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Orginal Article

Effect of environmental conditions on the characteristics of GFRP plates using non-destructive testing techniques

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Abstract: Glass fibre-reinforced polyester (GFRP) is widely used in industries such as aerospace, civil engineering and railway transportation due to its high specific strength, high specific modulus and excellent fatigue resistance. In civil engineering, GFRP is particularly employed for applications such as rebars, girders and other structural components. The objective of this research is to study the evolution of mechanical, physical and chemical properties of GFRP sheets using non-destructive testing methods, including the Barcol hardness test, water absorption test, infrared (IR) spectroscopy and scanning electron microscope (SEM) observation. These square-shaped GFRP sheets are manufactured through contact moulding and consist of isophthalic resins, glass fibres and additives such as catalysts and accelerators. These samples are exposed to three different environments: in the laboratory (control specimens), in potable water and in seawater. Laboratory tests are conducted on the GFRP samples at 30, 90, 180 and 365 days. The results indicate a significant decrease in hardness across all preserved samples. This reduction in GFRP rigidity can be attributed to water or moisture absorption, as evidenced by the obtained results. Furthermore, no changes in the chemical composition were observed on the surface of the tested samples.

Finally, the matrix/glass fibre bond remains in good condition, despite this material being exposed to a humid and/or sulphate-rich environment for one year.

Keywords: glass fibres, GFRP, seawater, infrared test, isophthalic resins

1. Introduction

Over the past 50 years, composite materials have been increasingly used in various industrial applications due to their high stiffness, flexural strength, corrosion resistance and strength-to-weight ratio [1-3]. Continuous glass fibres were first manufactured in the 1930s for high-temperature electrical applications [4]. Today, glass fibre-reinforced composite materials are widely used in various structures due to their favourable mechanical properties, including tensile strength, fracture toughness, flexural stress-strain behaviour and fracture resistance, as well as their ability to significantly reduce structural weight. A composite material consists of two main components: a matrix that surrounds and binds the reinforcement, and a reinforcing material (fibres) [5-7]. Traditionally, E-glass is used most commonly with a polyester or epoxy resin matrix. This glass is less strong and slightly less rigid than other commonly available glasses, but it is significantly less expensive. There are possibilities in terms of improved web configurations, weaving methods and even the use of other materials to form sandwiches [8]. The reinforcement of a composite is related to the percentage of fibres or the ratio (fibre/resin); generally, this ratio is greater than 50% fibres by weight. It is also influenced by the type of fibres and their orientation with respect to the direction of the fillers [9].

Effective and reliable non-destructive testing (NDT) techniques are essential throughout the life cycle of composite materials to minimise safety risks and maintenance costs [10]. Practitioners, researchers and academics use terms such as NDT and non-destructive examination (NDE), all of which refer to methods for analysing, testing or evaluating materials, components or assemblies to detect discontinuities or quality variations without compromising the functionality of the component or system. Various NDT methods, including ultrasound, stereography, tap test, acoustic emission, digital radiography and infrared thermography, are commonly employed. However, no single method provides a comprehensive evaluation of the structures being tested [2-11]. Research on the application of ultrasonic NDT to glass fibre-reinforced polyester (GFRP) hull structures has shown that structural design parameters such as the mass fraction of glass fibres, fabric combination, stacking sequences and the number of single-layer laminates can significantly influence mechanical properties such as structural strength and tensile modulus. Increasing the thickness of GFRP hull plates results in a greater number of glass fabric layers, creating interfaces between them [12]. Therefore, damage monitoring and assessment of composite materials are particularly important. Current NDT technologies for damage detection, including fibre optics, X-ray monitoring, infrared monitoring and acoustic emission, are considered reliable. However, the limitations of above-ground and offline damage monitoring technologies remain unresolved [13].

