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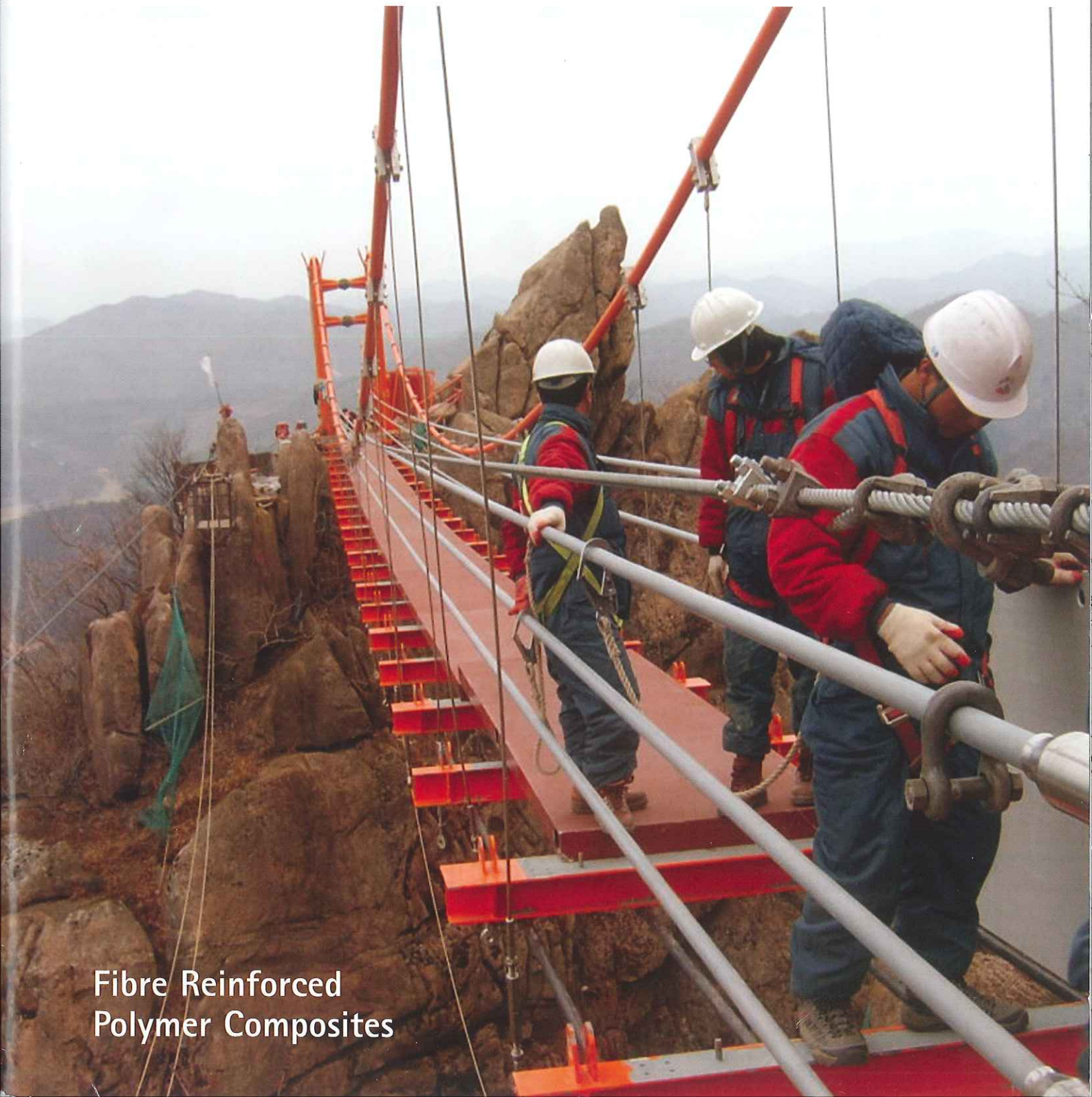

## Fibre Reinforced Polymer Composites

# Effects of Hygrothermal Ageing on the Mechanical Properties of Glass-Fibre-Reinforced Polymer Pultruded Profiles

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## Abstract

This paper presents the results of an experimental study on the physical and mechanical changes suffered by glass-fibre-reinforced polymer (GFRP) pultruded profiles, made of either unsaturated polyester or vinylester resins, after accelerated hygrothermal ageing. Specimens from both types of profiles, comprising identical fibre contents and architectures, were subjected to: (a) immersion in demineralized water; (b) immersion in saltwater at temperatures of 20, 40 and 60°C for 12 months and; (c) continuous condensation at 40°C for 9 months. Batches of test specimens from both profiles, conditioned in those accelerated exposure environments, were periodically monitored with respect to: (a) mass changes; (b) variation in glass transition temperature evaluated through dynamic mechanical analysis (DMA) and; (c) degradation of mechanical properties, assessed by means of tensile, flexural and interlaminar shear tests.

**Keywords:** GFRP; unsaturated polyester matrix; vinylester matrix; pultruded profiles; hygrothermal ageing; mechanical properties.

## Introduction

Fibre-reinforced polymer (FRP) materials in general, and glass-fibre-reinforced polymer (GFRP) pultruded profiles in particular, are being used increasingly in civil engineering applications as an alternative to traditional materials, such as steel, reinforced concrete and timber. This growing acceptance of FRP structures, particularly in corrosive applications, can be attributed to their improved durability and low maintenance requirements, in addition to other intrinsic advantageous properties of advanced composite materials that include high strength, lightness and low thermal conductivity.[1,2]

In regard to durability, the long-term use of FRP materials in vessels, pipelines, storage tanks and chemical-resistant equipment of the oil industry provides evidence of their improved performance in relatively harsh and corrosive environments, when compared to traditional materials. However, for civil engineering applications; owners, designers and contractors request comprehensive and validated data on durability, since the service life of mainstream structures is generally expected to exceed 50 years. As most FRP civil engineering structures are quite recent[3] and research already carried out on this topic is still limited, such information correlating the effects of environmental degradation on the physical, chemical and mechanical properties of FRPs is currently not available. The development of reliable degradation models, similar to those already available for traditional materials, involves gathering such comprehensive data on durability. It is also worth mentioning that comparative studies on the performance of alternative matrix formulations used in FRP materials are also scarce. In this context, paradoxically, the widespread acceptance of FRP materials is delayed because of concerns about durability. In this regard, several authors have recently identified durability as one of the most critical gap between perceived need for information and available information, and as a crucial area of focus for future research on FRP materials.[4,5]

