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Combined effects of saline solution and moist concrete on long-term durability of GFRP reinforcing bars

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HIGHLIGHTS

- ▶ A durability study of GFRP bars submitted to salt solution and concrete is proposed.
- ▶ Mechanical and physical characterizations were performed on aged bars.
- ▶ GFRP bars have shown high tensile strength retention after aging.
- ▶ No chemical degradation of the polymer as detected after aging.
- ▶ Prediction of long-term tensile strength were performed.

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ABSTRACT

This paper presents the mechanical, durability, and microstructural characterization of unstressed glass-fiber-reinforced-polymer (GFRP) reinforcing bars exposed to concrete environment and saline solutions under accelerating conditions. These conditionings were used to simulate the effect of seawater or deicing salts on GFRP bars. The pre- and postexposure tensile strengths of the bars were used for long-term property predictions based on the Arrhenius theory. The results revealed no significant differences in the durability of the concrete-wrapped GFRP bars whether immersed in salt solution or tap water and the very high long-term durability of the GFRP bars in salt solution. According to the predictions, even after a service life of 100 years, the tensile-strength retention of the tested GFRP bar would still be 70% and 77% for mean annual temperatures of 50 °C (the mean annual temperature and the marine environment of the Middle East and warm regions) and 10 °C (mean average temperature of northern regions), respectively, which are higher than the design tensile strength according to the ACI 440.1R.

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1. Introduction

In recent decades, fiber-reinforced-polymer (FRP) composites have been promoted as a solution to the deterioration of bridges, buildings, and other structures made with concrete reinforced with traditional materials, such as steel. Fiber-reinforced composites offer better resistance to environmental agents as well as high stiffness-to-weight and strength-to-weight ratios when compared with conventional construction materials. Unfortunately, the long-term performance of GRFP under some special harsh environment conditions—such as exposure to high alkalinity, seawater, or

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deicing salts—remains unresolved. The strength of the glass fibers and the resin matrix—two GFRP constituents—can decrease when subjected to the combined effect of wet alkaline and saline environments.

Our study aimed at assessing the environmental durability of GFRP bars used as internal reinforcement of concrete subjected to a saline solution and predicting their long-term behavior in such environments. The study simulated rather aggressive conditions by immersing concrete-wrapped bars in a salt solution at different elevated temperatures for 365 d. The tensile strength was considered the primary structural parameter, and hence was used an indicator of degradation due to exposure. Additional microstructural and physical characterizations were performed and service-life models were established.

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2. Background and research to date

The strength of glass fibers and the resin matrix-two GFRP constituents-can decrease when subjected to wet alkaline or saline environments. Thus, an adequate durability study of GFRP materials should be performed for FRP reinforcing bars to gain wide acceptance in the construction industry. Considerable research has been conducted in the past decade to assess the suitability of FRP reinforcement in reinforced-concrete structures [1–4]. The work of these researchers has highlighted the short-term performance of FRP-reinforced concrete structures or the durability of FRP reinforcing bars subjected to aging in alkaline solutions. Some researchers have reported on the durability of GFRP bars embedded in moist concrete, which simulates actual application conditions, and on the adverse effects of cracks and microcracks in GFRP bars on their long-term durability [5]. Nevertheless, the data on the durability of GFRP bars subjected to the combined effect of moist concrete and saline solution is very limited.

The resins widely used for FRP composites include polyester, vinylester, and epoxy. Weak adhesion of polyester or vinylester can result in serious deterioration when hydroxyl ions penetrate the structure [6]. On the other hand, a considerable drawback of epoxy is that it can absorb from 1% to 7% moisture by weight, which plasticizes the matrix, inducing differential swelling stresses, and generally degrades the physical properties [7]. In general, the matrix could be damaged through cracking and microcracking due to volume expansion during moisture absorption, whereas its stiffness could be reduced by plasticization. A subsequent mechanism of degradation resulting from the breaking of polymer chains triggered by hydrolysis and the leaching out of low molecularweight material from the bulk resin could further damage the matrix [8-10]. The matrix formed by vinylester, which contains much fewer ester units compared to polyester, is hardly deteriorated by hydroxyl ions compared to a polyester matrix.

E-glass fibers are the most susceptible to degradation due to moisture and alkalinity [11]. Dejke [12] reported that glass fibers are known to degrade in the presence of water, and that moisture can decrease the glass transition temperature (T_g) of the resin and act as a plasticizer, potentially having significant effect on the strength of GFRP materials. The reaction of GFRP composite with the alkali in concrete is a major durability concern. Typically, concrete environments have high alkalinity, depending on the design mixture and type of cement used [13,14]. This alkaline environment damages glass fibers through loss in toughness and strength and through embrittlement. Glass fibers are damaged due to the combination of two processes: (1) chemical attack on the glass fibers by the alkaline cement environment, and (2) concentration and growth of hydration products between individual filaments [15]. Fiber embrittlement is due to the nucleation of calcium hydroxide on the fiber surface. Hydroxylation can cause fiber surface pitting and roughness, which act as flaws, severely reducing fiber properties in the presence of moisture. In addition, calcium, sodium, and potassium hydroxides in the concrete pore solution are aggressive to glass fibers [16]. Therefore, the degradation of glass fibers depends not only on a high pH level, but also on the combination of alkali salts, pH, and moisture.