GFRPs are susceptible to various factors that can lead to deterioration and failure, including manufacturing defects such as foreign material inclusions and improper thermal cycling, as well as operational issues such as low-speed impacts and delamination defects [14]. The mechanical behaviour of fibre-reinforced composite primarily depends on fibre strength and modulus, chemical stability, matrix strength and fibre/matrix interface bonding,

which enables stress transfer [15]. Prolonged exposure of GFRP composites to different environmental conditions – such as ultraviolet radiation, high temperature, humidity, chemical exposure and thermal cycling – combined with sustained loads, can result in colour change, surface debonding, crack propagation within the matrix, hydrolysis, plasticisation and swelling, and fibre/matrix debonding, all of which can extend into the inner layers of the composites [16-17]. Studies on moisture absorption in GFRP composites suggest significant differences in diffusion behaviour between the fibre and transverse directions. Specifically, diffusion along the fibre direction can be up to ten (10) times higher than in other directions within the laminates [18].

When used in marine applications, it is essential that GFRP composites retain their mechanical properties and do not degrade when submerged in seawater for a long time. A significant problem with the use of GFRP composites in seawater is that the fibre/matrix interface is degraded by a hydrolysis reaction of unsaturated groups within the resin [19]. Humidity-induced swelling introduces stresses both in the resin due to network inhomogeneities and at the fibre/matrix interface. Water can cause chemical degradation of glass fibres, resulting in lower fracture energies in the presence of moisture [20]. Hydrothermal ageing, which involves exposing composites to high temperatures and humidity, is a critical factor influencing the long-term performance of GFRP composites. The penetration of water molecules into the resin matrix causes hydrolysis reactions that break polymer chains and reduce the bond strength between molecules. Glass fibre leaching occurs when glass dissolves in water, leading to the extraction of alkalis from the glass structure, generating hydroxides and raising the pH above nine (9). This, in turn, degrades the silicon networks (Si–O–Si and Si–O–Na/K) in the glass. As a result, Si–OH, a gelatinous product less dense than the original glass, is formed, facilitating the transport of water and alkalis, thus accelerating fibre degradation. Furthermore, hydrothermal ageing accelerates these degradation processes, making it essential to study the mechanical behaviour of GFRP composites under such conditions to expand their application spectrum [21-22].

Duo et al. (2021) collected data from 557 experiments on the tensile strength and elastic modulus of GFRP and basalt fibre-reinforced polymer (BFRP) bars exposed to different harsh environments (aqueous, acidic, saline and alkaline media) from the existing literature. The results showed that the tensile strength of GFRP and BFRP bars decreased more rapidly in alkaline and aqueous media, followed by acidic solution, while their durability was highest in saline solution. Additionally, GFRP bars exhibited better corrosion resistance than BFRP bars in alkaline, saline and acidic solutions [23]. Vizentin and Vukelic (2022) investigated the effects of prolonged seawater immersion (6 and 12 months) on glass fibre-reinforced polyesters and glass fibre-reinforced epoxy samples. They observed an increase in mass due to seawater absorption and the growth of microorganisms in the organic resins used as matrix materials. The rate and extent of tensile strength degradation depended on the fibre configuration. Optical and scanning electron microscope analysis revealed significant morphological changes in the matrix, primarily caused by salt crystal formation and the integration of marine microorganisms into the resin [24]. According to Kim et al. (2007), the stiffness of GFRP increases by about 16% when the temperature is decreased to –150°C, and it can also be noted that the rate of increase in stiffness is higher between ambient temperature and –50°C [25]. Phifer (2003) concluded that immersing E-glass/vinyl ester composite in fresh water for two years caused a 60% and 10% reduction in tensile strength and stiffness respectively [26-27]. Aditya et al. observed a 54% and 27% reduction in stiffness and bending respectively when symmetrical and anti-symmetrical GFRP laminates were exposed to a 98% humid environment for 2000 hours [27-28]. This research aims to study the evolution of

mechanical, physical and chemical (IR analysis and SEM observation) characteristics of glass fibre-reinforced polymer (GFRP) samples. These samples are made of polyester resin and reinforced with a combination of E-glass mat, weave and C-type glass fibre fabric, and are exposed to real environments for a period of 12 months.

2. Materials used

2.1. Glass fibres

The reinforcements used in the GFRP plates are a combination of a mat and weaving (Combo Mat 600/300) of E-glass, and a type C glass fibre fabric. The latter has a unidirectional distribution of continuous glass fibres with a basis weight of 30 g/m².