This paper presents results of an experimental study on the physical and mechanical changes suffered by GFRP pultruded profiles, made of either unsaturated polyester or vinylester resins with identical fibre contents and architectures, following accelerated hygrothermal ageing. Specimens from both types of profiles were subjected to immersion in demineralized water and saltwater for temperatures of 20, 40 and 60°C and, in addition, to continuous condensation at 40°C, simulating the ageing conditions in wet environments (e.g. placed under water or subjected to high levels of moisture), in coastal areas or where the use of de-icing salts is common. Other environmental degradation agents, not investigated in the present study, include acid or alkaline fluids, thermal cycles, freeze–thaw cycles, ultraviolet radiation and elevated temperature.[4] Batches of test specimens from both types of profiles, placed in the above-mentioned degradation environments, were periodically removed and monitored regarding: (a) mass changes; (b) variation in glass transition temperature evaluated through dynamic mechanical analysis (DMA) and; (c) degradation of mechanical properties in tension, flexure and shear. This paper provides extensive data on the effects of hygrothermal ageing on the performance of GFRP pultruded profiles, thereby contributing to shortening of the above-mentioned gap between perceived need for information and available information on durability. In addition, as similar fibre contents/architectures were used in this study, results obtained allow for a direct comparison between the performances of unsaturated polyester and vinylester resins.

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## Experimental Programme

### *Materials*

The material studied was obtained from two commercial GFRP pultruded tubular profiles (50 × 50 mm, thickness 5 mm). This material consists of alternating layers of unidirectional E-glass fibre rovings and strand mats embedded in either unsaturated polyester resin (profile "UP") or vinylester resin (profile "VE"). The former resin is used in most structural applications when there are no particular requirements in terms of environmental aggressiveness, whereas the latter is often selected for applications in relatively harsh or corrosive environments. The two profiles were produced with the same glass fibre content and architecture (*Figs. 1 and 2*), thus allowing comparison of the durability performance of the polyester and vinylester resins used in these *off-the-shelf* standard profiles.

### *Initial Characterization*

The chemical, physical and mechanical characterization of both types of materials was carried out using the following techniques:

1. *Chemical composition:* Infrared spectra of the materials were studied in the 450 to 4000 $cm^{-1}$ region, according to ASTM E 1252 standard.[6] For these measurements, powder samples scraped from the surfaces of test specimens were mixed with dry spectroscopic-grade potassium bromide and pressed into pellets. 32 scans were collected and averaged at a spectral resolution of 4 $cm^{-1}$, in a *Thermo Scientific Nicolet* spectroscope. The glass fibre content was determined by the calcination method described in ASTM D 3171 standard.[7]
2. *Physical properties:* Density was measured according to ISO 1183 standard[8] (immersion method). Glass transition temperature ($T_g$) was determined by DMA, in accordance with ISO 6721 standard.[9] Three-point bending type clamped specimens of 5 × 15 × 60 mm were tested at constant frequency of 1 Hz and strain amplitude of 15 μm, using a DMA analyser. The analysis was carried out from room temperature up to 200°C, at a rate of 2°C/min. Three replicates were tested for each type of material.
3. *Mechanical properties:* Tensile tests were conducted according to ISO 527—parts 1 and 5 standard[10] in rectangular test specimens (5 × 25 × 300 mm), without end tabs, using an universal testing machine with a load capacity of 100 kN. Three-point bending flexural tests were performed according to ISO 14125 standard,[11] in rectangular test specimens (5 × 15 × 150 mm) with a span of 100 mm using a system constituted by a hydraulic press with a 10 kN load capacity. Interlaminar shear tests were carried out in accordance with ASTM D 2344 standard[12] in rectangular test specimens (5 × 10 × 30 mm), loaded in a 20 mm span with the same system used in the bending tests. Compressive properties were determined according to ASTM D 695 standard[13] in rectangular specimens (5 × 10 × 30 mm).

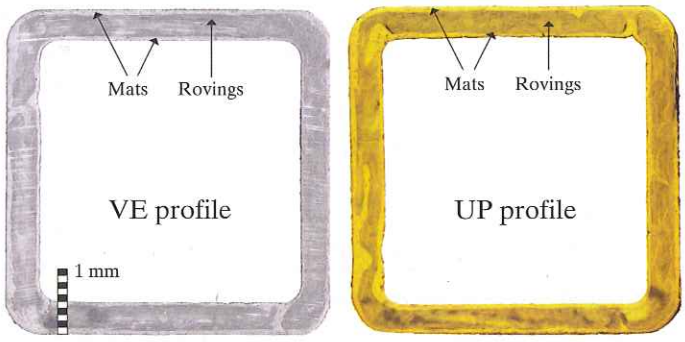


*Fig. 1: Cross section and fibres architecture of UP and VE profiles (UP = Unsaturated polyester resin; VE = Vinylester resin)*

*Fig. 2: Outer mats and inner rovings of a burnt laminate (VE profile)*

### *Exposure Environments*

In order to study the potential degradation of the two types of profiles in typical environments of civil engineering applications, test specimens were subjected to the exposure conditions described in *Table 1*.

The experimental procedures used in the immersion ageing conditions, both in water and in saltwater, were based on ISO 175 standard,[14] with the concentration of salt in the saltwater medium being in agreement with ASTM D 1141 standard[15]—for both media, the cut edges of the test specimens were completely immersed. The ageing performed in the continuous condensation chamber was carried out according to the procedures described in ISO 6270 standard.[16]

### *Experimental Characterization after Hygrothermal Ageing*

After exposure to the different ageing conditions described in *Table 1*, batches of aged test specimens obtained from each type of profile were subjected to the following characterization techniques:

1. *Mass changes:* Control specimens with geometry similar to that of specimens used in DMA were removed periodically from the different exposure environments in order to evaluate their mass changes. After removal from the exposure environments, the surface of the specimens was dried with a cloth in order to remove any residual free moisture. Specimens were then immediately weighed using a 0,0001 g precision scale.
2. *Dynamic mechanical analysis:* The $T_g$ was measured according to the same procedure used in the initial characterization tests. Three replicates were tested for each type of

material and ageing condition (duration and exposure environment).

