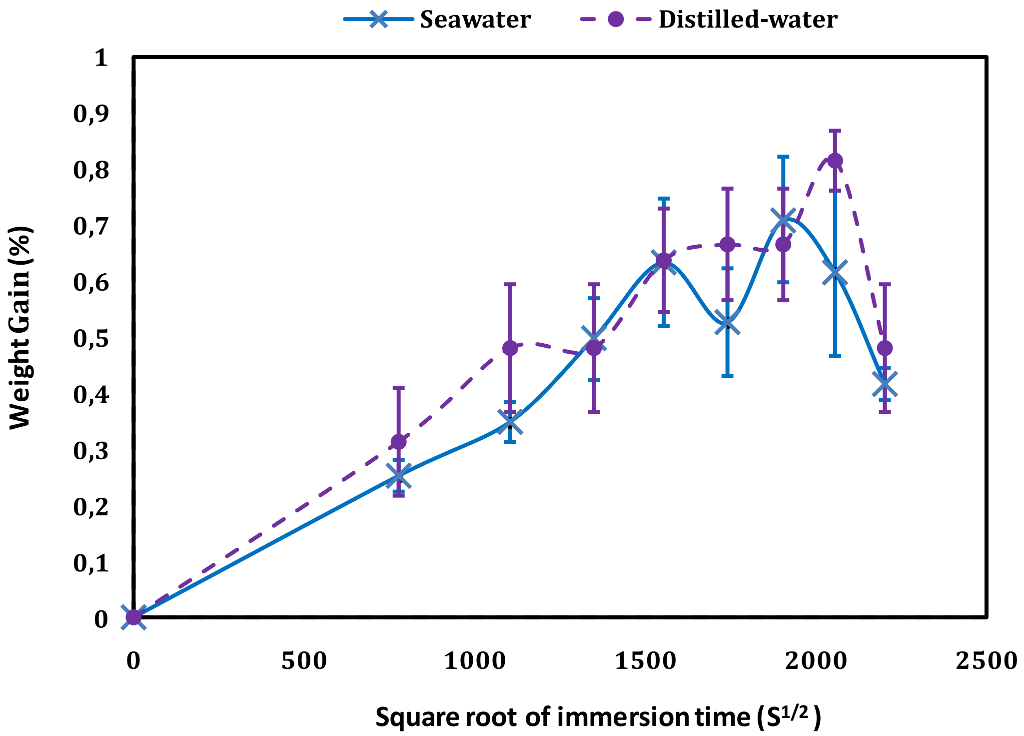



Fig.5. Weight gain as a function of square root of immersion time for composite.

These findings imply that the environmental medium greatly affects the moisture absorption properties of the composite, which can affect its mechanical proprieties and durability performance under maritime service settings, [10] note that mixed short and woven fibre glass reinforced unsaturated polyester composite exhibited quick moisture absorption at first, then $20$ days after stabilized. Consequently over prolonged periods of time, the composites will stabilize or slightly decrease in distille water and saltwater.

Figure 6 shows the weight gain $(\%)$ of the composite after $1$ and $2$ months of immersion in two different environments At $1$ month in distilled water and seawater, the composite show similar absorption ($\sim 0.65-0.7\%$ weight gain), although distilled water appears slightly higher, but within error margins so the difference might not be statistically significant. At $2$ months, both groups show a decrease in weight gain compared to $1$ month, at the beginning of ageing, salt water or distilled water diffuses into the composite and fills all the cavities. The material becomes saturated. Upon saturation, the water triggers physicochemical reactions that attack the resin, causing hydrolysis. These reactions lead to leaching, which manifests itself as weight loss, more significant in salt water due to the salts, as shown in Fig.6, so the samples in distilled water retain slightly more weight gain $(\sim 0.45-0.5\%)$ compared to seawater $(\sim 0.4\%)$.

In the initial phases, water ions rapidly penetrate the unsaturated polyester matrix, filling micro-voids by diffusion-driven mechanisms, Subsequent to the initial saturation; the material may experience structural relaxation. Certain tiny molecules such as those from unsaturated polyester may be leached out into the solution, resulting in a net weight loss that counteracts additional water absorption.