2.2. Additives (catalyst and accelerator)

The catalyst used is of the methyl ethyl ketone peroxide type (MEKP 50), liquid and colourless. The polymerisation accelerator is added to the mixture daily (resin and catalyst); in this study, a solution of Cobalt Octoate (PC006) is used as an accelerator [29].

2.3. Resin

In this study, an isophthalic-type unsaturated polyester resin (PRE-67) is used. It is characterised by low viscosity, short gel time, the ability to impregnate and form thick laminates, excellent bonding power and reinforcement with glass fibres. The mechanical characteristics of the resin used, according to the technical data sheet, are presented in Table 01 [29-30].

Table 1. Mechanical properties of isophthalic resin [30]

Properties	Values	Properties	Values
BARCOL hardness	40	Tensile strength (MPa)	70
Flexural resistance (MPa)	120	Tensile modulus (MPa)	3500
Flexural modulus (MPa)	3600	Elongation at break (%)	3

3. Preparation of the specimens

The glass/polyester plates were manufactured using the manual contact moulding technique. These plates have an average thickness of 7 mm and were cut into rectangular shapes with dimensions of 80 × 80 cm, using a diamond disc in accordance with European standard ISO 1268-2 [31]. The plates were manufactured by placing five layers of the Combo Mat and two layers of the fabric on the surfaces, using isophthalic resin prepared according to European standards ISO 584 and ISO 2535 [32-33]. The GFRP composite plates were immersed in drinking water (PW) and seawater (SW) (see Fig. 1) for 365 days at room temperature in tanks large enough to allow direct contact and total immersion of all surfaces of each plate.

Fig. 1. GFRP plates immersed in seawater (SW)

4. Results and interpretation

4.1. Barcol hardness test

The Barcol portable sclerometer is a device used to assess the hardness of GFRP plates, whether applied to the surfaces of fibre-reinforced plastic composites or not, in accordance with ASTM D2583-13a [34]. To carry out this test, the sample is placed under the indicator of the Barcol hardness tester, and uniform pressure is applied until the indicator reaches a maximum. The penetration depth is converted into an absolute Barcol value (see Fig. 2). This test is applicable when the sample has a minimum thickness of 1.60 mm. The hardness value is the average of three (03) measurements at each test interval. The results of the Barcol hardness test of GFRP specimens stored in different media are shown in Fig. 3.

According to Fig. 3, the hardness of the R plates is higher than that of the PW and SW plates at 180 and 365 days. The SW specimens show the lowest hardness values compared to the other specimens at 365 days. At the same storage age, the hardness values of the R, PW and SW specimens are 44.40, 44.33 and 44 respectively. This loss of rigidity in the immersed GFRP can be attributed to the effect of water or humidity absorption. According to Phifer [26], immersion of E-glass/vinyl ester resin composite in drinking water for two years caused a stiffness reduction of about 10%.