3. *Mechanical behaviour:* Tensile, flexural and interlaminar shear tests were performed according to the above-mentioned standards. At least five replicates were tested in the longitudinal direction for each material and ageing condition.

Excluding the study of the mass changes, after being removed from the different exposure environments and prior to further testing, specimens were placed inside polyethylene bags. These were hermetically closed, in order to maintain the moisture content of the material, and then placed inside a room with temperature controlled at 20 (±2)°C. Prior to testing, specimens were removed from the polyethylene bags and immediately tested without any further conditioning.

## Results and Discussion

### *Initial Characterization*

The results of initial chemical, physical and mechanical characterization of both profiles are listed in *Table 2*.

Chemical composition determined by Fourier transform infrared spectroscopy (FTIR) (*Fig. 3*) showed little differences between the two materials analysed. In fact, the spectra of both profiles were quite similar. The localizations and intensity of the peaks confirmed the presence of ester, as well as aromatic and aliphatic structures, which are common in the molecular structure of both unsaturated polyester and vinylester resins. FTIR spectra also showed the existence of calcium carbonate (as filler) and silica (from the glass fibres).

The glass fibre content and density of the VE profile were slightly higher than those of the UP profile. On the other hand, the $T_g$ (obtained from both the storage modulus, $E'$, and the loss factor, $\tan\delta$) of the VE profile was lower than that of the UP profile. From the mechanical aspect point of view, the UP and VE profiles started to lose their initial performance at temperatures above 108 and 99°C, respectively (*Fig. 4*).

With regard to the mechanical behaviour, in all characterization tests (tension, flexure, interlaminar shear and compression), both types of profiles exhibited a well defined and typical linear elastic behaviour up to failure. A comparative analysis of the mechanical behaviour exhibited by both profiles shows that they are quite similar in their tensile properties (both strength, $\sigma_{tu,x}$, and modulus, $E_{t,x}$) and interlaminar shear strength ($\sigma_{u,sbs}$). However, in flexure, the VE profile showed superior initial performance, for both strength ($\sigma_{fu,x}$,) and stiffness ($E_{f,x}$). Owing to the relatively high scatter in the results obtained for the compressive strength ($\sigma_{cu,x}$), it was decided to exclude the compressive properties from this durability study.

### *Moisture Uptake with Hygrothermal Ageing*

*Figure 5* illustrates the mass variation exhibited by both profiles for the different immersion media (solutions of demineralized water, *W*, and saltwater, *S*) and temperatures

| Type of exposure | Duration | Conditions |
|---|---|---|
| Immersion in water (W-20), (W-40), (W-60) | 3, 6, 9 and 12 months | Composition: demineralized water<br>Temperatures: 20 (±2)°C, 40 (±1)°C and 60 (±1)°C |
| Immersion in saltwater (S-20), (S-40), (S-60) | | Composition: 35 g/L NaCl<br>Temperatures: 20 (±2)°C, 40 (±1)°C and 60 (±1)°C |
| Continuous condensation (CC-40) | 3, 6 and 9 months | Temperature: 40 (±2)°C<br>Relative humidity: 100% |

*Table 1: Exposure ageing conditions*

| Property | Test method | | Profile UP | Profile VE |
|---|---|---|---|---|
| Chemical composition | FTIR | | FTIR spectra consistent with unsaturated polyester or vinylester, with presence of calcium carbonate and silica | |
| Glass fibre content (%) | Calcination | | 68,4 ± 1,8 | 68,7 ± 0,4 |
| Density (g/cm$^3$) | Immersion | | 1,869 ± 0,113 | 2,028 ± 0,052 |
| $T_g$ (°C) | DMA | $E'_{initial}$ | 107,9 ± 10,8 | 98,6 ± 7 |
| | | $\tan\delta$ | 146 ± 2,3 | 126,9 ± 2,3 |
| Mechanical properties | Tension | $\sigma_{tu,x}$ (MPa) | 406 ± 31 | 393 ± 51 |
| | | $E_{t,x}$ (GPa) | 37,6 ± 2,6 | 38,9 ± 4,1 |
| | Flexure | $\sigma_{fu,x}$ (MPa) | 417 ± 65 | 537 ± 73 |
| | | $E_{f,x}$ (GPa) | 20,0 ± 6,9 | 28,4 ± 3,4 |
| | Interlaminar shear | $\sigma_{u,sbs}$ (MPa) | 38,5 ± 2,7 | 39,2 ± 4,2 |
| | Compression | $\sigma_{cu,x}$ (MPa) | 280 ± 123 | 360 ± 131 |