The deterioration at the interfaces between the fibers and the matrices involves a much more complex mechanism [17]. The interface is a nonhomogeneous region about 1 μ m thick. This layer is weakly bonded and most vulnerable to deterioration [17]. The three dominant deterioration mechanisms include matrix osmotic cracking, interfacial debonding, and delamination [18]. The moisture diffusion into FRP composites could be influenced by the material's anisotropic and heterogeneous character. Along with diffusion into the matrix, wicking through the fiber/matrix

interface in the fiber direction could be a predominant mechanism of moisture ingress [19,20]. Nonvisible dissociation between fibers and matrix could lead to rapid losses of interfacial shear strength [9].

In order to evaluate long-term durability performance of FRP in harsh environments, extensive studies have been conducted to develop accelerated aging procedures and predictive models for longterm strength estimates, especially for GFRP bars [21-24]. These models are based on the Arrhenius model [25]. Research on the effects of temperature on the durability of FRP bars in concrete alkaline environments indicates that an acceleration factor for each temperature difference can be defined using Arrhenius laws. These factors differ for each product, depending on the types of fiber and resin, and bar size. In addition, these factors are affected by environmental conditions, such as surrounding solution media, temperature, pH, moisture, and freeze-thaw conditions. Predictive models based on Arrhenius laws make the implicit assumption that the elevated temperature will only increase the rate of degradation without affecting the degradation mechanism or introducing other mechanisms. Gerritse [26] indicated that at least three elevated temperatures were necessary to perform an accurate predication based on Arrhenius laws. Moreover, the measured data should be in continuous time intervals. We followed those recommendations for this study.

2.1. Research gaps and statement of the problem

Several studies have addressed the durability of GFRP reinforcing bars [1,2,24], including FRP-wrapped concrete cylinders [27-30]. Very limited studies, however, have been conducted on the durability of GFRP reinforcing bars subjected to saline solution or to the combined effect of saline solution and the alkaline environment of the concrete surrounding the bar. The properties of the pultruded products (void content, interface quality, and fiber distribution) and the nature of the aggressive environment can lead to important changes in the behavior and durability of the final product. As such, the available knowledge on the durability of GFRP reinforcing bars subjected to typical alkaline solutions as specified by ACI 440.3R-04 [31] may not be directly applicable to GFRP bars subjected to salt and concrete at the same time. In fact, FRP reinforcing bars can be subjected to aggressive alkaline environments from the concrete and to an aggressive external saline environment in marine applications or from deicing salts. No studies have focused on this possible combined effect. In addition, engineers now aim to design structures with service lives of from 75 to 150 years, thereby requiring studies that predict the durability and service life of the new GFRP materials used in concrete infrastructure.

3. Experimental approach

3.1. Material

Sand-coated GFRP bars were used in this study. The bars were made of continuous E-glass impregnated in a vinylester resin using the pultrusion process. The fiber mass fraction was 77.9% as determined by thermogravimetric analysis according to ASTM E1131 [32]. The relative density of the GFRP bars according to ASTM D792 [33] was 1.99. The bars had a nominal diameter of 12.7 mm. The mechanical and physical properties of the GFRP reference bars are summarized in Table 1. All bars were cut into 1440 mm lengths, as specified by ACI 440.3R-04 B2 [31]. The bars were divided into two series: (1) unconditioned reference samples; and (2) conditioned samples (130 bars) embedded in concrete and aged in a saline solution. The mortar mixture consisted of 3 parts sand, 1 part type 1 cement (according to ASTM C150 [34]), and a water–cement ratio of 0.40, which yielded a concrete pH of 12.15, measured by extracting interstitial solution after the aging process. The concrete (or mortar) was cast only around the middle third of the bars to avoid any degradation at the ends, which were used as grips during tensile testing according to ACI 440.3R-04 B2 [31]. The concrete mold was made of wood with

Table 1Tensile properties and physical properties of the 12.7-mm-diameter GFRP bars.

	Property	Unit	Value
Tensile properties	Mean tensile strength, $f_{u \text{ ave}}$ (1)	MPa	786
	Guaranteed tensile strength, $f_{f_l}^*$ (1)	MPa	708
	Design tensile strength f_{60}^a	MPa	496
	Average tensile modulus, $E_{f,ave}$ (1)	GPa	46.3
	Tensile strain, epsilon, $\varepsilon_{u,ave}$ (1)	%	1.70
Physical properties	Longitudinal coefficient of thermal expansion	×10 ^{−6} /°C	5.5
	Transverse coefficient of thermal expansion	×10 ^{−6} /°C	29.5
	Moisture absorption	%	0.38
	Fiber content	wt%	77.9

(1) According to ACI 440.1R-06.



Fig. 1. View of mortar-wrapped GFRP bar specimen.

a 48-mm square section, which provided a minimum concrete cover of 18 mm. Fig. 1 shows a picture of a mortar-wrapped GFRP bar.

