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Durability of FRP Immersed in Water. Changes in Mechanical Properties

Ernest Bernat-Maso[1], Manuel J. Lis[2], Luis E. Mercedes[3] and Lluís Gil[4]

[1] Serra Húnter Fellow. Department of Strength of Materials and Engineering Structures, Universitat Politècnica de Catalunya-BarcelonaTECH, ESEIAAT, 08222-Terrassa, Spain, ernest.bernat@upc.edu

[2] Department of Chemical Engineering, Universitat Politècnica de Catalunya-BarcelonaTECH, ESEIAAT, 08222-Terrassa, Spain, manuel-jose.lis@upc.edu

[3] Department of Strength of Materials and Engineering Structures, Universitat Politècnica de Catalunya-BarcelonaTECH, ESEIAAT, 08222-Terrassa, Spain, luis.enrique.mercedes@upc.edu

[4] Department of Strength of Materials and Engineering Structures, Universitat Politècnica de Catalunya-BarcelonaTECH, ESEIAAT, 08222-Terrassa, Spain, lluis.gil@upc.edu

Abstract. *Fibre Reinforced Polymers (FRP) have been widely used to strengthened construction structural elements in the last years because of their mechanical pros. However, the durability of these materials is always controversial. In particular, the effect of long-term contact with water on the mechanical properties of FRPs is studied in this research throughout the implementation of accelerated degradation tests. Samples of Carbon FRP and Glass FRP were immersed into supply water, water with salts and surfactants and highly chlorinated water. In all cases, electrical current passing through the samples was also imposed. Tensile tests on pristine and degraded samples were carried out to determine the influence of these aggressive environments on the tensile strength and the Young's modulus of the specimens. Finally, superficial (ATR) FT-IR analyses were conducted to assess possible chemical changes in the samples surfaces. Results indicated that the chemical composition of used resins was not modified due to the water exposure. No hydrolysis process took place during testing time on the surface. However, mechanical properties were reduced, especially when samples were exposed to plain supply water, which may be related to the physical degradation caused by moisture intake by diffusion.*

Keywords: *Composites, Hydrolysis, Mechanical Properties, Accelerated Degradation, Waste Water.*

1 Introduction

Fibre Reinforced Polymers have been commonly used to strengthen existing building structures in the last years. Their significant stiffness, outstanding strength and low weight make FRP an interesting building material for retrofitting, rehabilitation or strengthening concrete or masonry structures. In addition, one of the main advantages pointed out by FRP suppliers is its corrosion resistance in wet environments, although this statement is not always proved.

In fact, FRP durability have been a controversial topic from the very beginning because of the organic nature of the matrix where fibers are embedded into. In this line, several researches may be found in the literature.

Some researchers investigated the durability of FRP components. In this line, carbon fiber has been proved to be resistant to acid and alkali environments and it can only be oxidized by strong oxidants (Zhu and Hu, 2017). In contrast, glass fiber is known to degrade in presence of water, especially in alkaline environments (Bank, Gentry, and Barkatt, 1995), where greater alkalinity is directly correlated with faster rate of glass fiber erosion. The strength of glass fiber is permanently reduced after soaking in water because of the chemical reaction of glass fiber and water (Zhu and Hu, 2017). This fact is increased by alkalinity. Regarding corrosion, glass fiber can be affected by hydrofluoric acid but it shows a good corrosion resistance.

According to (Department of Defense USA, 2002) epoxy shows good chemical resistance but its mechanical properties are clearly reduced in the presence of moisture because it is composed by a large number of polar OH groups that facilitate attractive interaction with polar molecules like water (Panda and Mamta, 2010). Polyester durability mostly depend on their typology. Hence, orthophthalic polyester is far more affected by water presence than isophthalic polyester. According to Shaoru Zhu *et al.* (Zhu and Hu, 2017), the chemical medium can penetrate into the polymer, react with it and cause the polymer to swell. This process can produce salts, hydrolysis, saponification, sulfonation, oxidation or nitrification, which causes the breaking of the main valence bond. In general, resins have a significant cross-linking degree that brings resistance to medium corrosion. Hence, controlling curing degree is essential and it is mainly related to the hydrolytic activation energy of its hydrolyzed groups in the corresponding acid-base medium. Thus, corrosion resistance of the matrix highly depends on the curing/hardening agent.