*Table 2: Initial physical, chemical and mechanical properties*

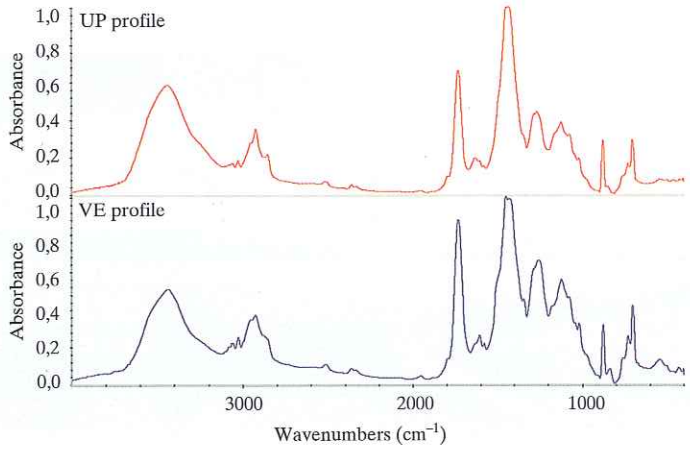


*Fig. 3: FTIR spectra of UP and VE profiles*

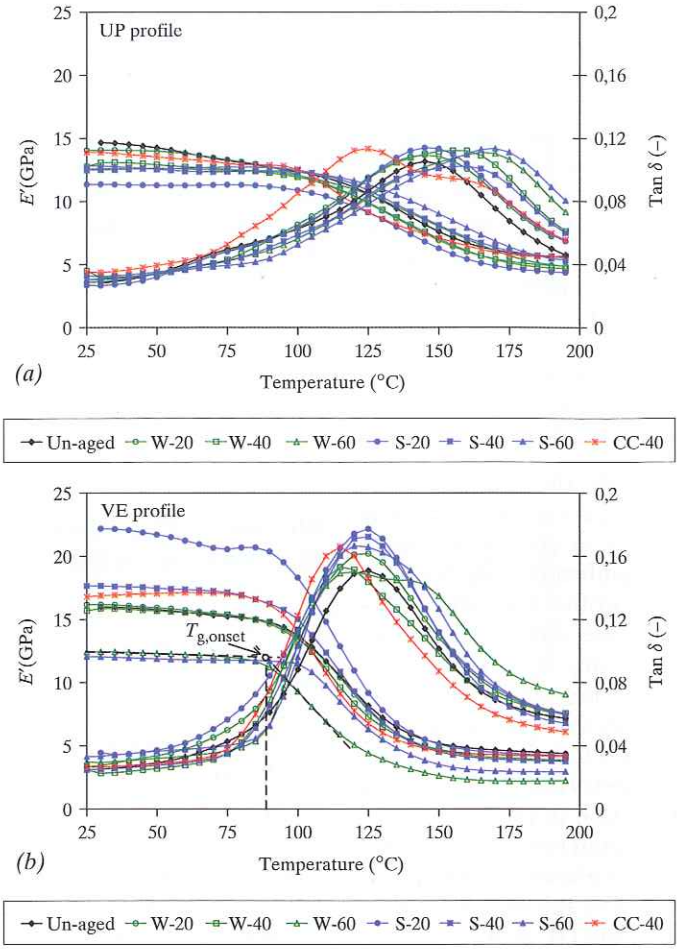


*Fig. 4: DMA 3-point bending curves of UP (a) and VE (b) profiles before and after hygrothermal ageing*

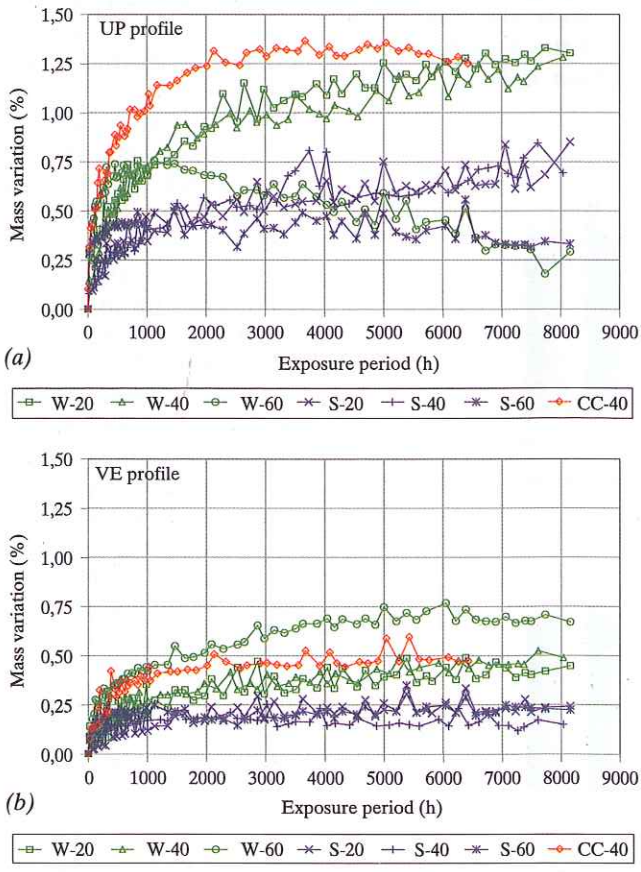


*Fig. 5: Mass variation of UP (a) and VE (b) profiles for different hygrothermal ageing conditions*

(20, 40 and 60°C), as well as in continuous condensation (*CC*) at 40°C.

*Figure 5* shows that the evolution of all mass variation curves follow roughly a *Fickian* response (i.e. a fast initial mass gain that slows as saturation approaches), with rates of mass uptake increasing with temperature, particularly in the beginning of the exposure. It can also be seen that, for similar ageing conditions (immersion media and temperatures), the comparison of the mass variation exhibited by both profiles depicts significant differences, with the mass uptake for the VE profile being considerably lower than that exhibited by the UP profile for all hygrothermal ageing conditions; these differences, already reported by Chin *et al.*[17], stem mainly from the distinct water absorption capacities of both resin systems, in particular, the higher hydrolytic stability of VE resins. *Figure 5* also shows that, for similar temperatures, mass uptake in saltwater was always lower than that in demineralized water, for both UP and VE profiles. Finally, one can readily observe that the increasing immersion temperature does not have a direct correlation with the increased level of mass uptake and this result should be attributed to the potential mass loss by extraction of low molecular components, an effect that is expected to increase with the immersion temperature. In fact, weight changes in these ageing processes usually result from a balance between the water uptake due to moisture ingress and the loss of material. When compared with the immersion in demineralized water at 40°C, under continuous condensation at 40°C both materials exhibited a higher initial weight gain, although for longer periods, weight gains for those environments became quite similar.

### *DMA after Hygrothermal Ageing*

*Figure 4* shows the results of DMA after 12 months of immersion and 9 months of continuous condensation—for each condition, only one curve corresponding to a representative specimen is plotted. The left axis represents the variation of $E'$ curves with temperature, which exhibit a characteristic "step" in the glass transition region; the right axis shows the corresponding tan$\delta$ curves, which present a typical peak in that region.

The variation in the behaviour exhibited by the $E'$ curves at the transition region reflects mainly the changes

in the polymer matrix performance, which progresses from a glassy state to an elastomeric state, characteristic of its viscoelastic nature. In fact, the reinforced material (in this case, the glass fibres) does not suffer a stiffness reduction in this temperature range. Therefore, the DMA technique indicates the contribution of the viscoelastic nature of the matrix for the overall behaviour of the composite, and in the present study, this information is useful to help understand the actual influence of the matrix nature on the durability of the composite. In addition, the quality of the fibre–matrix interface can also influence DMA results.

*Figure 6* plots, in summary, the variation of the $T_g$ of both profiles (mean value ± standard deviation, determined based on the onset of $E'$), as a function of the type and duration of exposure.

