



Durability of GFRP pultruded profiles made of unsaturated polyester and vinylester resins

Rodrigo de Oliveira Martins da Câmara Borges

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DURABILITY OF GFRP PULTRUDED PROFILES MADE OF UNSATURATED POLYESTER AND VINYLESTER RESINS

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1 Introduction

The increasing maintenance and rehabilitation costs of steel and reinforced concrete structures built in the last decades has been promoting the use of alternative materials with increased durability in aggressive environments, such as glass fiber reinforced polymers (GFRP) [1, 2]. Pultruded GFRP profiles combine low self-weight with high strength, thermal and electromagnetic insulation and resistance to corrosion. However, they present some disadvantages such as low stiffness, brittle behaviour and poor mechanical performance when exposed to elevated temperatures and fire [3]. Although this kind of materials has been used for decades in the naval, automobile and aerospace industry, Civil Engineering applications present different loading and exposure conditions, in which experimental data on durability is still scarce [4].

This paper is the result of an experimental research, developed for over a year, on the changes of physical, mechanical and aesthetical properties of pultruded GFRP profiles made of unsaturated polyester and vinylester resins, when subjected to accelerated ageing in typical Civil Engineering exposure environments (exposure to water, salt water, moisture, natural weathering and thermal cycles). Before ageing, test specimens were dried at moderate temperature in an attempt to prevent post-curing effects during the exposure period. In order to study the reversibility of degradation due to water sorption, test specimens were also dried after the exposure period, before physical and mechanical testing.

The experimental study was developed within a collaborative project between *Instituto Superior Técnico* (IST) and *Laboratório Nacional de Engenharia Civil* (LNEC).

2 Materials

The materials used in the experimental programme were obtained from two commercial GFRP pultruded bar profiles (32 mm x 5 mm, supplied by *Alto Perfis Pultrudidos Lda. Portugal*), one made of unsaturated polyester resin (UP profile) and the other made of

vinylester resin (VE profile). Both materials present alternate layers of unidirectional E-glass fiber rovings and strand mats embedded in the resin.

3 Methods

3.1 Exposure environments

To simulate the effect of typical Civil Engineering degradation agents, test specimens were subjected to different exposure environments, as listed in table 1.

Table 1 – Description of exposure environments and conditions

Exposure environment		Duration	Conditions
Immersion in demineralized water	W20	3, 6, 9 and 12 months (a)	W20/S20 – T = 20 (± 2) °C, W40/S40 – T = 40 (± 2) °C, W60/S60 – T = 60 (± 5) °C. Salt water composition: NaCl 35 g/l
	W40		
W60			
Immersion in salt water solution	S20		
	S40		
	S60		
Continuous condensation	CC	3, 6, 9 and 12 months (a)	T = 40 (± 2) °C, HR = 100 %
Natural weathering exposure	EN	6, 12, 18 and 24 months (b)	Roof of the main LNEC building. Environmental conditions continuously monitored.
Thermal cycles	CT	200, 400 and 600 cycles (c)	6 hours at – 5 °C + 6 hours at 40 °C

Batches of aged material tested in this study: (a) 3 and 6 months, (b) 6 months, (c) 200 cycles

3.2 Experimental procedures

Test specimens were grouped for ageing in order to optimize the use of the provided material, as individual specimen cutting was done only after the exposure periods. An additional 20 mm were added to the test specimens' length in each surface subjected to cutting in order to avoid direct access of moisture to the individual specimen's boundaries.

Test specimens were dried at 80 °C until no significant mass changes were registered (according to ASTM D 5229 standard [5]) before ageing in an attempt to prevent post-curing effects. This procedure was repeated after exposure, prior to physical and mechanical testing, to assess the reversibility of the degradation. After drying, test specimens were conditioned in a room with controlled temperature (T = 20 (±2) °C) and

transported in hermetically closed polyethylene bags to prevent changes in moisture content.