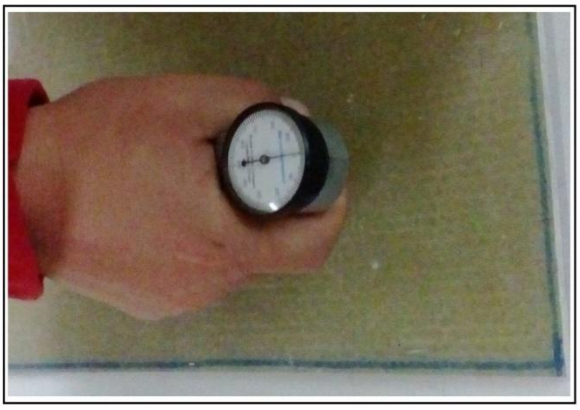

Fig. 2. Barcol hardness determination test

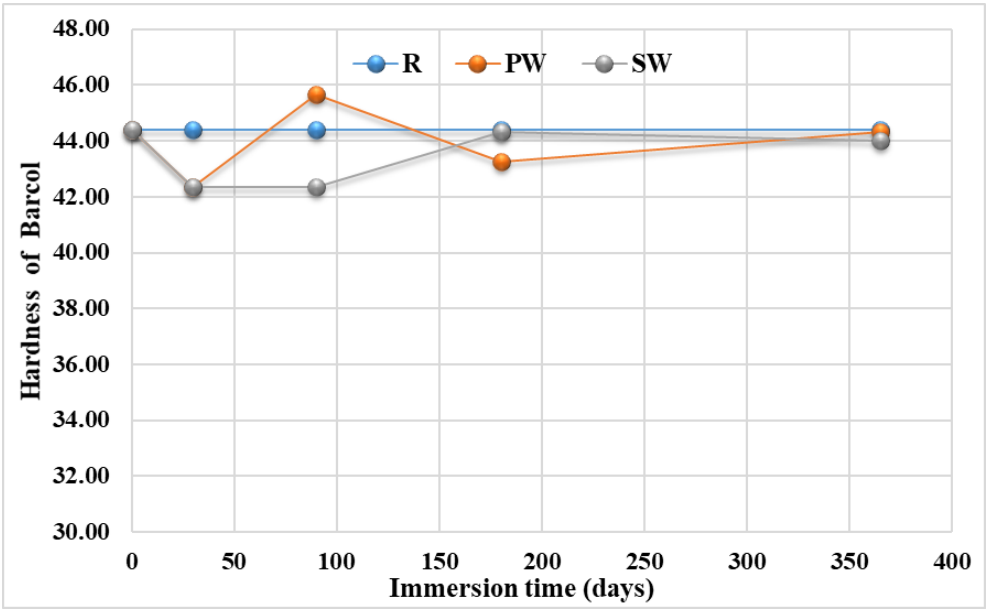

Fig. 3. Barcol hardness of GFRP preserved in different environments

4.2. Water absorption test

This study was conducted in the laboratory using samples with dimensions of 50 × 50 × 7 mm³, in accordance with ASTM C 413-01 standard [35]. The dry specimens were immersed in a container filled with potable water for a duration of 24 hours, after which the samples were weighed to determine their weight after immersion. The water absorption value is the average of five (05) measurements in each test series. The water absorption results of the specimens stored in different environments are presented in Fig. 4.

Figure 4 shows that the water absorption curves of GFRP specimens stored in different environments continuously increase up to 365 days. The SW specimens exhibit maximum absorption at 90 days of storage, reaching 0.57 g/cm², while the PW specimens show a maximum absorption of 0.42 g/cm² at the same storage age. The SW specimens have higher absorption values compared to the other specimens from 90 to 180 days, whereas the R specimens show lower absorption values, except at 365 days. These results can be attributed to the saturation of GFRP after 365 days of immersion in seawater or potable water, which aligns with findings in the literature [20-24], where it was reported that composites with isophthalic polyester resin matrices do not stabilise after reaching the water saturation level.