For the UP profile, immersion in both demineralized water and saltwater caused, in general, a decrease in the value of $T_g$. It is seen that the maximum reduction in $T_g$ occurred for specimens immersed in demineralized water, whereas the minimum reduction corresponds to immersion in saltwater. After 12 months of exposure, $T_g$ seems to increase with the immersion temperature for both media; for saltwater immersion at 60°C, the $T_g$ becomes even higher than that of the un-aged material, most likely due to a post-curing phenomenon, induced by the increased temperature. For the UP profile, the tan$\delta$ curves for continuous condensation, and immersion in demineralized water at 60°C show the appearance of a second "peak" at higher temperatures (*Fig. 4*). The occurrence of this second peak, associated to the widening of its base, suggests that the ageing of the material involves a plasticization mechanism. The occurrence of two "peaks" in the tanδ curve may be attributed to the different mobility of two kinds of segments in the polymeric matrix, caused by their different extents of plasticization.

For the VE profile, the variation of $T_g$ was less dependent on the immersion temperature and, in general, its variation was less significant than that verified in the UP profile. The tan$\delta$ curves for the VE profile did not show any widening, suggesting that the molecular structure did not suffer significant changes. The only exceptions were the immersions at 60°C in both media, in which an asymmetry could be observed in the configuration of the tan$\delta$ curves, near their maximum value. This result is consistent with the lower water uptake ability exhibited by this material, when compared with the UP profile.

Water uptake by unsaturated polyester and vinylester composites is known to cause plasticization in the short term and hydrolysis over the long term through attack of the ester linkages.[18] As the ester group is located in the middle of the molecular structure of polyester, and in the ends of the molecular structure of vinylester, in principle, the later resin is more resistant to the above-mentioned plasticization mechanisms. Both these phenomena induce higher levels of molecular mobility, resulting in a consequent decrease in the $T_g$, although such decrease can often be offset through residual curing of the resins in aqueous media. These competing phenomena result in fluctuations in the $T_g$ as a function of the exposure period; in the experiments reported herein, such behaviour was shown, in particular, by the UP profile.

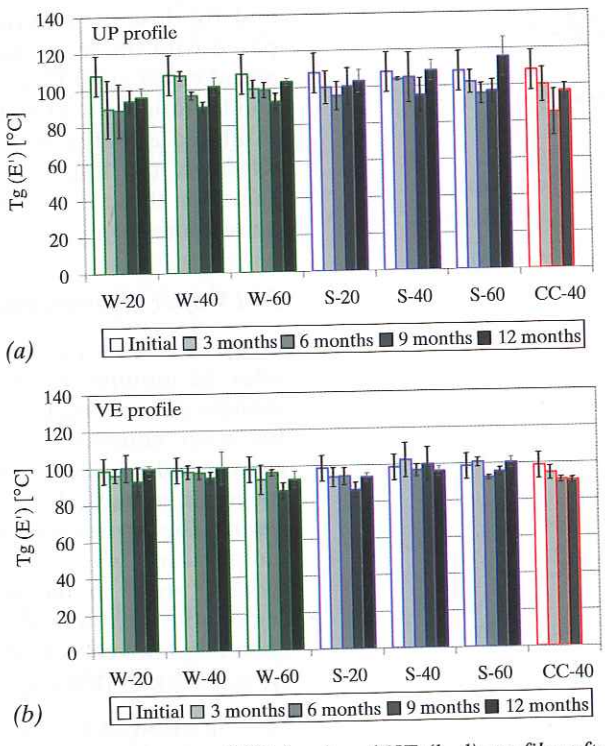


*Fig. 6: Glass transition temperature of UP (a, c) and VE (b, d) profiles after hygrothermal ageing*

### *Mechanical Performance after Hygrothermal Ageing*

#### *Tensile Properties*

The results obtained from tensile tests on both materials, namely, the tensile strength and the tensile modulus as a function of time and hygrothermal conditions, are presented in *Fig. 7*.

*Figure 7* shows that for all ageing conditions and for both materials there was an overall decrease in the average tensile strength with the duration of exposure (the only exception was the VE profile after 12 months of exposure in demineralized water at 20°C). As expected, the level of degradation of the tensile strength increased consistently with the temperature of the immersion medium, with maximum reductions occurring at 60°C—after 12 months of exposure, the lowest levels of retention were 64 and 75% for the UP and VE profiles, both immersed in demineralized water. The general higher aggressiveness of demineralized water compared to saltwater was consistent with previous investigations (e.g. those reported by Van de Velde and Kiekens[19]) and could be attributed to osmotic effects. For all hygrothermal ageing conditions and periods of exposure, the tensile strength retention of the VE profile was consistently higher than that of the UP profile. Chu *et al.*[20] reported tensile strength reductions in pultruded E-glass vinylester laminates that follow the overall trend of the present tests—the strength retention presented by those authors was considerably smaller, but so was the thickness of the tested material and, consequently, the maximum moisture uptake.

The variation exhibited by the average tensile modulus with the exposure period (*Fig. 7*), which was much more irregular and associated with