Physical-chemical characterization of both materials in their initial state was conducted using the following methods:

- (i) **Glass fiber content:** test specimens with 20 mm x 10 mm x 5 mm were tested in accordance with ISO 1172 standard [6], through the use of the calcination method.
- (ii) **Chemical characterization by Infrared spectroscopy (FTIR):** this test was conducted in accordance with ASTM E 1252 standard [7] by mixing particles obtained from the interior of test specimens with potassium bromide and pressing them into pellets. A *Bruker Tensor 27* spectroscope was used, in the 450 cm⁻¹ to 4000 cm⁻¹ region at a spectral resolution of 4 cm⁻¹.
- (iii) **Density:** this property was determined using test specimens with 30 mm x 15 mm x 5 mm, in accordance with ISO 1183 standard [8] (method A).

Physical, mechanical and aesthetical properties of both materials were assessed in their initial state and after ageing using the following techniques:

- (i) **Sorption behaviour:** control specimens placed in immersion and continuous condensation exposures (with dimensions 100 mm x 32 mm x 5 mm) were periodically monitored in terms of mass changes throughout the exposure period, using an electronic scale, with precision of 0,1 mg.
- (ii) **Dynamic mechanical analysis (DMA):** viscoelastic response and glass transition temperature (T_g) of both materials was assessed using DMA technique, in accordance with parts 1 and 5 of ISO 6721 standard [9, 10]. Three-point bending type clamp specimens (60 mm x 15 mm x 5 mm) were tested at a constant frequency of 1 Hz and strain amplitude of 15 μ m. The analyses were conducted from 25 °C up to 200 °C at a rate of 2 °C/min using a *Q800* model of *TA Instruments*. Three replicates from each ageing condition were tested.

- (iii) **Aesthetical characterization:** five samples from each material aged in natural weathering exposure destined to tensile tests were used to assess colour and gloss changes:
- **Colour changes** were determined in accordance with parts 1 and 2 of ISO 7724 standard [11, 12], using the CIE 1976 (L*a*b*) colorimetric system. A *MinisScan XE Plus* portable colorimeter of *Neurtek Instruments* was used in this test.
 - **Gloss changes** were assessed in accordance with ISO 2813 standard [13]. A *Novo-Gloss Statistical Glossmeter* was used to measure specular gloss at the incidence angles of 60 ° and 85 °.
- (iv) **Mechanical behaviour:** six samples from each material and ageing conditions were subjected to mechanical testing.
- **Flexural properties** were assessed in three-point bending tests in accordance with ISO 14125 standard [14] using test specimens with 150 mm x 15 mm x 5 mm in a 100 mm span. Tests were conducted in a *Seidner Form Test* at a rate of 0,1 kN/s.
 - **Tensile properties** were determined according to parts 1 and 4 of ISO 527 standard [15, 16]. Specimens with 300 mm x 25 mm x 5 mm were tested in an *Instron 1343* universal testing machine with a load capacity of 250 kN at a rate of 2 mm/min.
 - **Shear properties** were determined by interlaminar shear testing in accordance with ASTM D 2344 [17] and ISO 14130 [18] standards using test specimens with 30 mm x 10 mm x 5 mm and a 20 mm span. Tests were conducted in a *Seidner Form Test* at a rate of 0,1 kN/s.

4 Results and discussion

4.1 Materials characterization before ageing

Physical, chemical and mechanical properties of both unsaturated polyester (UP) and vinylester (VE) profiles before ageing are presented in table 2. Concerning mechanical testing, both profiles exhibited linear elastic behaviour to failure.

Table 2 – Physical, chemical and mechanical properties of GFRP profiles (un-aged)

Property		UP profile	VE profile
Glass fiber content [%]		65,3 ± 1,8	67,9 ± 1,8
Chemical composition		FTIR spectra consistent with unsaturated polyester, with calcium carbonate and silica	FTIR spectra consistent with vinylester, with calcium carbonate and silica
Density [g/cm ³]		1,92 ± 0,00	1,96 ± 0,00
T_g [°C]	$E'_{initial}$	112,3 ± 3,6	106,6 ± 1,3
	$\tan \delta$	136,4 ± 1,3	124,1 ± 0,3
Flexural properties	σ_{fu} [MPa]	502,7 ± 41,5	495,4 ± 42,3
	E_f [GPa]	20,1 ± 2,3	22,4 ± 1,0
Tensile properties	σ_{tu} [MPa]	444,3 ± 51,8	389,8 ± 29,0
	E_t [GPa]	37,4 ± 2,3	35,0 ± 1,4
Interlaminar shear	τ_u [MPa]	33,4 ± 4,8	37,8 ± 1,7