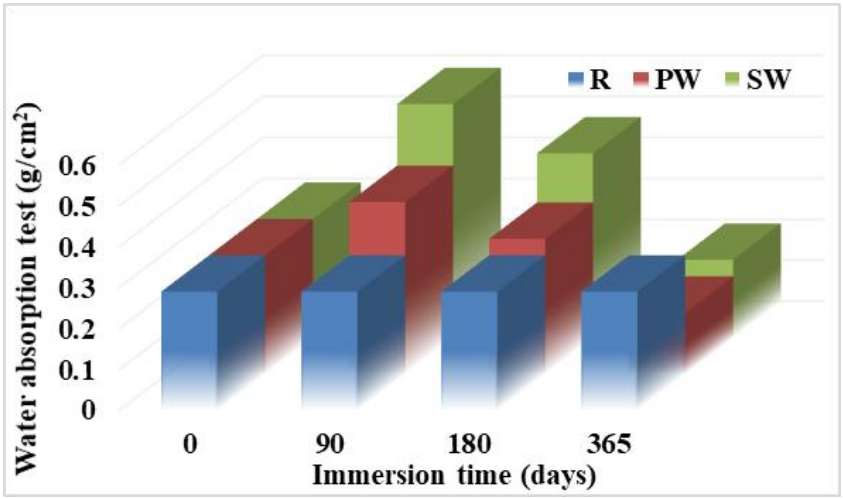

Fig. 4. Water absorption test of GFRP preserved in different environments

4.3. Visual observations of specimens stored in different environments

In this part, the surfaces of GFRP specimens stored in different media for a period of 365 days were visually observed. It was noticed that the surface of the GFRP specimens stored in drinking water developed a white colour (likely due to the precipitation of carbonate minerals), as shown in Fig. 5.A. On the other hand, a white-coloured layer (salt precipitates from sea salts or sodium chlorides) was observed on the surface of the test specimens stored in seawater (see Fig. 5.B).

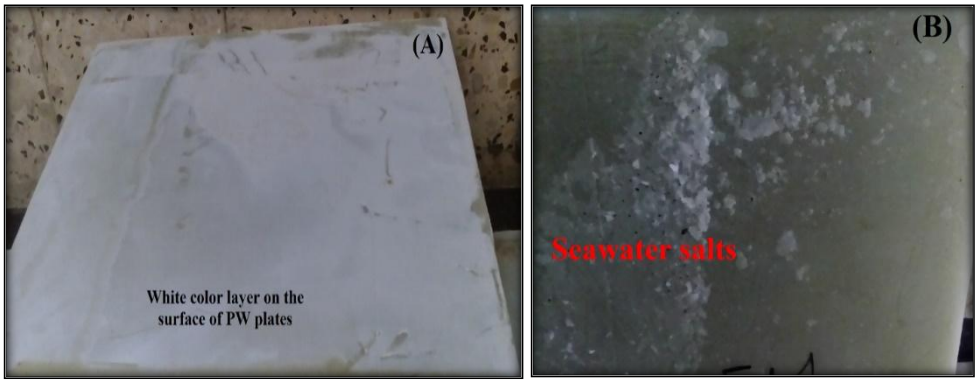

Fig. 5. Surfaces of specimens stored in different media over a period of 365 days

4.4. Infrared (IR) spectra analysis

The results of the infrared (IR) spectra analysis of the surface of the GFRP specimens preserved in different environments at 365 days are shown in Fig. 6.

