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Technical Report

Effects of sea water environment on glass fiber reinforced plastic materials used for marine civil engineering constructions

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ABSTRACT

Glass fiber composites (GFRP) are common in civil engineering projects, but not in marine structures. One reason is that seawater effects degrade GFRP composites mechanical properties and interlaminar shear strength (ILSS). Here, influence of seawater environment is studied to determine the best composite materials for marine civil engineer applications, studying the influence of several factors in their mechanical properties. This is to determine safety factors to use in the design of structural calculations for marine applications. Glass/epoxy composites are the safest materials to use in marine civil structures as mechanical properties degradation becomes stabilized after moisture saturation level. UV and water cyclic analysis must be done to determine affection to transversal strength. Only vinylester GFRP has problems with biodegradation. GFRP fatigue performance is not influenced by seawater environment.

1. Introduction

Glass fiber composite materials have been well known in certain maritime applications for the last 25 years as they started to be used in offshore oil platforms in the early nineties. They are also well known in the naval sector where ships are commonly built with these materials. There are other quite common applications like water storage vessels, pipelines for water desalinization plants and tidal current blades systems for energy generation [1]. In all these applications, corrosion resistance of GFRP materials makes them very effective.

There also exist very well-known civil engineering applications where composites have been applied, like building composite bridges [2–3], FRP pedestrian footbridges [4] or repairing and strengthening of bridge concrete structures [5]. In these cases, carbon fiber reinforced plastics (CFRP) have been commonly used because of low flexural modulus of glass fiber composites (GFRP) that cause problems with deflection in composite beam applications. In spite of this, GFRP costs are much lower than CFRP and this is a very important factor to use this material in applications where low flexural modulus and high deflections of GFRP structures do not determine application use. One application where GFRP rebars are used is to reinforce structural concrete where environmental concrete rebar strength is important like ice effect on steel reinforced concrete bridge slabs [6].

Despite the corrosion resistance of FRP materials is well know, there are few experiences where GFRP materials are used for maritime civil engineer constructions. The only references are found for certain marginal applications like composite elements build for the protection of sea shores and engineering structures against the impact of waves in the Tuapse–Adler railway which runs along the Russian Black Sea coast [7]. Another application is reinforced composite sheet piling of multiple panels to build retaining sea walls [8–10], used in some applications like the construction of 141 m seawall in Martinez Marina in Canada or the construction of 421 m of shore protection in Keyport in New Jersey, USA.

The main reason why GFRP is not used in maritime civil construction applications is because sea water environment effects degrade long term mechanical properties of GFRP composites and interlaminar shear strength (ILSS) [11]. Effects of seawater are different depending on the type of resin used. There are several kinds of resin that could be used for maritime structures like phenolic, polyurethane, polyester, vinylester and epoxy. Resins of polyester, vinylester and epoxy are the most commonly used and are fully studied in several scientific journal publications where different aspects of seawater effects are studied and different conclusions are obtained. However, there is no scientific publication that analyses the most important facts to design civil engineer marine construction applications and, at the same time, helps to

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select the most appropriate resin to use in civil engineer applications.

The aim of this publication is to analyze what kind of resin is the most suitable for civil engineer marine constructions and to study what is going to have long term mechanical properties on seawater environments in most important material design variables used in civil engineering construction.

2. Analysis

2.1. Water absorption. Influence of moisture

In case of exposition to humid air or water environments, many polymer matrix composites absorb moisture by instantaneous surface absorption and diffusion. Usually, the moisture concentration initially increases with time and finally approaches the saturation point (equilibrium) after several days of exposure to humid atmosphere. The time to reach the saturation point depends on the composite thickness and the ambient temperature. Drying can reverse the process but may not result in complete attainment of original properties. The uptake of water by polymer composites follows the generalized Fick's law of diffusion. However, the exact rate of moisture uptake depends on several factors including void content, fiber type, resin type, fiber orientation/architecture, temperature, applied stress level, presence of microcracks, and thermal spikes.

Fick's law could model most of polymeric resin composites. Gellert et al. studied water intake curves of polyester and vinylester resins [12]. Fig. 1 shows resin water intake curves from most usual resins used in civil engineer applications. Zafar et al. analyzed water intake of epoxy resins [13] showed in Fig. 2. Alia et al. [14] studied fickian's water intake performance of vinylester resin, but also studied some non-fickian's resins as polyurethane. As we will see, water intake has a strong influence in evolution of mechanical properties of composite in seawater environment.