4.2 Sorption behaviour

Figures 1 and 2 show the experimental curves of mass change for both UP and VE profiles, respectively, for different immersion media (W for demineralized water and S for salt water, at 20 °C, 40 °C and 60 °C) and continuous condensation (CC) at 40 °C.

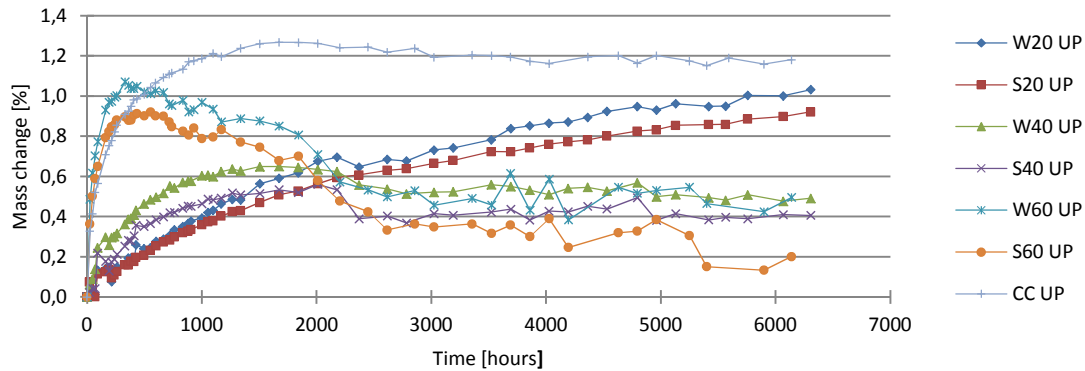


Figure 1 – Mass changes for different hygrothermal ageing conditions – UP profile

Both profiles exhibited an approximately *Fickian* response, except for the immersions at 60 °C for the UP profile (and also at 40 °C although less significantly), in which significant mass loss was observed after a 400 hours exposure. According to Chin *et al.* [19], this phenomenon may be due to leaching of soluble degradation or hydrolysis products. Overall, demineralized water immersion exhibited greater mass uptake than salt solution immersion for each temperature. Elevated temperatures led to high initial mass change rates for both profiles and an overall greater mass uptake in the case of the

VE profile. The UP profile showed higher mass changes in comparison with the VE profile, with a maximum of 1,2 % for continuous condensation exposure, opposed to a maximum of 0,6 % for the VE profile (W60-VE).

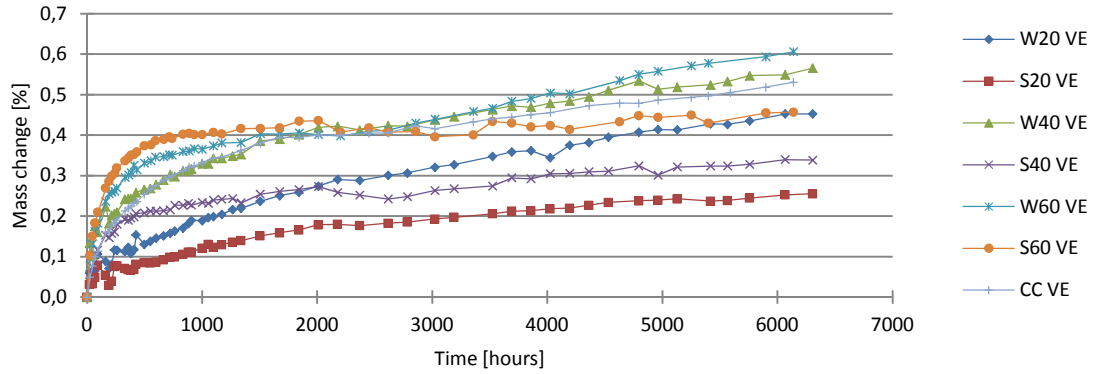


Figure 2 – Mass changes for different hydrothermal ageing conditions – VE profile

4.3 Dynamic mechanical analysis

Figures 3 and 4 present changes in T_g ($\tan \delta$) for the UP and VE profiles, respectively, regarding hydrothermal ageing and natural weathering. Figure 5 plots changes in this property (for both profiles) after exposure to thermal cycles.