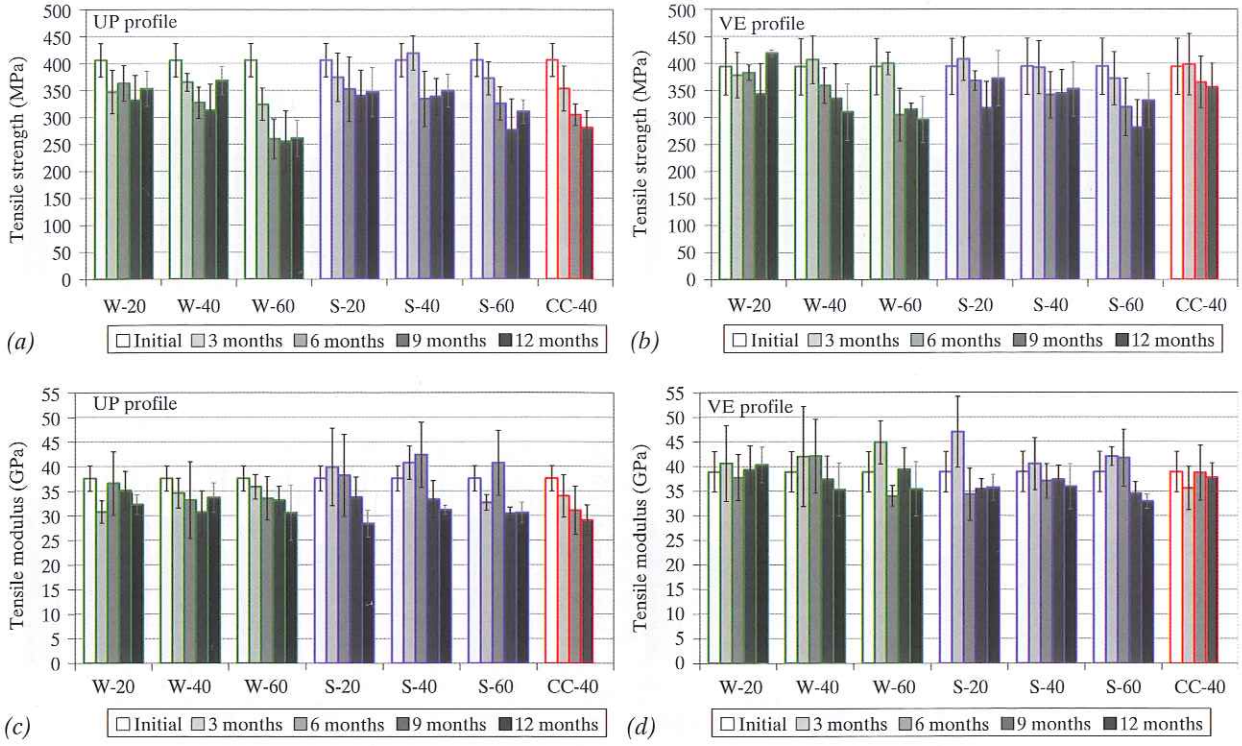


*Fig. 7- Tensile strength and modulus of UP (a, c) and VE (b, d) profiles after hygrothermal ageing*

higher coefficients of variation (when compared to the tensile strength), makes it more difficult to establish systematic analyses and comparisons between the two materials. However, for all exposure conditions and durations, one can conclude that the stiffness retention was considerably higher than the corresponding strength retention—the minimum levels of retention after 12 months were 76% for the UP profile (saltwater at 20°C) and 85% for the VE profile (saltwater at 60°C). In addition, and similar to the tensile strength, the stiffness retention of the VE profile was always higher than that exhibited by the UP profile. Finally, when compared to strength, stiffness retention appeared to be much more insensitive to the temperature and composition of the immersion media.

For both profiles the strength and stiffness retention of specimens immersed in demineralized water at 40°C was comparable to that of specimens under continuous condensation (particularly for the VE profile) and this result agrees well with the water uptake measurements.

### *Flexural Properties*

The results obtained from flexural tests, namely the flexural strength and the flexural modulus, on both materials are presented as a function of time and hygrothermal conditions in *Fig. 8*.

In general, the level of degradation of the flexural strength of both profiles increased with the temperature of the immersion medium, being maximum at 60°C—this result was in agreement with the behaviour already reported for the tensile strength and with results obtained by other authors with GFRP pultruded profiles.[19,21] As for the tensile strength, for similar temperatures, strength reduction in demineralized water was usually lower than that in saltwater (it should be mentioned that this latter result differs from those reported by Liao *et al.*[22]) Unlike the behaviour exhibited in the tensile tests (essentially dominated by the fibres), in flexure (also significantly influenced by the matrix and the fibre–matrix interface) the VE profile did not present a better mechanical performance than the UP profile for all ageing conditions; in fact, for most exposure conditions and durations, the strength retention of the VE profile was considerably smaller than that of the UP profile—after 12 months of exposure, the lowest levels of retention were 66% for the UP profile and 58% for the VE profile, both immersed in demineralized water. This result may be due, at least to some extent, to some post-curing effect on the UP profile, which was identified in the DMA tests, and, in addition, to the considerable scatter of the results obtained in the initial characterization flexural tests. In this regard, it is worth mentioning that Kootsookos and Mouritz[23] also reported higher flexural strength retention in moulded glass–polyester laminates, compared with glass–vinylester laminates having similar fibre architectures.

Flexural modulus after 12 months of exposure decreased in all ageing conditions, for both profiles (*Fig. 8*). Similar to strength, in general, stiffness retention in demineralized water was lower than that in saltwater and, in addition, the UP profile presented better performance than the VE profile—the lowest levels of retention were 69% for the UP profile and 58% for the VE profile, both immersed in demineralized water. Similar to the tensile modulus, the flexural stiffness retention appeared to be more insensitive to the temperature of the immersion media, when compared to strength.

As for tensile performance, the variation of flexural properties in specimens subjected to continuous condensation was roughly similar to that of specimens immersed in demineralized water at 40°C.

### *Interlaminar Shear Strength*

*Figure 9* illustrates the variation of the interlaminar shear strength (a matrix dominated property) of both profiles as a function of the hygrothermal conditions and the period of exposure.