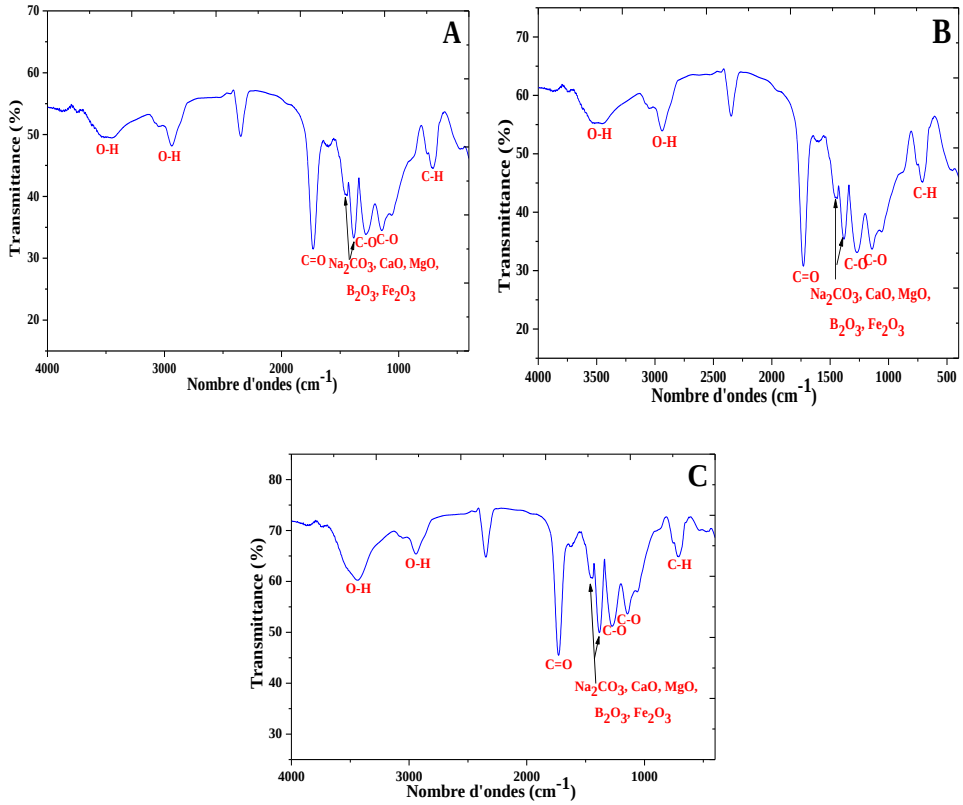

Fig. 6. IR results of preserved GFRP from (A) seawater, (B) potable water, and (C) controls at 365 days duration

From the results obtained in the figures below, it was recorded that storage in drinking water and seawater did not influence the chemical formations on the surface of the GFRP specimens after one year of immersion. In addition, two vibration bands were identified: a narrow O–H stretching band of alcohol and a broad acid band between 2500–3200 cm^{-1} and 3580–3670 cm^{-1}, respectively. A sharp and intense band at 1750 cm^{-1} is attributed to the stretching of the C=O double bond in the COOH functional group of carboxylic acid. The broad and intense band between 1450 and 1550 cm^{-1} is attributed to the stretching of AR glass fibre chemical components involving double bonds (C=O, Ca=O, Mg=O, B=O, and Fe=O). Two moderate C–H single bond stretching bands were identified between 680 and 725 cm^{-1}. Two bands around 1040 and 1450 cm^{-1} correspond to the broad and strong symmetric and antisymmetric valence vibrations of C–O single bonds.

4.5. Scanning electron microscope (SEM) observations

The observation of GFRP samples by scanning electron microscopy (SEM) is illustrated in Fig. 7. In this test, GFRP samples aged 365 days and exposed to different curing environments were examined using SEM. The figure shows that the fibres in the Combo Mat layer are in good condition, with no visible damage, except for a few micron-sized spots on the fibre surface, which may be related to the fibre manufacturing process. Additionally,

platelets in the form of hardened resin crystals are observed on the fibre surface, indicating a strong bond between the fibres and the matrix. Furthermore, good fibre–matrix interface adhesion in the GFRP composite is noted. Consequently, storage in a humid and sulphate-rich environment for 365 days does not appear to affect the GFRP composite. However, these results do not fully confirm the findings of previous tests.

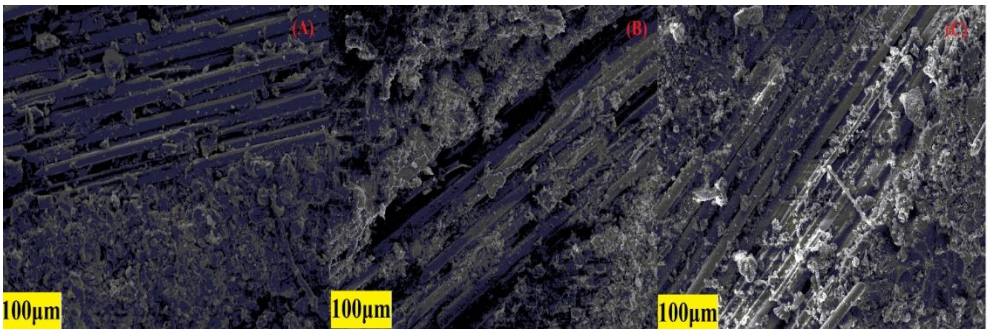

Fig. 7. SEM observation of GFRP from (A) controls, (B) potable water, and (C) seawater at 365 days duration

5. Conclusion

From this study, it was concluded that glass fibre-reinforced polymer (GFRP) is considered a chemically stable material. However, it is generally underutilised in the maritime field, as seawater can negatively influence its long-term mechanical properties. In addition, the bond between the glass fibres and the GFRP matrix remains in good condition, despite the material being stored for one year in a humid and aggressive environment (seawater). Finally, despite variations in hardness and water absorption values, particularly at 90 days, the structure of the GFRP – especially the glass fibres – remains in good condition.

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