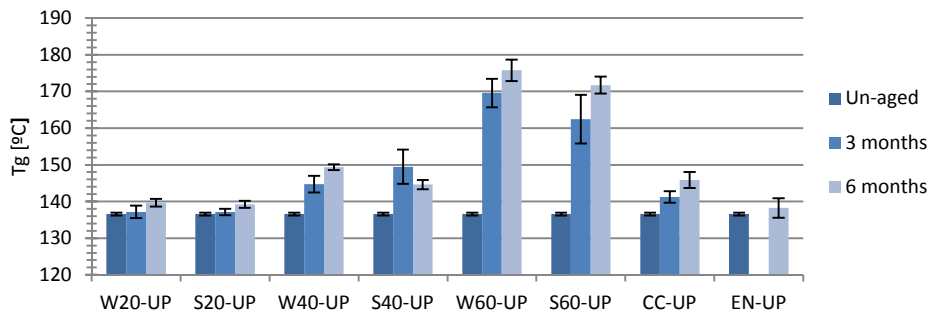


Figure 3 – T_g ($\tan \delta$) variation after hydrothermal ageing and natural weathering – UP profile

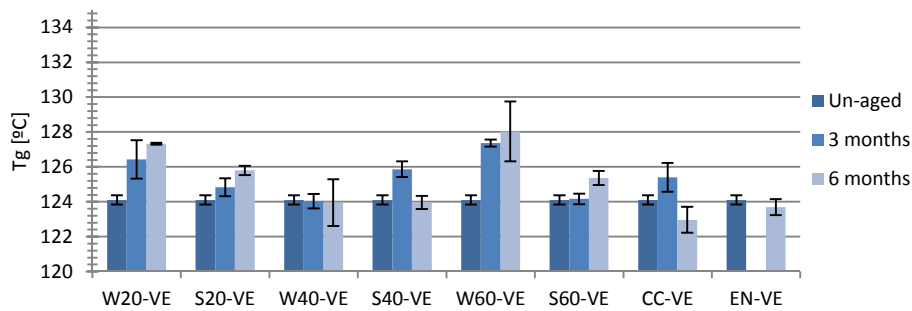


Figure 4 – T_g ($\tan \delta$) variation after hydrothermal ageing and natural weathering – VE profile

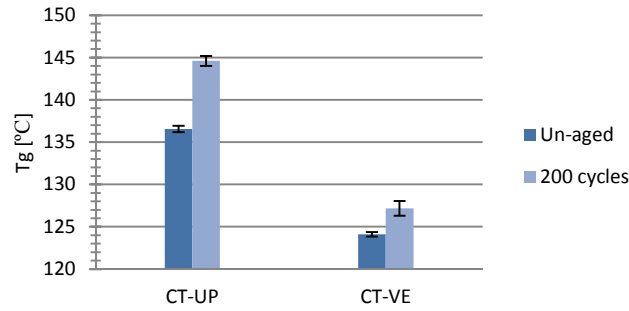


Figure 5 – T_g ($\tan \delta$) variation after thermal cycles – UP and VE profiles

Obtained results show that, for both profiles, no significant degradation in glass transition temperature was experienced. According to Chu and Karbhari [20], water sorption leads to degradation in this property, due to matrix plasticization. However, drying of test specimens after ageing may have caused damage reversal.

Significant increases in glass transition temperature were exhibited after immersion at 60 °C, especially for the UP profile. This suggests that post-curing effects may have occurred despite the initial drying process. In the VE profile these effects were less significant, although some increases were observed. Irreversible degradation, which is expected to occur in most aggressive exposures, may have been outdrawn by these post-curing effects.