Regarding the durability of the FRP composite material, it is stated (Cromwell, Harries, and Shahrooz, 2011; Karbhari *et al.*, 2003) that hydrothermal effects are dominant. Water or moisture absorbed by the FRP matrix can result in physical changes to the matrix (including plasticization and a reduction in glass transition temperature) which result in a breakdown of the resin matrix that makes it possible further affectation of fiber and matrix-fiber interface. According with (Karbhari *et al.*, 2003), moisture diffuses into all organic polymers, leading to changes in thermophysical, mechanical, and chemical characteristics. Additionally, the primary effect of the absorption is on the resin itself through hydrolysis, plasticization, saponification, and other mechanisms, which cause both reversible and irreversible changes in the polymer structure.

Several absorption studies, like (Sun and Li, 2011) proved that the diffusive and capillary processes were the main ways composites absorb moisture. The existence of water molecules in the FRP can weak the performance of interface between the fiber and matrix. This effect can reduce the shear performance of the FRP and cause the progression of delamination between layers.

Beside moisture, chemical attack (*e.g.* acid and alkali solutions) also contributes to degradation of FRP by accelerating the hydrolysis process (Karbhari *et al.*, 2003; Liu, He, and Xiong, 2017). It is demonstrated that the tensile strength of FRP composites immersed in acid and alkali solutions decreases faster than those immersed in distilled water (Liu *et al.*, 2017). Additionally, scanning electron microscope (SEM) analysis shows that immersion in alkali solution causes degradation of the fiber-matrix interface and that degradation leads to significant reduction in the tensile properties of basalt and glass FRP composites. Moreover, ingress of alkaline media into fiber can cause surface pitting, hydroxylation, hydrolysis and leaching that not only affect the integrity of fiber but also expose fiber to further degradation. This was especially observed for glass fiber composites because the reaction between glass fibers and alkali substances led to increase water uptake (Sun and Li, 2011). Similar response was observed for acidic media (Liu *et al.*, 2017). According to the wet-dry cycles test results, degradation of aramid and basalt FRP sheets in sulfate and chloride solutions were more significant than in alkali and acid solutions because sulfate and chloride solution promoted crystallization, which accelerated the degradation. Carbon and aramid FRPs were more stable although. In contrast, glass FRPs were susceptible to moisture extracting ions from glass fiber showing lower chemical resistance.

Two processes are observed when a FRP is exposed into an aggressive media: physical adsorption of the medium caused by swelling and resulting in the destruction of the resin structure; and chemical effect on the bonds of resin molecules resulting in a performance decrease (Zhu and Hu, 2017). It is also stated that the chemical attack involves specific chemical reaction of the polymer with the fluid in the case of polyesters. In this case, the most common failure mode is the hydrolysis by water, acids and alkalis. Esters, and carbonate groups are particularly susceptible to this hydrolysis process (Bagherpour, 2012).

Hydrolysis is a reaction that involves the breaking of a bond in a molecule using water. Molecule polarity promotes moisture sensitivity. Therefore, using hardening or catalytic systems which provide a less polar molecular structure are preferred to avoid water absorption and reduce hydrolysis problems (Ellis, 1993).

Regarding the effect of saline environment, it was proved (Bank *et al.*, 1995) that the rate of strength degradation of aramid/epoxy composites in saline solution was less than that in distilled water. This behavior was justified because the presence of "massive" salt molecules slowed down the absorption rate of water, resulting in a slower rate of hydrolysis process. This fact was also proved by (d'Almeida, 1991).

Regarding the effect of chlorinated environment, it is known that chlorinated water is normally more corrosive than distilled water because of the higher conductivity and the penetrating power of the chloride ion through surface films on metals. The rate of corrosion is controlled by the chloride content, oxygen availability, and the temperature. However, the effect of the presence of chlorides is not specifically investigated for FRPs.