3.2. Environmental aging

Two types of accelerated aging in saline solution of 3% NaCl were used in this study: (1) accelerated aging of GFRP reinforcing bars embedded in concrete designed to simulate an aggressive alkaline environment of saturated concrete at moderate temperatures (23 °C, 40 °C, and 50 °C), and (2) accelerated aging of GFRP reinforcing bars embedded in concrete designed to simulate very humid and warm environment of application (70 °C). For the first type of aging, the specimens were completely immersed at three different temperatures (23 °C, 40 °C, and 50 °C) and were removed from the water after four different periods of time (60, 120, 210, and 365 d) to lead to predictions about long-term properties. For the second type of aging, the embedded specimens were immerged in a saline solution or tap water, and then heated to 70 °C for 120 d. The 3% NaCl concentration was used to simulate a marine environment or the use of deicing salts in northern regions [35,36]. The pH of the solution surrounding the bars resulted from the concrete absorbing water, thereby releasing alkaline ions from the concrete directly into the bar environment. The aging was performed by immersing the mortar-wrapped GFRP bars in wood containers specially manufactured for the study (Fig. 2). The containers were tightly closed with a polyethylene-film lining. A polyethylene sheet was also placed on top of the wood containers to avoid excessive evaporation of water during conditioning. The bars were spaced apart and from the bottom of the container to allow the solution to freely circulate between and around the bars. Furthermore, the water level was kept constant throughout the study to avoid a pH increase, which could result from decreased water level, and a significant increase of alkaline ions in the



 $\pmb{\text{Fig. 2.}}$ Wood container built for aging of the cement mortar-wrapped GFRP bar specimens.

solution. The immersion temperatures were chosen to accelerate the degradation effect of aging. They were not so high, however, as to produce any thermal-degradation mechanisms [37].

For predicting long-term properties, six GFRP bars (in most cases) were removed from the saline solution after every period and tested under tension to compare their tensile-strength retention values to those of the reference specimens. The surface of the GFRP bars evidenced no significant changes after specimen immersion.

3.3. Water-immersion test

The moisture uptake at saturation of GFRP bars was determined before and after conditioning according to ASTM D570 [38], except that the immersions were performed in tap water instead of distilled water. Three 50-mm-long specimens were cut, dried, and weighed prior to immersion in water at 50 °C for 3 weeks. The samples were removed from the water after 3 weeks, surface dried, and weighed.

The water content at saturation in weight percent (W_s) was calculated using the following equation:

$$W_s = 100 \cdot (P_s - P_d)/P_d \tag{1}$$

where P_s and P_d are the sample weights in saturated and dry states, respectively.

The percentage of moisture uptake was calculated, and the gain in mass was corrected to take into account possible specimen mass loss due to various dissolution phenomena during the aging procedure (such as hydrolysis) by completely drying the immersed specimens, placing them in an oven at 100 $^{\circ}\text{C}$ for 24 h, and comparing their dried masses to their initial masses.

3.4. Tensile tests

All bars were tested under tension according to ACI 440.3R-04 B2 [31]. Each specimen was instrumented with two linear-variable differential transformers (LVDTs) to capture elongation during testing. The average value of the two measurements was used for the calculation of the modulus of elasticity. The test was carried out with a Baldwin testing machine and the load was increased until failure. For each tensile test, the specimen was mounted on the press with the steel-pipe anchors gripped by the wedges of the machine's upper and lower jaws. Just before the test, the concrete cover was carefully removed from the middle third of the specimens with a hammer to avoid damaging the bars. The rate of loading ranged from 250 to 500 MPa/min. The applied load and bar elongation were recorded during the test with a data-acquisition system monitored by a computer. Due to the brittle nature of GFRP, no yielding occurred and the stress-strain behavior was linear.

3.5. Long-term predictions

Eq. (2) expresses the Arrhenius relation in terms of the degradation rate [39]:

$$k = A \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where k is the degradation rate (1/time); A the constant relative to the material and degradation process; E_a the activation energy of the reaction; R the universal gas constant; and T is the temperature in Kelvin. The primary assumption of this model is that only one dominant degradation mechanism of the material operates during the reaction and that this mechanism will not change with time and temperature during the exposure [24]. Only the rate of degradation accelerated with the temperature increase. Eq. (2) can be transformed into:

$$\frac{1}{k} = \frac{1}{A} \exp\left(\frac{E_a}{RT}\right) \tag{3}$$

$$\ln\left(\frac{1}{k}\right) = \frac{E_a}{R} \frac{1}{T} - \ln(A) \tag{4}$$

From Eq. (3), the degradation rate k can be expressed as the inverse of time needed for a material property to reach a given value [24]. Eq. (4) further shows that the logarithm of time needed for a material property to reach a given value is a linear function of 1/T with a slope of E_a/R [24]. E_a and A can be easily calculated with the slope of the regression and the point of intersection between the regression and the Y-axis, respectively.