*Figure 9* shows that very significant reductions occurred in the interlaminar

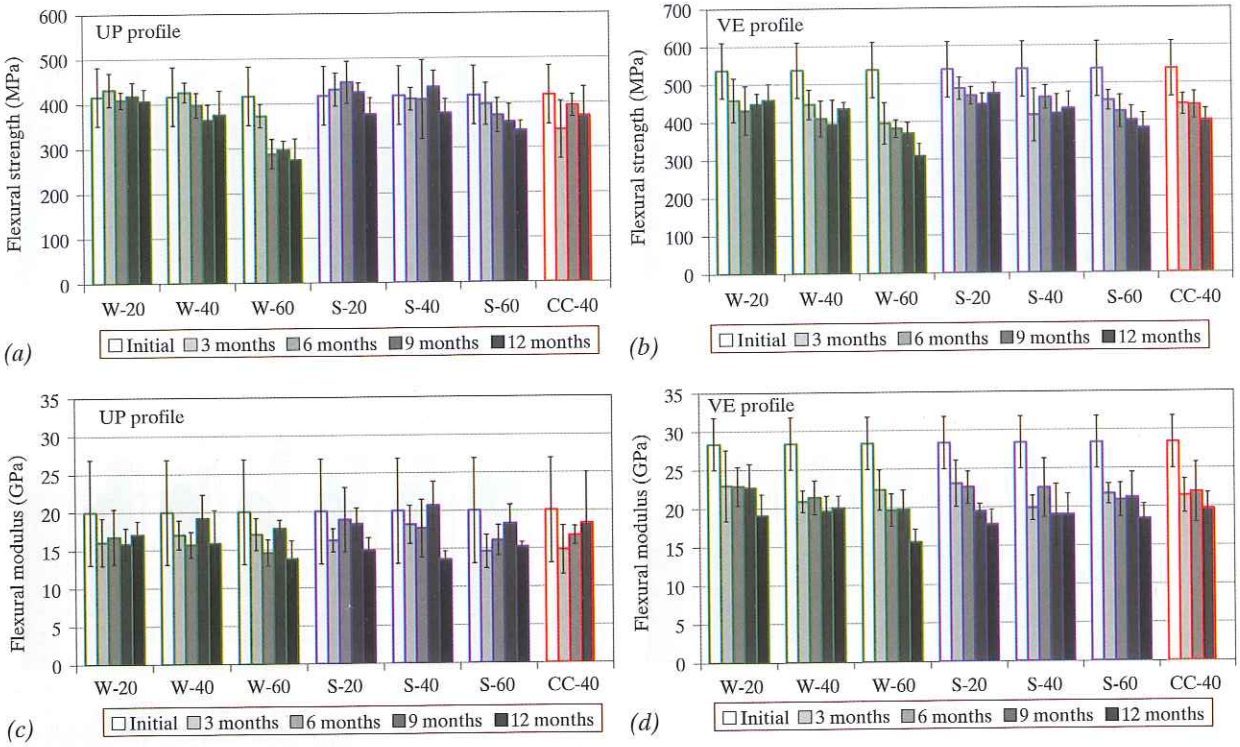


*Fig. 8– Flexural strength and modulus of UP (a, c) and VE (b, d) profiles after hygrothermal ageing*

shear strength of both profiles as a function of time. As for the other two mechanical tests, and similar to results reported earlier by Kharbari,[24] the interlaminar shear strength retention decreased consistently with the immersion temperature. After 12 months of exposure at 60°C, the strength retention in demineralized water was approximately 55% for the UP profile and 61% for the VE profile. For saltwater immersion, the corresponding values were slightly higher, with strength retentions of 60 and 62% for the UP and VE profiles, respectively. As for the two other mechanical tests, the variation of the interlaminar shear strength for immersion in demineralized water at 40°C was roughly analogous to that under continuous condensation. Strength reductions exhibited by the VE profile immersed in demineralized water at the three different temperatures followed a trend similar to those reported by Chu *et al.*[20]—these authors obtained higher strength retentions but, as already discussed, the results of the two studies are not directly comparable. Finally, the better performance exhibited by the VE profile for all hygrothermal ageing conditions and periods of exposure is outlined.

## Conclusion

This paper presented results of an ongoing research project on the environmental degradation suffered by GFRP pultruded profiles made of either UP or VE resins, with similar fibre contents and architectures. On the basis of results obtained for an exposure of 12 months in demineralized water and saltwater at 20, 40 and 60°C, as well as 9 months in continuous condensation at 40°C, the following conclusions can be arrived at:

1. The water uptake capacity of GFRP profiles and their temperature dependency are strongly dependent on the nature of the polymeric matrix—for similar ageing conditions, the VE profile exhibited considerably lower mass uptake than the UP profile.
2. The UP profile was the one that presented signs of plasticization in

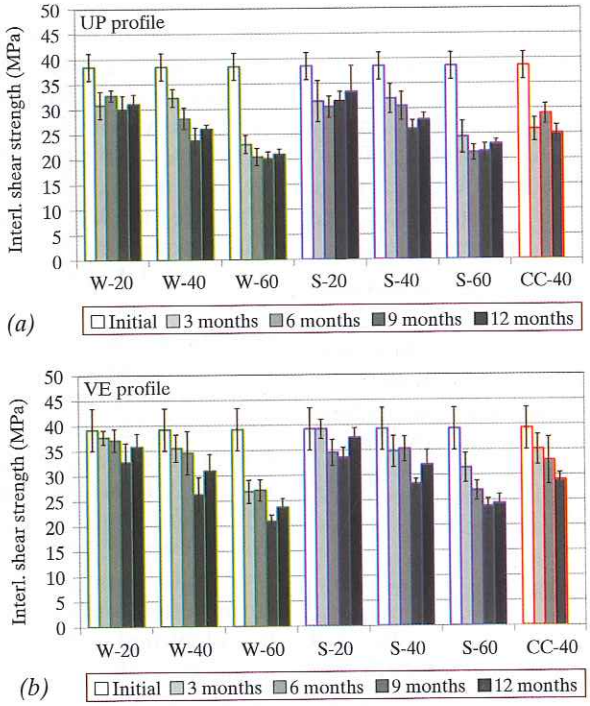


*Fig. 9: Interlaminar shear strength of UP (a) and VE (b) profiles after hygrothermal ageing*

DMA, and as a consequence of such plasticization mechanism the values of $T_g$ in aged specimens suffered a general reduction. In spite of this, for some ageing conditions, namely for higher temperatures, such reduction was offset because of the occurrence of resin post-curing. These competing phenomena resulted in fluctuations in the $T_g$ as a function of the period of exposure. For the VE profile, variations of $T_g$ were much lower, with DMA not suggesting any appreciable changes in the molecular structure.

3. The mechanical properties of GFRP profiles constituted by both types of resins were noticeably affected, even for immersion at 20°C (*Fig. 10*). For most of the hygrothermal ageing conditions and periods of exposure, the retention of both tensile strength (a fibre-dominated mechanical property) and interlaminar shear strength (matrix dominated) of the VE profile was considerably higher than that of the UP profile—degradation increased with the temperature of the immersion medium, with demineralized water being generally more aggressive than saltwater. In flexure, the tendency of the results was not so clear and, to some extent was contradictory to results of the other mechanical tests, as the VE profile showed a generally worse performance than the UP profile. It is believed that flexural results may have been influenced by the post-curing phenomen on observed in the UP profile.
4. The above-mentioned degradation was mainly due to physical phenomena, such as plasticization of the polymeric matrix, since no appreciable chemical degradation was detected through FTIR analyses.[25,26] Nevertheless, this degradation may influence the use of GFRP profiles in wet environments (structures placed underwater or subjected to high levels of moisture) and especially in tropical zones (where, in addition, temperatures are high), where the use of different resin systems and/or superficial protections (such as paintings or gel coats) shall be considered for improved performance.