Regarding the effect of degradation of the mechanical properties, tensile strength of FRPs is more affected than elastic modulus because of environmental exposure, as stated by (Cromwell *et al.*, 2011).

As a conclusion of the literature review, it is stated that chemical and physical affectations are possible on FRPs exposed to aggressive media, mostly involving resin matrix. Studying the particular effects of salts and surfactants rich water and highly chlorinated water is necessary for the application of these materials on water treatment plants.

2 Materials and Methods

Two types of FRPs were produced and tested: glass fiber and polyester resin FRP (GFRP) and carbon fiber and epoxy resin FRP (CFRP). Tensile tests were performed on unaltered samples, samples immersed in supply water, samples immersed in water with salts and surfactants representing increased aggressivity of waste water and water highly chlorinated to represent a long term effect of chloride in supply water.

2.1 Materials

The used glass fiber was E-Glass Chopped Strand Mat with no orientation and a density of 225g/m^2. Filaments of the fibers were covered by silane to enhance chemical compatibility with polyester resins. The used carbon fiber was unidirectional 300g/m^2 0.165mm thickness fiber.

The polyester was an unsaturated resin of orthophthalic type and standard glycols, dissolved in styrene (acts as hardener). The catalyst was methylethylketone peroxide. Epoxy resin was a combination of formaldehyde (polymer with 2-(chloromethyl)oxirane and phenol) and bisphenol A epichlorohydrin polymer. As hardener for the epoxy resin, a mixture of Isophoronediamine and Trimethylolpropane was used.

2.2 Sample Production

FRPs were manually laminated on a glass plate previously prepared with unmolding agents. Four layers of carbon fiber and seven layers of glass fiber were respectively used. Over each fiber layer the corresponding resin was manually applied with a brush (see Figure 1 (a)) at a ratio of 50% fiber and 50% resin. Finally, perforated release film and non-woven breather felt were placed below weight application tools to absorb excessive resin during curing process.

Resulting CFRP plate was 1mm thickness whereas GFRP plate was 4mm thickness. These plates were manually cut to the desired dimensions of 12.5mm x 200mm in the case of CFRP and 25.0mm x 200mm in the case of GFRP. Twelve specimens of each FRP type were obtained. These were divided in four groups of three samples. Each group was subjected to a different media type (unaltered specimens, supply water, waste water and chlorinated water) before tensile testing.

2.3 Degradation Method

Artificial concentrated wastewater containing 100g of urea, 50g of detergent powder (25% of sodium carbonate, 10% of sodium percarbonate, 10% of benzensulfonic acid, 3% of no ionic surfactant, 3% of silicic acid), 35g of NaCl per 1L of supply water was produced according with typical compounds found in wastewater as by (Garcia, 1985). Artificially highly chlorinated water was produced by adding 35g of NaCl per liter of supply water. Additionally, three samples of each FRP were also immersed into supply water for comparison with artificial concentrated wastewater and highly chlorinated water.

All immersed samples were subjected to an imposed electrical current according with (International Standardisation Organisation, 2017) which corresponded to 2.4mA for CFRP samples and 20mA for GFRP samples. Immersion lasted two weeks. Surface of GFRP specimens showed different coloring depending on the treatment as presented in Figure 1(b).

(a) (b)

Figure 1. (a) CFRP production and (b) GFRP specimens state before tensile tests; from left to right supply water, wastewater, chlorinated water and untreated.

2.4 Tensile Testing

Before performing tensile tests samples were prepared to avoid local stress concentration failure mode. This was achieved by covering the endings of the samples by two thin aluminum sheets bonded to both sides of the sample with epoxy resin. These sheets avoided clamp indentation on the sample during tensile test.

Tensile tests were performed with an electromechanical press at a constant displacement rate of 2mm/min, acquiring force and displacement at 50Hz until tensile failure.