3.6. Differential scanning calorimetry (DSC)

DSC was used to obtain information on the thermal behavior and characteristics of polymer materials and composites, such as glass transition temperature (T_g) , melting point, curing process, crystallinity, thermal stability, and relaxation. In our study, specimens weighing 12–15 mg were cut from different GFRP samples (unconditioned GFRP specimens aged in saline solution and moist mortar at 50 °C for 365 d, and GFRP specimens aged in saline solution and moist mortar at 70 °C for 120 d), placed in aluminum pans, and were analyzed using a TA Instruments DSC Q10 calorimeter. Specimens were heated from 25 °C to 195 °C at a rate of 5 °C/min. The glass transition temperature of the specimens was determined in accordance with ASTM E1356 [40]. A decrease in T_g observed for the conditioned samples was deemed an indication of the plasticizing effect or chemical degradation. Aged samples maintaining T_g lower than the reference displayed irreversible chemical degradation.

3.7. Microstructural observations

Scanning-electron-microscopy (SEM) observations and image analysis were also performed to examine specimen microstructure before and after aging for different times. Samples observed under SEM were unconditioned specimens, GFR specimens aged in saline solution and moist mortar at $50\,^{\circ}\mathrm{C}$ for $365\,\mathrm{d}$, and GFRP specimens aged in saline solution and moist mortar at $70\,^{\circ}\mathrm{C}$ for $120\,\mathrm{d}$. All the specimens observed under SEM were first cut, polished, and coated with a thin layer of gold–palladium with a vapor-deposition process. Once the surfaces were coated, the transversal and longitudinal surfaces were examined with a JEOL JSM-840A SEM. These observations were conducted to check for any potential degradation of the glass fibers or interfaces.

3.8. Fourier-transform infrared spectroscopy (FTIR)

FTIR analysis of unconditioned bars and 12.7-mm mortar-wrapped bars aged in saline solution at 50 °C for 365 d was conducted. This analysis was performed to determine if hydrolysis reactions occurred in the polymer resin, which can lead to an important loss of mechanical properties. FTIR spectra were recorded using a Nicolet Magna 550 spectrometer equipped with an attenuated total reflectance (ATR) device. Fifty scans were routinely acquired with an optical retardation of 0.25 cm to yield a resolution of $4\,\mathrm{cm}^{-1}$.

4. Experimental results

4.1. Tensile-strength retention

Tensile testing of the unconditioned and aged GFRP specimens showed an approximately linear behavior up to failure. Specimens failed from fiber rupture. The failure was accompanied by delamination of fibers and resin, as shown in Fig. 3. No chemical deposit

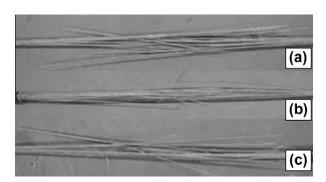


Fig. 3. Typical failure mode of GFRP bars for: (a) an unconditioned GFRP specimen;(b) a mortar-wrapped GFRP bar aged in the saline solution for 365 d at 50 °C; and (c) a mortar-wrapped GFRP bar aged in the saline solution for 120 d at 70 °C.

Table 2 Experimental tensile strength of the reference GFRP bars and GFRP bar specimens aged in the saline solution at 23 $^{\circ}$ C, 40 $^{\circ}$ C, 50 $^{\circ}$ C, and 70 $^{\circ}$ C.

Immersion	Temperature	Mean tensile	Standard
duration (d)	(°C)	strength (MPa)	deviation (MPa)
0	23	788	54
60	23	781	32
	40	777	42
	50	764	23
120	23	772	26
	40	760	43
	50	753	20
	70	744	34
210	23	763	38
	40	745	38
	50	744	40
365	23	726	13
	40	712	53
	50	702	22

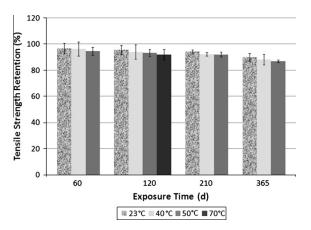


Fig. 4. Tensile-strength retention of the GFRP bars aged in the saline solution at 23 °C, 40 °C, 50 °C, and 70 °C.

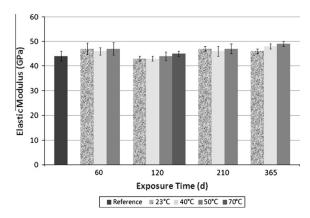


Fig. 5. Elastic modulus of GFRP bars aged in the saline solution at 23 °C, 40 °C, 50 °C, and 70 °C.

was observed on bar surfaces before testing. Micelli and Nanni [4] observed similar tensile failure modes with GFRP bars.

Table 2 provides the experimental results from tensile testing related to the ultimate strength of aged GFRP bars tested after accelerated aging at 23 $^{\circ}$ C, 40 $^{\circ}$ C, and 50 $^{\circ}$ C. Table 2 shows that the tensile strength for unconditioned the GFRP bars was

Table 3Water absorption at saturation before and after conditionings in the solution.