The tendencies stated in the aforementioned conclusions will be assessed and eventually confirmed in the forthcoming experiments to be carried out within this research project. Additional experiments are also being carried out in order to evaluate the reversibility of the degradation suffered by both profiles—in these new experiments, specimens will be submitted to mechanical tests after being dried, as against the present experiments, in which they were tested in a saturated state. The next steps will also include the development of analytical models in order to simulate the observed degradation suffered by both types of profiles.

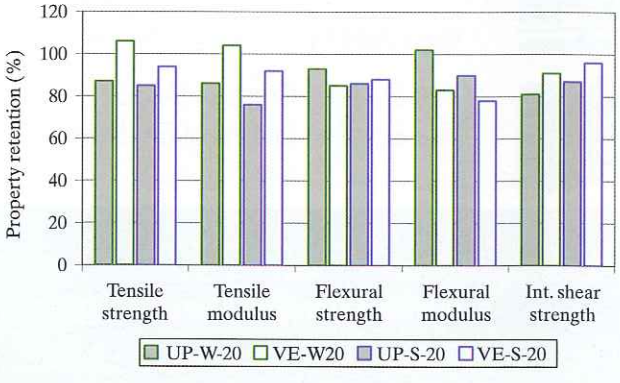


*Fig. 10: Retention of mechanical properties after 12 months of immersion at 20°C*

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## References

[1] Correia JR. GFRP pultruded profiles in civil engineering: hybrid solutions, bonded connections and fire behaviour, PhD Thesis, IST, Technical University of Lisbon, 2008.

[2] Correia JR, Cabral-Fonseca S, Branco FA, Ferreira J, Eusébio MI, Rodrigues MP. Durability of glass fibre reinforced polyester (GFRP) pultruded profiles for construction applications. *Mech. Compos. Mater.* 2006; **42**(4): 325–338.

[3] Keller T, Bai Y, Vallée T. Long-term performance of a glass-fiber-reinforced polymer truss bridge. *J. Compos. Const.* 2007; **11**(1): 99–108.

[4] Kharbari VM, Chin JW, Hunston D, Benmokrane B, Juska T, Morgan R, Lesko JJ, Sorathia U, Reynaud D. Durability gap analysis for fiber-reinforced polymer composites in civil infrastructure. *J. Compos. Const.* 2003; **7**: 238–247.

[5] Harries KA, Porter MA, Busel JP. FRP materials and concrete research needs. *Concr. Int., ACI* 2003; **October**: 69–74.

[6] ASTM~E~1252. *Standard Practice for General Techniques for Obtaining Spectra Qualitative Analysis*. American Society for Testing and Materials, West Conshohocken, PA, 1998.

[7] ASTM~D~3171. *Standard Test Methods for Constituent Content of Composite Materials*. American Society for Testing and Materials, West Conshohocken, PA, 2009.

[8] ISO~1183—Plastics. *Methods for Determining the Density of Non-Cellular Plastics. Part 1: Immersion Method, Liquid Pyknometer Method And Titration Method*. International Organization for Standardization, Brussels, 2004.

[9] ISO~6721—Plastics. *Determination of Dynamic Mechanical Properties. Part 1: General Principles; Part 5: Flexural Vibration- Non-Resonance Method*. International Organization for Standardization, Brussels, 2001.

[10] ISO~527—Plastics. *Determination of Tensile Properties. Part 1: General Principles; Part~5: Test Conditions for Unidirectional Fiber-Reinforced Plastic Composites*, International Standards Organization, Brussels, 1997.

[11] ISO~14125. *Fiber-Reinforced Plastic Composites—Determination of Flexural Properties*, International Standards Organization, Brussels, 1998.

[12] ASTM~D~2344. *Standard Test for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates*, American Society for Testing and Materials, West Conshohocken, PA, 2006.

[13] ASTM~D~695. *Standard Test Method for Compressive Properties of Rigid Plastics*. American Society for Testing and Materials, West Conshohocken, PA, 2008.

[14] ISO~175—Plastics. *Methods of Test for the Determination of the Effects of Immersion in Liquid Chemicals*. International Organisation for Standardization, Brussels, 1999.

[15] ASTM~D~1141. *Standard Practice for the Preparation of Substitute Ocean Water*. American Society for Testing and Materials, West Conshohocken, PA, 2008.

[16] ISO~6270—Paints and varnishes. *Determination of Resistance to Humidity. Part 1: Continuous Condensation*, International Standards Organization, Brussels, 1998.

[17] Chin JW, Nguyen T, Aouadi K. Effects of environmental exposure on fiber-reinforced plastic (FRP) materials used in construction. *J. Compos. Technol. Res.* 1997; **19**(4): 205–213.

[18] Chu W, Karbhari VM. Effect of water sorption on performance of pultruded E-glass/vinylester composites. *J. Mater. Civil Eng.* 2005; **17**(1): 63–71.

[19] Van de Velde K, Kiekens P. Effects of chemical environments on pultruded E-glass reinforced polyesters. *J. Compos. Technol. Res.* 2001; **23**(2): 92–101.

[20] Chu W, Wu L, Kharbari VM. Durability evaluation of moderate temperature cured E-glass/vinlyester systems. *Compos. Struct.* 2004; **66**(1–4): 367–376.

[21] Nishizaki I, Meiarashi S. Long-term deterioration of GFRP in water and moist environment. *J. Compos. Const.* 2002; **6**(1): 21–27.

[22] Liao K, Schultheisz CR, Hunston DL. Effects of environmental aging on the properties of pultruded GFRP. *Compos. B: Eng.* 1999; **30**(5): 485–493.

[23] Kootsookos A, Mouritz AP. Seawater durability of glass- and carbon-polymer composites. *Compos. Sci. Technol.* 2004; **64**(10–11): 1503–1511.

[24] Kharbari VM. E-Glass/vinylester composites in aqueous environments: effects on short-beam shear strength. *J. Compos. Const.* 2004; **8**(2): 148–156.

[25] Costa R. *Durability of Glass Fibre Reinforced Polyester Pultruded Profiles*. MSc Thesis, IST, Technical University of Lisbon, 2009 (in Portuguese).

[26] Carreiro A. *Durability of Glass Fibre Reinforced Vinylester Pultruded Profiles*. MSc Thesis, IST, Technical University of Lisbon, 2010 (in Portuguese).