2.5 ATR FTIR Testing

Samples were subjected to Fourier-transform infrared spectroscopy analysis (FTIR) after tensile test. This test was conducted to observe if there were changes of chemical bonds on the specimens after being treated by supply water, waste water or chlorinated water. Attenuated total reflection (ATR) technique was used because it is able to examine directly the sample without further preparation but obtaining only the chemical characteristics of the surface of the sample. The FTIR spectrometer used in this study was FTIR-8300.

3 Results

Quantitative results from the tensile tests and qualitative observations of the FTIR analysis are summarized in this section.

3.1 Tensile Strength

The tensile strength (f_t) of each sample was calculated assuming a uniform stress distribution on the cross section, so dividing the maximum applied force by the cross area of the specimen. All specimens broke by material tensile failure so no sliding respect clamps neither local stress effects were observed. Tensile strength results are summarized in Table 1.

Table 1. Results of the tensile tests.

	Supply water		***Wastewater***		***Chlorinated water***		***Untreated***	
	f_t *(MPa)*	*E (MPa)*	f_t *(MPa)*	*E (MPa)*	f_t *(MPa)*	*E (MPa)*	f_t *(MPa)*	*E (MPa)*
CFRP	1108	34364	1294	30556	1331	26912	1311	25967
	921	31561	1246	34375	1020	24359	1495	30351
	1049	28378	1413	28399	1246	27616	1033	26257
GFRP	139.3	3333	143.0	3590	150.1	4043	164.2	3613
	149.1	3784	115.7	2881	138.7	2765	159.9	3711
	157.4	3824	160.0	3243	155.8	3522	147.4	3120

3.2 Elastic Modulus

Elastic modulus (E) was calculated as the slope of the linear part of the stress-strain curve, which was set between 20MPa and 100MPa for GFRP and between 100MPa and 600MPa for CFRP. Strain was calculated as the measured axial displacement divided by the total length of the sample. Results are summarized in Table 1.

3.3 FTIR Analysis

Representative FTIR analysis results are showed Figure 2. The analyses have to be performed by qualitative comparison of the presence/absence of particular peaks in the specific ranges of the corresponding compounds. Hydroxyl groups, which are related with hydrolysis processes, are supposed to appear around 3500 cm^1 (red line in Figure 2).

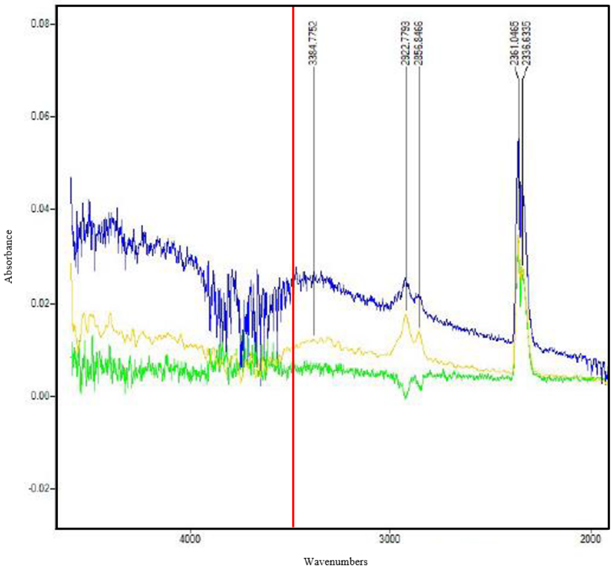

Figure 2. Effect of waste water and supply water on CFRP (left). Yellow for untreated, blue for waste water and green for supply water treated specimens.

4 Discussion

Regarding quantitative results about tensile strength and elastic modulus it is observed that immersing GFRP with an electrical current causes the decrease of the tensile strength in all cases. This strength reduction is equivalent for specimens immersed into supply water and into chlorinated water (-5.5% and -5.7% respectively), so adding NaCl makes no apparent effect on the tensile strength reduction of GFRP. Immersing GFRP in wastewater brought the higher tensile strength reduction (-11.2%). It is also associated with the most significant reduction of the elastic modulus (-7.0%) whereas immersion of GFRP in chlorinated water has no effect (-1.1%) on this parameter and immersion in supply water showed an increase (+4.8%).