Conditioning	Temperature (°C)	Duration (d)	Moisture uptake (%)
Unconditioned			0.14
Embedded in concrete and immersed in the saline solution	50	365	0.15
Embedded in concrete and immersed in the saline solution	70	120	0.13

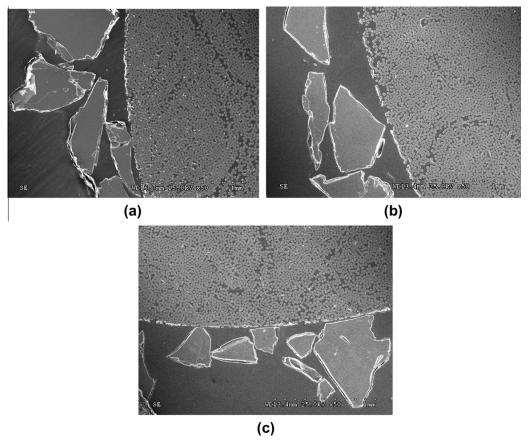


Fig. 6. Micrograph of the bar/coating interface (×50) of: (a) an unconditioned GFRP bar; (b) a mortar-wrapped GFRP bar aged in the saline solution for 365 d at 50 °C; and (c) a mortar-wrapped GFRP bar aged in the saline solution for 120 d at 70 °C.

 788 ± 54 MPa. Note that the tensile strength dropped to 702 ± 22 MPa for bars immersed for 365 d in salt solution at 50 °C. Robert et al. [2] reported that the tensile strength of similar bars dropped to 665 ± 62 MPa after 240 d of exposure to water at 50 °C, indicating that immersion in the saline solution had no more impact on the durability of GFRP bars than immersion in tap water.

The tensile strength of the GFRP bars subjected to very high temperatures (70 °C) for 120 d decreased to 744 MPa \pm 34 MPa, which is similar to the tensile strength (747 \pm 11 MPa) of similar bars embedded in concrete and aged in tap water under the same immersion conditions.

Fig. 4 shows the retention of the ultimate strength of aged GFRP bars according to the duration of immersion at various temperatures. Fig. 4 shows a slight decrease in the ultimate tensile strength of GFRP bars as the length of immersion increased. Furthermore, immersion temperature clearly affected loss of strength. The Fig. 4 shows that the loss of strength was 14%, 12%, and 10% at 50 °C, 40 °C, and 23 °C, respectively, for 12 months of immersion. This phenomenon is due to the increasing diffusion rate of the solution inside the sample and to the acceleration of the chemical

reaction of degradation with immersion temperature, leading to a higher absorption rate of the solution for the same time of immersion and accelerated degradation reaction. The absorption of solution can lead to degradation of the fibers and fiber/matrix interface, leading to a loss in ultimate tensile strength. In a similar study, Robert et al. [2] recorded losses of resistance of 16%, 10%, and 9% after 240 d of aging of embedded GFRP bars immersed in tap water at 50 °C, 40 °C, and 23 °C, respectively.

4.2. Effect on Young's modulus

Fig. 5 shows the change in the elastic modulus of the aged GFRP bars according to length of immersion at various temperatures. Indeed, the measured results show that, even after 365 d, the losses in elastic modulus of the GFRP bars were negligible and that all aged bars were not affected by the higher temperatures or the exposure to the saline solution when embedded in concrete. This result indicates that the elastic modulus of GFRP bars is not affected by aging in a concrete environment with saline solution simulating seawater or deicing salts.

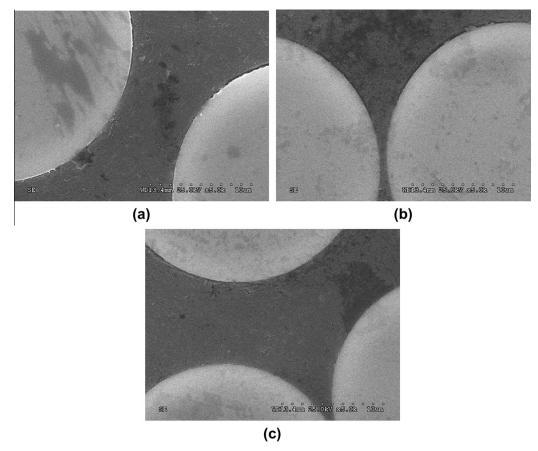


Fig. 7. Micrograph of the bar/coating interface (\times 5000) of: (a) an unconditioned GFRP bar; (b) a mortar-wrapped GFRP bar aged in the saline solution for 365 d at 50 °C; and (c) a mortar-wrapped GFRP bar aged in the saline solution for 120 d at 70 °C.

4.3. Results of water-immersion testing

Table 3 presents water uptake at saturation of GFRP bars embedded in mortar before and after conditioning in saline solution. The results presented in Table 3 are the average values obtained from five test specimens. These results show that the moisture absorption at saturation of the GFRP bars was not affected by aging in saline solution. The measured moisture uptake at saturation of the GFRP bars was 0.14%, 0.15%, and 0.13%, before immersion in the saline solution for 365 d at 50 °C, and after immersion in the saline solution for 120 d at 70 °C, respectively. The slight variation of moisture absorption is related to the precision of the balance used for the measurement.