The polymer chains may rearrange, decreasing the free volume and hindering more water absorption. Salts in saltwater can diminish the chemical potential of water molecules, so impeding their diffusion into the composite. Furthermore, salt ions might create a surface barrier restricting water entrance a process known as salting-out effect.

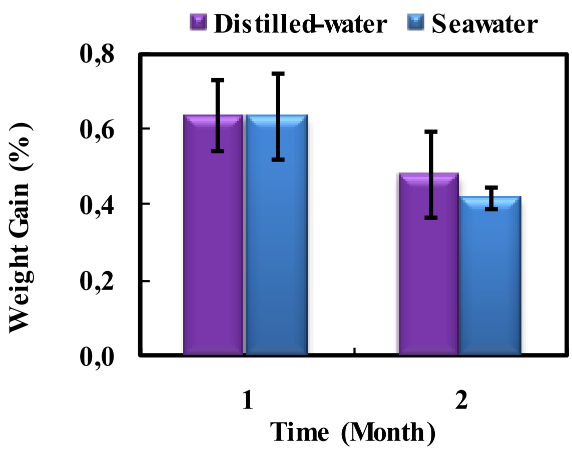



Fig.6. Weight gain of composite after 1and 2 months of immersion in environments.

### 3.2. Charpy properties

Figure 7 shows first state of both samples before immersion have a great ability for energy absorption, $195.89\ \frac{kJ}{m^2}$, this is the baseline impact strength of the virgin composite material. After one month immersion in solutions, there is a notable reduction in the impact strength by the glass/ unsaturated polyester composite in both settings; in distilled water the value decreases to around $156.54\frac{kJ}{m^2}$, and in seawater the value decreases little to around $150.78\frac{kJ}{m^2}$, this signifies a decrease of around $18-23\%$ from the original value, reflecting a deterioration in toughness or impact resistance during one month of immersion. The decline is slightly more pronounced in the marine environment.

Figures 5 and 7 show that there is a direct relationship between water uptake and impact strength. The greater the water uptake, the lower the impact strength, both for distilled water and salt water. This water uptake causes chemical reactions between the resin and the various aqueous media by breaking the various bonds within the resin, which is caused by hydrolysis, which will break the ester bonds. This hydrolysis is harmful to the composite and especially to the resin. It will degrade the mechanical properties of the composite, by detaching the fibers from the matrix, creating Delamination and decohesions. It makes the composite more fragile, therefore more brittle, which is shown in Fig.7. Figures 5 and 7 also show, after one month of aging in distilled water and in salt water, an increase in impact resistance, following a decrease in water absorption, which is consistent with the start of aging. The energy absorption capacity for both environments shows a slight increase beyond the one-month threshold. In distilled water, the impact resistance rebounds to about $168\frac{kJ}{m^2}$, a little less in salt water, where it is around $162\frac{kJ}{m^2}$. But these values remain $13$ to $16\%$ lower than the initial measured impact resistance (impact resistance of control samples without immersion in an aqueous environment). This difference in impact resistance is due to the irreversibility of the degradation of the resin.

The sample in distilled water exhibits somewhat greater recover than the one in saltwater, the little rise in impact energy noted between $1$ and $2$ months is less common than the early deterioration but may occur under specific situations, such as saturation effect, stress relaxation/redistribution, or plasticization dominance. Although interfacial weakening and hydrolysis diminish toughness, the plasticization effect may marginally enhance the material's ductility in some instances.

The persistent plasticization enables the compromised material to absorb slightly more energy prior to total failure compared to its condition after one month. This impact is often subordinate to the general deterioration or the experimental variability.