4.4 Aesthetical characterization

4.4.1 Colour changes

Tables 3 and 4 show the variation of colour space system coordinates for UP and VE profiles, respectively, after natural weathering exposure.

Table 3 – Colour space system coordinates after natural weathering exposure – UP profile

UP profile	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Un-aged	$79,67 \pm 0,89$	$-1,24 \pm 0,24$	$12,84 \pm 1,39$	-	-	-	-
EN (6 months)	$78,10 \pm 1,29$	$-1,13 \pm 0,19$	$11,74 \pm 1,35$	-1,57	0,11	-1,10	1,92

Table 4 - Colour space system coordinates after natural weathering exposure – VE profile

VE profile	L^*	a^*	b^*	ΔL^*	Δa^*	Δb^*	ΔE^*
Un-aged	$74,45 \pm 0,24$	$-1,49 \pm 0,04$	$7,14 \pm 0,45$	-	-	-	-
EN (6 months)	$70,80 \pm 0,77$	$-0,92 \pm 0,22$	$15,75 \pm 0,93$	-3,66	0,57	8,61	9,37

Both profiles experienced changes in superficial colour after 6 months of exposure to natural weathering. Highest degradation of this property was observed for the VE profile, with a significant increase in the b^* coordinate, which is consistent with the visible yellowing of the composite's surface. The results are consistent with those presented by Bogner and Borja [21], who also experienced greater colour degradation on a vinylester composite, compared to an unsaturated polyester composite, for an exposure of 24 months to natural weathering on a similar climate.

4.4.2 Gloss changes

Table 5 presents changes in gloss values for 60° and 85° incidence angles after 6 months of exposure to natural weathering. The VE profile showed significant gloss loss for both incidence angles, with a property retention of approximately 20%. Changes in the UP profile were less significant, with retentions over 60%.

Table 5 – Gloss changes after natural weathering exposure – UP and VE profiles

	UP profile		VE profile	
	60°	85°	60°	85°
Un-aged	18,4 ± 2,8	27,0 ± 3,4	16,4 ± 2,0	22,2 ± 3,9
EN (6 months)	16,8 ± 4,0	17,3 ± 4,7	3,6 ± 0,6	4,2 ± 0,7

4.5 Mechanical behaviour

4.5.1 Flexural properties

Changes in flexural properties for the UP profile after hygrothermal ageing and natural weathering exposure are plotted in figures 6 and 7. Changes for the vinylester profile are presented in figures 8 and 9. Figure 10 shows changes in flexural properties for both profiles, regarding exposure to thermal cycles.

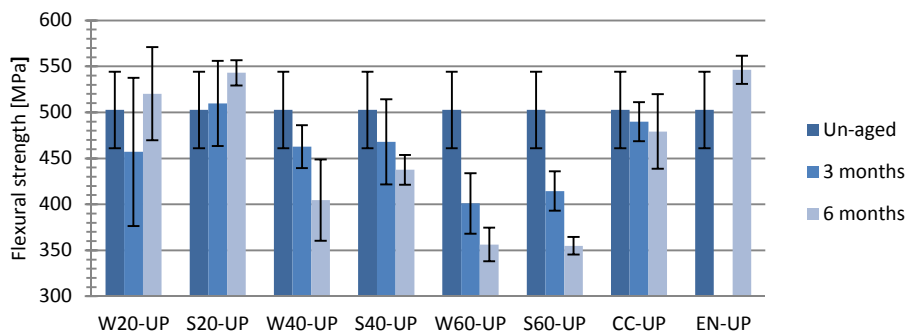


Figure 6 – Flexural strength changes after hygrothermal ageing and natural weathering exposure – UP profile