4.4. Microstructural effects

The visual and microstructural observations of the GFRP bars showed no significant damage after 365 d of immersion in the saline solution at $50\,^{\circ}\text{C}$ or after 120 d of immersion at the highest temperature ($70\,^{\circ}\text{C}$). The micrographs in Fig. 6 show the interface between the mixture of fibers and resin and the silica coating of the GFRP bars for (a) an unconditioned GFRP bar, (b) a mortar-wrapped GFRP bar aged in the saline solution for 365 d at $50\,^{\circ}\text{C}$, and (c) a mortar-wrapped GFRP bar aged in the saline solution for 120 d at $70\,^{\circ}\text{C}$. Fig. 7 shows micrographs of the fiber/matrix interface for the GFRP bars for (a) an unconditioned GFRP bar, (b) a mortar-wrapped GFRP bar aged in the saline solution for 365 d

at 50 °C, and (c) a mortar-wrapped GFRP bar aged in the saline solution for 120 d at 70 °C.

Observation of these interfaces and the microstructure in general demonstrate that conditioning of mortar-wrapped bars in water did not affect the microstructural properties of the GFRP bars. This is in accordance with what Robert et al. [2] reported when similar mortar-wrapped GFRP bars were immersed in tap water. This phenomenon clearly illustrates that GFRP bars are not significantly affected by accelerated aging in saline solution.

4.5. Bar/concrete interface

If there were any degradation in the GFRP-bar resin or fibers at the interface between the bar and concrete, it is expected that bond mechanisms and the durability of reinforced member would be affected. Fig. 8 shows the GFRP bar/concrete interface for (a) an unconditioned reference bar, (b) a specimen embedded in concrete and aged in saline solution at 50 °C for 365 d, and, (c) a specimen embedded in concrete and aged in saline solution at 70 °C for 120 d. Moreover, there was no significant damage to the bar/concrete interface after aging in saline solution, even at high temperature (70 °C).

4.6. Effects on polymer matrix

FTIR analysis of unconditioned bars and 12.7-mm mortar-wrapped bars aged in saline solution at $50\,^{\circ}\text{C}$ for 365 d was conducted (Fig. 9). This analysis was performed to determine if

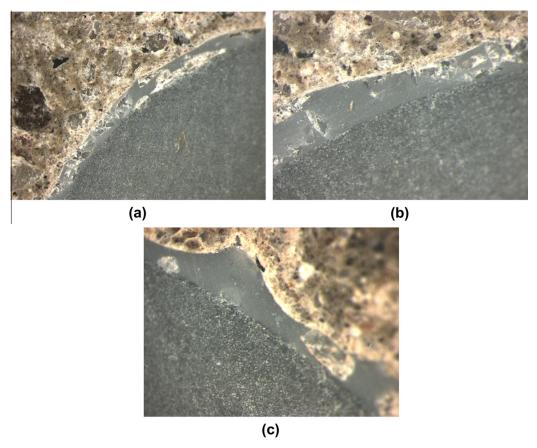


Fig. 8. Micrographs of the GFRP bar/concrete interface of: (a) an unconditioned specimen; (b) a conditioned bar specimen aged in the saline solution at 50 °C for 365 d; and (c) a conditioned bar specimen aged in the saline solution at 70 °C for 120 d.

hydrolysis reactions occurred in the polymer resin, which can lead to an important loss of mechanical properties. When a hydrolysis reaction occurs, new hydroxyl groups are formed and the corresponding infrared band increases. Changes in the peak intensity were quantified by determining the ratio of the OH peak to the resin's carbon–hydrogen stretching peak, which is not affected by conditioning. The experimental ratio of the OH peak to the resin's carbon–hydrogen stretching peak for the 12.7-mm-diameter mortar-wrapped GFRP samples immersed in saline solution for 365 d to °C was 0.29 compared to 0.30 for the unconditioned samples. So, the hydroxyl peak did not show any significant changes. This indicates no significant hydrolysis of GFRP bars in these environmental conditions.

DSC was also used to obtain information on the thermal behavior and characteristics of polymer materials and composites, such as glass transition temperature (T_g) and cure ratio. A decrease in T_{σ} for the conditioned samples was deemed indication of plasticizing effect or chemical degradation. These degradation phenomena could confirm the presence of irreversible degradation phenomena at high temperatures. Aged samples with a T_g lower than for the reference showed irreversible chemical degradation. Table 4 presents the glass-transition-temperature (T_g) values for the first and second heating of unconditioned and aged samples as well as the cure ratio for both sample types. Note that, for the unconditioned and aged GFRP samples, the T_g corresponding to the second heating run was close to the T_g corresponding to the first scan. These results confirm the high cure ratio of 99% measured by DSC and shown in Table 4. Nevertheless, the results in Table 4 reveal no significant changes in the T_g value of the GFRP bars after

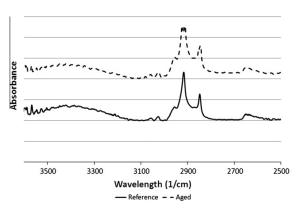


Fig. 9. FTIR spectra for unconditioned and aged samples.

aging in saline solution at 50 °C for 365 d. Even after 120 d of immersion in saline solution at high temperature (70 °C), the T_g of the GFRP bars embedded in moist mortar remained constant. This result reveals no major effect on the thermal properties of the resin, which could occur after conditioning of the mortar-wrapped FRP bars, was detected by DSC.