Fick's second law to model mathematically water intake is:

$$\frac{M_t}{M_\infty} = \frac{4}{l}\sqrt[2]{\frac{Dt}{\pi}} \quad if \quad \frac{Dt}{l^2} > 0.05 \tag{1}$$

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} e^{-\left(\frac{\pi^2 Dt}{l^2}\right)} \quad if \quad \frac{Dt}{l^2} < 0.05 \tag{2}$$

where

- $M\%$: percent weight change

$$M\% = \frac{M_t - M_0}{M_0} * 100 \tag{3}$$

- M_0: initial weight (g)
- M_t: weight of the specimen at each immersion time (g)
- M_∞: weight of the specimen at saturation (g)
- D: diffusion coefficient (mm^2/sg)
- t: time (sg)
- l: thickness of specimen (mm)

Moisture has important effects in composite performance because it causes degradation, especially in polymeric matrix of composite. It is commonly known that glass fibers can be damaged by prolonged exposure to water; on the other hand, moisture does not have any known degrading effects on carbon fibers. Alia et al. [14] state that three well-differentiated zones can be identified in the polymer that is related to the water concentration reached and the chemical changes caused:

- Zone 1 is where the absorbed water has not exceeded the critical concentration of water, and therefore the initial properties of the polymer remain unchanged.
- Zone 2 is the region in which seawater has penetrated and concentrations are above the critical concentration, chemically linked to the polymer, and the polymer properties are irreversibly degraded.
- Zone 3 is the region in which salt deposits occur because the solubility product of dissolved salts in seawater has been reached locally. These deposits constitute a physical barrier to the ingress of water.

2.2. Mechanical properties vs moisture

It is certainly known that sea water long term effects affect composites mechanical properties. Degradation is strongly linked to water intake characteristics of composites. It is possible to analyze the relationship between moisture (%) and mechanical properties with time exposition to sea water. Fig. 3 shows the relationship between glass/polyester composite water intake (moisture) and variation of tensile strength, flexural strength and modulus.

Moisture saturation of glass/polyester composite B is 0.58% [15]. After moisture achieves saturation level (30 days), degradation of tensile slope decreases and becomes nearly stabilized. On the other hand, at moisture saturation level of polyester composite (1.25% for 65 days) flexural variation slope increases. This means than transversal performance of glass/polyester composite does not stabilize after moisture saturation level.

Fig. 4 represents the relationship between water intake of glass/vinylester composite and mechanical properties variation [16]. Moisture saturation of composite A and B is 0.44% for 210 days. After achieving saturation level, variation of flexural decrease

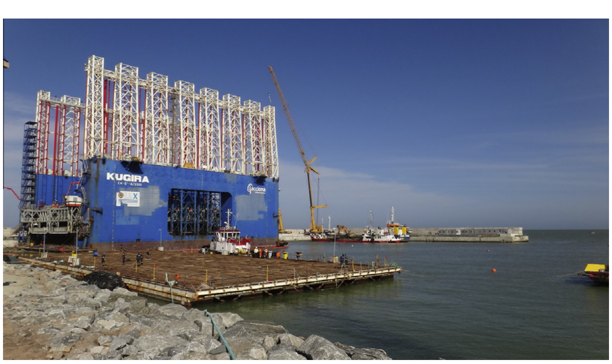

Fig. 1. Construction of breakwaters for a shipyard in São João da Barra, in Brazil.

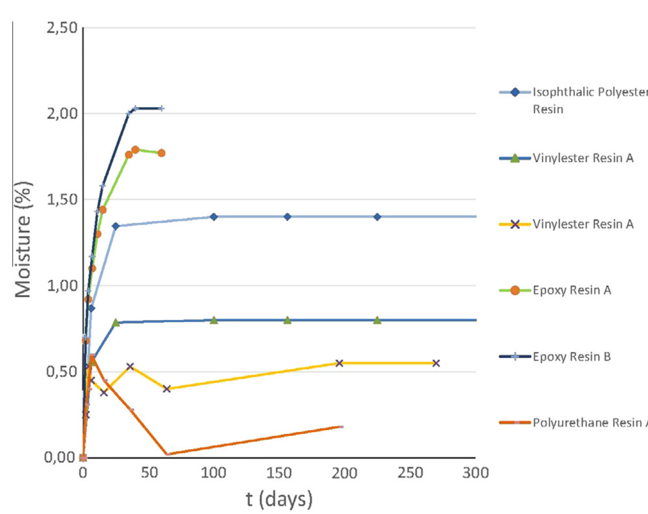

Fig. 2. Water intake evolution of pure resin matrices.