In relation with CFRP specimens, the greater reduction of the tensile strength (-19.8%) is observed for specimens immersed in supply water. Treatment in chlorinated water also causes a decrease of this parameter (-6.3%) whereas immersion into wastewater showed an apparent increase (+3.0%) of the tensile strength. Elastic modulus of CFRP is increased when immersing it into supply water (+14.2%) or wastewater (+13%) with no significant difference among them. However, it is reduced when immersed in chlorinated water (-4.5%).

Looking at the results on the whole, it may be stated that chlorinated water caused the reduction of tensile strength and elastic modulus for both FRPs. Wastewater causes the reduction of mechanical properties of GFRP but increases the ones of CFRP. Finally, exposure to supply water reduces the tensile strength but increase the elastic modulus.

Incorporating the results of the ATR-FTIR analysis, it is noted that no hydrolysis happened because hypothetically resulting hydroxyl group was not detected in any case. The corresponding peak ($3500cm^{-1}$, red line in plot of Figure 2 as example) were not qualitatively observed in any case. Results of CFRP may indicate the physical resin adsorption of the medium, which caused the swelling of polymer, also induced by the electrical field. This adsorption is restrained by the presence of massive ions like salts and surfactants at the sample surface. In this line, surfactants are really likely to move on to the exposed sample surface. In addition, the imposed electrical current would have polarized the specimen surface, changing the properties of the solid-liquid interface and making it easier for the salt ions to adhere on to this surface. The combination of electrical polarization, so promoting ions adhesion to the surface, and superficial attachment of surfactants explained the lower water adsorption, so the lower reduction or even increase of the tensile strength for CFRP immersed in chlorinated and wastewater, respectively. The same tendency should be valid for glass fiber. In fact, surfactants were detected in resin surface of GFRP specimens. However, in the case of GFRP another process plays an important role in the opposite direction: glass fiber is sensitive to alkaline environments and higher alkalinity of wastewater may explain the greater degradation of the specimens immersed in this media because of fiber degradation. Supply water and chlorinated water showed similar tensile strength reduction because of the sensitivity of glass fiber to the moisture, which had greater effect than water adsorption restrain for chlorinated water.

Finally, inclusion of water molecules into resin structure of the matrix may explain the apparent increase of the elastic modulus, which is more evident for the cases in which water molecules adsorption was not limited, so for specimens immersed in supply water. Similar effect was observed for CFRP into wastewater but, in contrast, glass fibers really degraded in this alkaline media so a reduction of elastic modulus of GFRP was observed. Finally, variation of the elastic modulus of specimens immersed in chlorinated medium was not significant, reaching a balance between stiffening because of hypothetic adsorption of water molecules and degradation of material for both FRPs.

5 Conclusions

Combining mechanical analysis and chemical ATR FTIR analysis makes it possible to understand the underlying causes of the observed changes in the mechanical properties of FRPs immersed in aggressive water environments. The following conclusions are obtained:

- Exposure to supply water reduces the tensile strength and increases the elastic modulus of GFRP and CFRP. In contrast, exposure to chlorinated water causes the reduction of both parameters, whereas wastewater causes the reduction of mechanical properties of GFRP but increases the ones of CFRP.
- Water adsorption causes the swelling of the polymer, which is accelerated by the polarization induced by the electrical field, reducing the tensile strength.
- Media with massive ions or surfactants that tend to adhere resin surface, even more under an imposed electrical field, showed lower water adsorption by the matrix, so less degradation of the tensile strength results.
- Inclusion of water molecules into resin structure may result in a stiffer response of FRPs although further research is required to confirm this point.

As practical conclusion, plain water is showed to be the most aggressive media for the matrix resin and a real problem to be faced for improving FRPs durability.

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ORCID

Ernest Bernat-Maso: http://orcid.org/0000-0002-7080-0957
Manuel J. Lis: http://orcid.org/0000-0002-2026-085X
Luís E. Mercedes: http://orcid.org/0000-0003-2520-8599
Lluís Gil: http://orcid.org/0000-0002-2007-4846

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