4.7. Prediction of long-term behavior

Predictions of the service life of the GFRP bars at mean annual temperatures (MATs) of 10 °C and 50 °C were performed according

 Table 4

 Results of differential-scanning-calorimetry (DSC) analysis.

Conditioning	Temperature (°C)	Duration (d)	T _g run 1 (°C)	T _g run 2 (°C)	Cure ratio (%)
Unconditioned Embedded in concrete and immersed in the saline solution	50	365	116 115	117 118	99 99
Embedded in concrete and immersed in the saline solution	70	120	117	118	99

to the procedure proposed in Appendix A based on previous work performed by Bank et al. [23]. The temperature of 10 °C corresponds well to the mean average temperature of northern regions, where deicing salts are often used. The temperature of 50 °C exacerbates the combined effect of the mean annual temperature and the marine environment of the Middle East, Caribbean, and Florida. The Arrhenius plot can be used to extrapolate the service life necessary to reach the established tensile-strength retention levels (PR) for any temperature. Consequently, predictions were made for tensile-strength retention as a function of time for immersions at 10 °C and 50 °C, and the general relation between the PR and the predicted service life at the average temperatures of 10 °C and 50 °C were drawn for the GFRP bars (Fig. 10). Fig. 10 shows that the predicted time to reach the determined strength-property retention level (PR) for the GFRP bars embedded in concrete and immersed in saline solution at an isotherm temperature of 10 °C is approximately 2 and 200 years for a PR of 90% and 75%, respectively. For the same bar immersed at an isotherm temperature of 50 °C, the service-life predictions are approximately 0.75 and 35 years for a PR of 90% and 75%, respectively. As expected, these results show that the long-term tensile strength of the GFRP bars was more affected by the saline solution and moist concrete in a warm climate. Robert et al. [2] showed that the predicted time to reach a PR of 90% and 75% for the same GFRP bars embedded in concrete and immersed in tap water at an isotherm temperature of 6 °C was approximately 1 and 210 years, respectively. This observation led to the conclusion that saline solution does not have a more significant effect on the long-term behavior of GFRP bars embedded in concrete. The predicted service life of GFRP bars embedded in concrete and aged in saline solution at an isotherm temperature of 10 °C to reach a PR less than 70% can be estimated to be infinite. Table 5 presents the tensile-strength retention after a service life of 75, 100, and 150 years at mean annual temperatures of 10 °C and 50 °C. Table 5 indicates that, even after a service life of 150 years, which corresponds to the longest design service life, the tensile-strength retention was still 68% and 75% for mean annual temperatures of 50 °C and 10 °C, respectively. These predictions show that the GFRP bars are durable with respect to the concrete

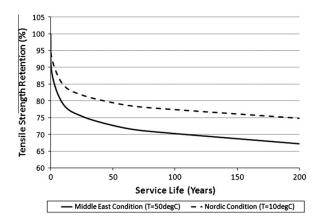


Fig. 10. General relation between the PR and the predicted service life at mean annual temperatures of 10 $^{\circ}\text{C}$ and 50 $^{\circ}\text{C}$.

Table 5Tensile-strength retention at different mean annual temperatures.

Service life (years)	Tensile-strength retention (%)		
	MAT = 10 °C (Northern regions)	MAT = 50 °C (Middle East and warm regions)	
75	78	71	
100	77	70	
150	76	68	

environment and saline environment, which is supposed to be simulated by immersion of the embedded GFRP bars in saline solution of 3% NaCl.

5. Summary and conclusions

In this research study, unstressed GFRP bars were embedded in concrete and exposed to salt solution of 3% NaCl at 23 °C, 40 °C, and 50 °C to accelerate the effect of the concrete environment and to simulate the effect of seawater or deicing salts. In addition, the GFRP bars were conditioned by subjecting them to an extreme temperature of 70 °C to screen for any potential effect of application in humid and warm environments. The pre- and postexposure tensile strengths of the bars were deemed indicative of specimen durability and were used for long-term property predictions based on the Arrhenius theory. In addition, Fourier-transform infrared spectroscopy (FTIR), differential-scanning calorimetry (DSC), and scanning electron microscopy (SEM) were used to characterize the aging effect on the GFRP reinforcing bars. Based on the results of this study, the following conclusions may be drawn:

- 1. The change in tensile strength of the tested GFRP bars was minor even at high temperatures (50 °C and 70 °C) making for a more aggressive environment (concrete and saline solution).
- 2. No significant microstructural changes were observed after 365 d of immersion of the GFRP bars embedded in concrete in the saline solution at 50 °C. The interfaces between the bars and concrete and between the resin and fibers appeared unaffected by moisture absorption and high temperatures.
- 3. The polymer matrix was not affected by moisture absorption and high temperatures: no changes in the glass transition temperature occurred, as observed by differential scanning calorimetry. FTIR did not show any significant changes in the polymer's chemical structure, i.e. degradation.
- 4. Predictions of the long-term behavior of the conditioned GFRP bars were made using a method based on the Arrhenius relation and were compared to predictions for similar mortar-wrapped GFRP bars immersed in tap water. These predictions provide information about the long-term tensile-strength retention. In order to use the Arrhenius relation, we suppose that the mechanisms of degradation stay the same during bar service life, but that they are accelerated by aging.
- 5. According to the long-term predictions, the tensile-strength retention of GFRP bars embedded in moist concrete and immersed in the saline solution will decrease by 25% after 200 and 35 years when immersed at an isotherm temperature

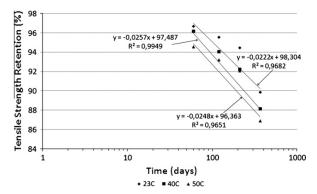


Fig. A1. Plot of the tensile strength retention as a function of time.

of 10 °C and 50 °C, respectively. It was shown that the service life needed to reach a tensile-strength retention of less than 70% at 10 °C should be infinite.