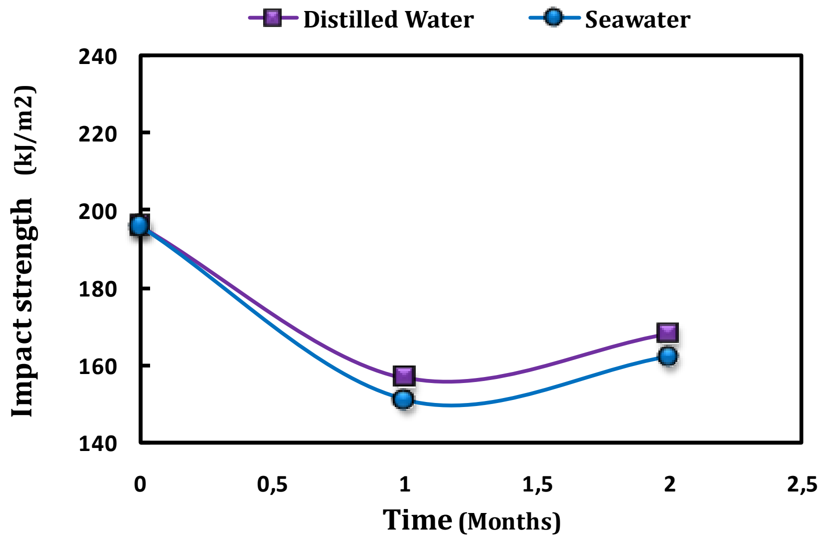



Fig.7. Impact strength of glass/unsaturated polyester composite in environments.

The data presented in Fig.8 shows the comparative impact strength of samples exposed to distilled water and seawater environments over $1$ and $2$ months. At $1$ month, composite immersed in distilled water and seawater energy absorption are close, but the composite after distilled water aging is slightly higher. At $2$ months both composite show slightly increased of impact strength compared to $1$ month, with distilled water again a bit higher. When composites are submerged in water (either distilled or seawater), water molecules infiltrate the matrix via diffusion, therefore functioning as a plasticizer inside the polymer matrix.

This process lowers internal stresses and may temporarily augment impact strength by increasing the ductility of the matrix. Distilled water facilitates pure plasticization without the introduction of salts or ions, whereas saltwater contributes salt ions that can induce micro-cracks and expedite matrix breakdown. Due to the absence of salts, distilled water primarily causes plasticization without significant chemical degradation in the unsaturated polyester.

Thus, a slight increase in toughness is observed and for the seawater introduces additional factors like ionic attack and salt crystallization, which can initiate micro-cracks within the matrix of unsaturated polyester. This reduces impact resistance compared to distilled water. Initially, water ingress improves the ductility. However, if the immersion continued much longer (beyond *2* months), we would expect a decline in impact strength due to long-term hydrolytic degradation. But clearly, the mechanical properties like tensile and flexural strength of aged glass/unsaturated polyester composite specimens after every time fall in comparison to virgin specimens.

The variations in this mechanical feature, however, seem to lack any obvious pattern. Similar behavior was seen by [12, 22]

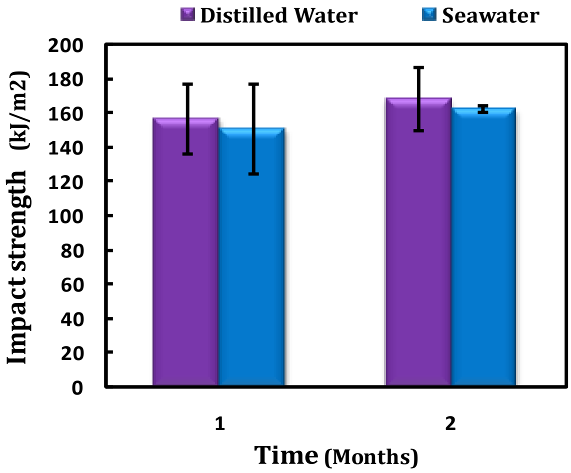



Fig.8. Impact strength of glass/ unsaturated polyester composite in each environment after *1* month and *2* months.

### 3.3. SEM micrographs

Figure 9 represent the micrograph on the surface before the immersion, The morphology of the control glass/ unsaturated polyester composite specimen exhibits a robust adhesion between the fiber and the matrix. Figures 10 and 11 represent the SEM micrographs on the surfaces of unsaturated polyester/glass composite after 4th months of seawater and distilled water immersion. Humidity aging is widely recognized as a main cause of the long-term deterioration of an polymers matrix exposed to the environment or in contact with watery solutions like distilled water or seawater, seawater penetration to the surface of the composite coupons and absorption by the unsaturated polyester over the course of four months led to a development of gaps in the unsaturated polyester and adversely affecting its mechanical properties. The process of these impacts necessitates further examination and research.