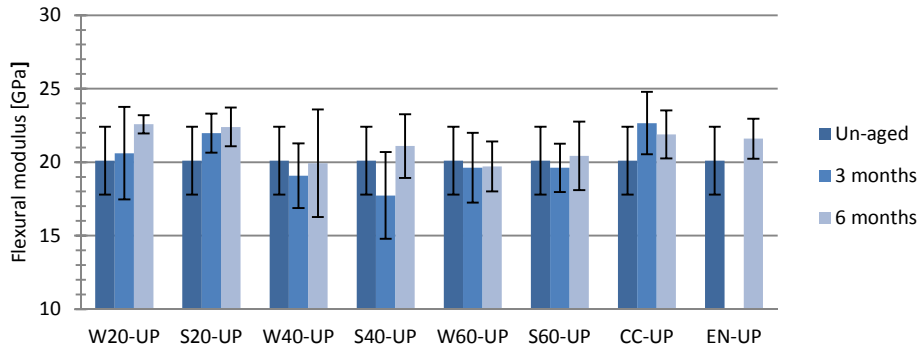


Figure 7 – Flexural modulus changes after hygrothermal ageing and natural weathering exposure – UP profile

Both profiles showed significant decreases in flexural strength, especially in the most aggressive environments, namely immersions at 40 °C and 60 °C. Losses were higher for the UP profile, with a maximum decrease of 29 % for immersion in both demineralized water and salt solution at 60 °C, which can be related to the mass loss phenomenon observed in this situation. The VE profile registered a maximum loss of 18 %, also in the immersion in demineralized water at 60 °C. Results suggest that irreversible degradation took place, more heavily in the immersions at elevated temperatures. Changes in flexural modulus were less significant for both profiles.

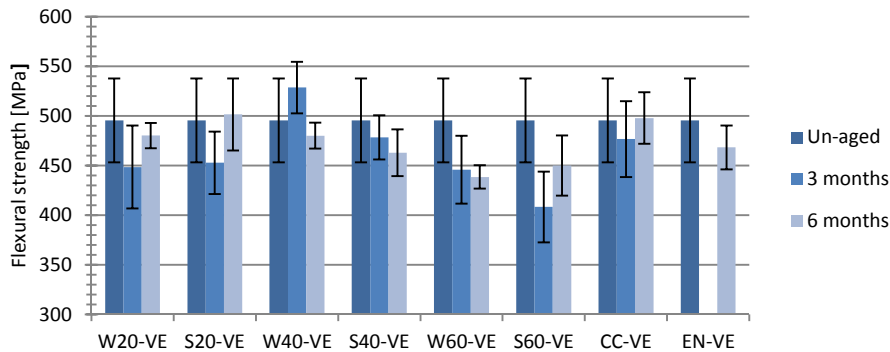


Figure 8 – Flexural strength changes after hygrothermal ageing and natural weathering exposure – VE profile

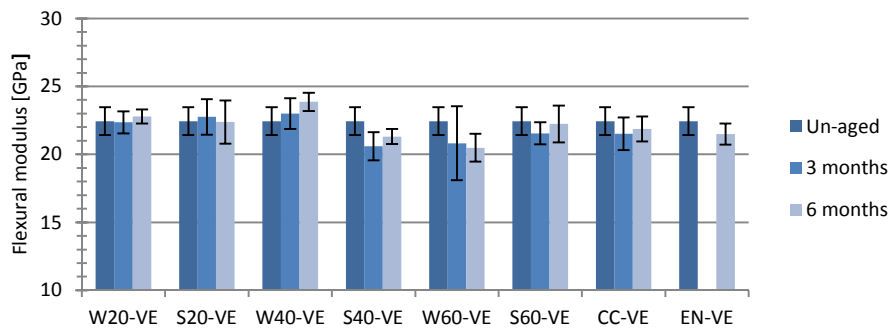


Figure 9 – Flexural modulus changes after hygrothermal ageing and natural weathering exposure – VE profile

Exposure to thermal cycles caused slight increases in the flexural properties of both

profiles. According to Dutta and Hui [22], this kind of exposure may lead to the stiffening of the polymeric matrix and a consequent improvement in flexural properties.