6. Civil engineers currently aim at designing structures for service lives of up to 100 years. According to the predictions, even after a service life of 100 years, the tensile-strength retention of the tested GFRP bar would still be 70% and 77% for mean annual temperatures of 50 °C and 10 °C, respectively, which are higher

than the design tensile strength according to the ACI 440 [41] (guaranteed tensile strength multiplied by the environmental reduction factor = $C_E \times f_{fi}^*$).

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Appendix A. Procedure for the long-term prediction of tensile strength

A.1. Introduction

The model used in this study to predict the tensile strength of aged specimens is based on the Arrhenius relation and is similar to that used for glass–fiber reinforced concrete (GRC) by Litherland et al. [25] and described by Bank et al. [23]. The procedure provides a predicted service life for the FRP composite material at a desired level of strength retention, or provides the level of strength retained at a desired service life. The method is based on the Arrhe-

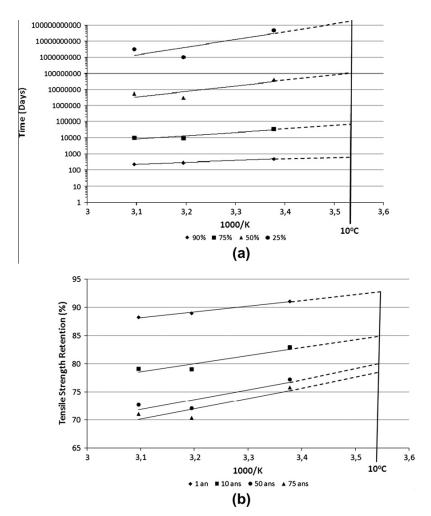


Fig. A2. Arrhenius plots for (a) service life as a function of temperature and percent retention and (b) property retention as a function of temperature and service life.

nius relation characterized by an activation energy that causes long-term chemical degradation in FRP materials. According to the Arrhenius law, elevated temperatures can be used as accelerating factors of the degradation of FRP materials and the change in mechanical properties of FRP materials can be measured as a function of conditioning time.

A.2. Summary of the method

A.2.1. The average tensile strength value for specimens tested at each temperature (23, 40 and 50 °C) and time of conditioning (60, 120, 210 and 365 d) were calculated. From these averages, the property retention (PR) values for each property as the average property value at the time of testing (t) divided by the average property value for the reference specimen (t = 0) were calculated.

A.2.2. These data were then plotted on a graph with time on the horizontal axis using a logarithmic scale, and the property retention value on the vertical axis using a linear scale (Fig. A1). Using linear regression, a line was fit through each set of data (one for each temperature of conditioning). The regression line must have a minimum r^2 of 0.80. In the present case, all the r^2 are higher than 0.96.

A.2.3. The Arrhenius plot have been constructed following two ways. First, the time have been plotted as a function of inverse absolute temperature for various percentages of property retention (Fig. A2a). Alternatively, property retention have been plotted as a function of inverse absolute temperature for various chosen lifetimes (Fig. A2b).

A.2.3.1. The time to reach different levels of property retention at each of the aging temperatures have been determined. These times have been calculated by substituting various values of tensile strength retention (90%, 75%, 50% and 25%) into the regression equations plotted in Fig. A1. Graphically, this is represented as drawing horizontal lines in Fig. A1 at 90%, 75%, 50% and 25% retention, and then drawing vertical lines from the intersection between these lines and the regression lines for the various temperatures. For each chosen level of property retention, the time in days has been plotted on a logarithmic scale as a function of the reciprocal of the absolute temperature (1000 K⁻¹) (Fig. A2a). The relationships between the time and the reciprocal of the absolute temperature for each level of property retention have been extrapolated (represented by dashed lines in Fig. A2a) to determine the time to reach the chosen levels of property retention at 10 °C.

A.2.3.2. Alternatively, service life times, represented by the time, have been substituted into the regression equations in Fig. A1 to find the tensile strength retention at different time at each of the aging temperature. Graphically, this is represented as drawing vertical lines in Fig. A1 at 1, 10, 50 and 75 years, and then drawing horizontal lines from the intersection between these lines and the regression lines for the various temperatures. For each chosen lifetime, the tensile strength retention in percentage has been plotted as a function of the inverse temperature (1000 K⁻¹) (Fig. A2b). The relationships between the tensile strength retention and the reciprocal of the absolute temperature for each service lifetime have been extrapolated (represented by dashed lines in Fig. A2b) to determine the levels of tensile strength retention at the chosen life times at 10 °C.

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