However, in the context of distilled water and the effect on the microscopic properties of composite materials, we observe almost the same effect as for seawater. Based on the morphology achieved, composite immersied in seawater and distilled water faileds by: dilamination between the lay-up of composite, change in the surface of unsaturated polyester matrix with crack propagations through the matrix. Debonding occurs between the fiber and matrix, corresponding these modes of failure rather well to the measured impact damage by [12], Clearly, moisture induces resin hydrolysis and debonding at the interface, which are the main deteriorating factors.

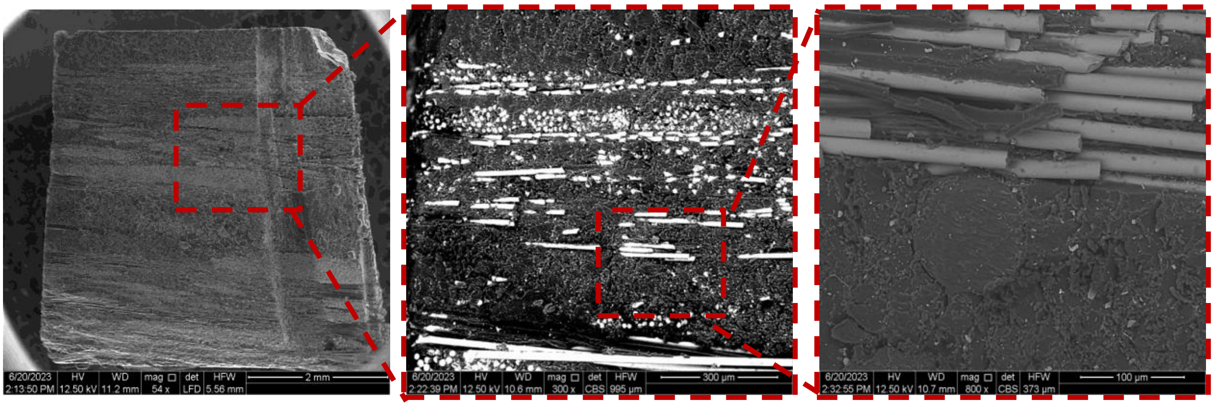


Fig.9. SEM micrograph of unsaturated polyester/glass composite before immersion.

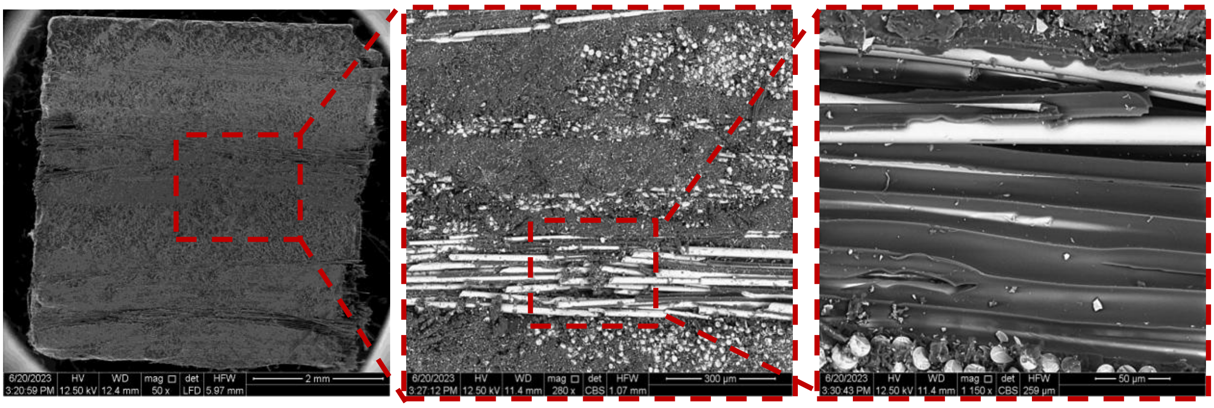


Fig.10. SEM micrograph of unsaturated polyester/glass composite after 4 months of immersion in seawater.

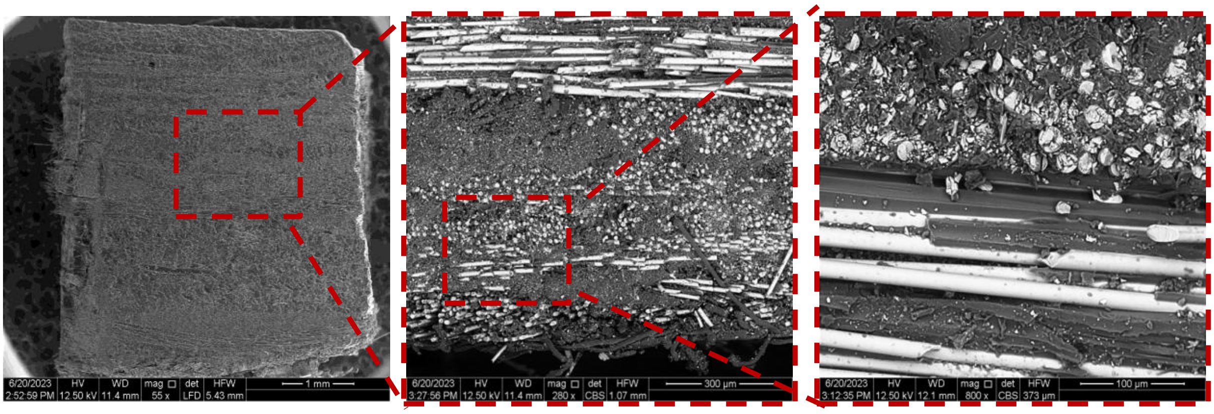


Fig.11. SEM micrograph of unsaturated polyester/glass composite after 4 months of immersion in distilled water.

## 4. Conclusion

Current investigation focuses on the influence of seawater and distilled water absorptions on glass fiber reinforcement unsaturated polyester composites and effects of ageing process in impact strength and the absorbed energy values, the following inferences are drawn.

- The glass/ unsaturated polyester composites absorbed more moisture initially, which reduced after *2* months and distilled water caused slightly higher moisture uptake than seawater.
- Short-term immersion ( *1 – 2* months) generally had a slight decrement in impact strength due to plasticization and mainly due to the formation of micro-cracks and voids in unsaturated polyester during immersion in aggressive solutions, and distilled water effect is almost aggressive as seawater, leading to decrement of impact properties.
- Almost the same between effects of distilled water and seawater in the microscopic observations of glass/ unsaturated polyester surface.
- The study's findings underscore the significance of alterations in salt ratio in environmental (type of the condition) and time of immersion in solutions for damage and of impact properties and energy absorption about material composites employed in the maritime environment, so this research had created a kind of model and basic database that can be used as a reference for the charpy impacts behavior of these types of resin transfer woven and non-woven glass/unsaturated polyester composite subjected to authentic maritime conditions, providing as an important tool to evaluate the longevity of composite marine constructions over their operational lifespan.

The low impact resistance of unsaturated polyester glass composite materials to distilled water and salt water is a real handicap for these materials. Further study with longer aging times is necessary to better understand the different degradation phenomena that reduce impact resistance. It is also advisable to use different additives in the resin to increase its impact resistance.

As future work, we are going to use different mechanical testes like tensile teste and micro-indentation tests to evaluate how the same harsh environments (seawater and distilled water) can influence the impact strength capacity and morphology structure for this type of glass/unsaturated polyester composite materials and another work to see the effects of other harsh conduction like engine oil ,diesel fuel and gasoline.

Based on this, another potential area of investigation which studies the long term effect and will be monitored and studied further until a full year of immersion in distilled water and seawater is reached, by having this, a better understanding on the resistibility of mix woven and non-woven glass/unsaturated polyester composites under long term water attack can be further comprehend.

## Acknowledgments

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## Nomenclature

| | |
|---|---|
| *BFRP* | – basalt fiber reinforced polymers |
| *FRP* | – fiber reinforced polymers |
| *GFRP* | – glass fiber reinforced polymers |
| *GRP* | – glass reinforced polymers |
| *ISO* | – International Organization for Standardization |
| $K_j$ | – kilo joule |
| $M_f$ | – mass ratio |
| *SEM* | – scanning electron microscopy |
| *SSC* | – supersulphated phosphogysum-slag cement |
| *VARTM* | – vacuum assisted resin transfer molding |
| $W_t$ | – weight at time *t* |
| $W_0$ | – weight at dry |

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