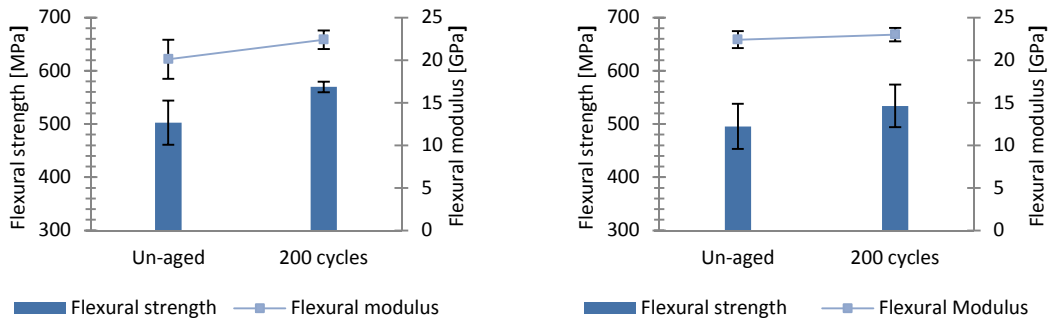


Figure 10 – Flexural strength and modulus after thermal cycles – UP (left) and VE (right) profiles

4.5.2 Tensile properties

Figures 11 to 14 show changes in tensile properties for both profiles after exposure to hygrothermal ageing and natural weathering. Figure 15 plots changes regarding exposure to thermal cycles.

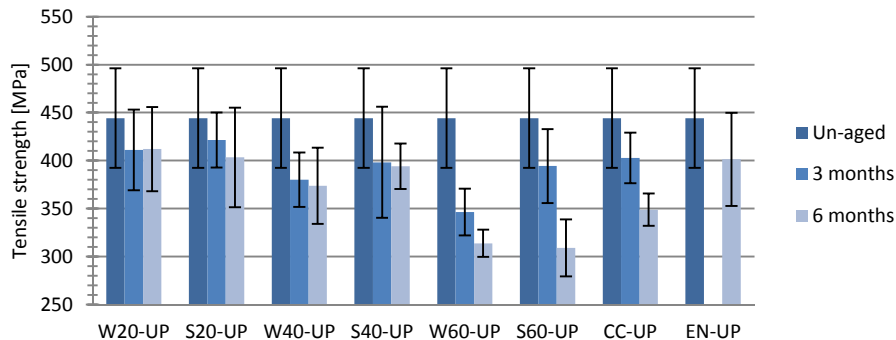


Figure 11 - Tensile strength changes after hygrothermal ageing and natural weathering exposure – UP profile

The UP profile showed an overall degradation tendency both on tensile strength and modulus, increasing with time and temperature. A maximum decrease of approximately 30 % was observed after 6 months of exposure to immersion in demineralized water and salt solution at 60 °C. Exposure to continuous condensation caused a decrease of 22 % in tensile strength, which suggests that the high moisture sorption observed may have caused irreversible degradation on the fiber and interphase levels. Regarding the VE profile, decreases in tensile strength were considerably lower, with a maximum loss of 9 % registered for immersion in demineralized water at 40 °C.

Higher degradation in the elevated temperature immersions is consistent with the results presented by Chu and Karbhari [20], who stated that the irreversible portion of

degradation decreases with time and temperature of immersion.

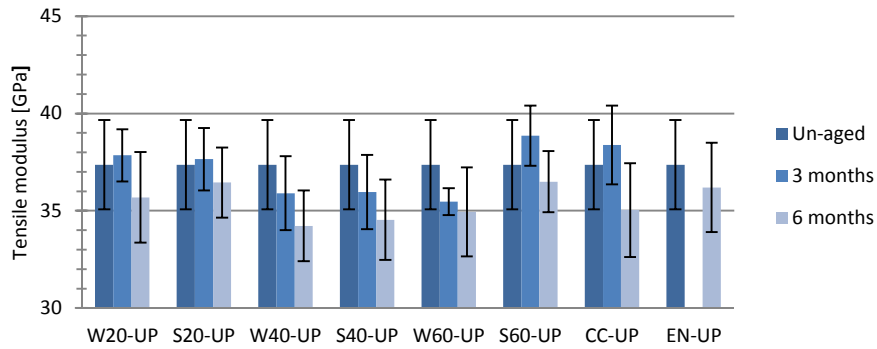


Figure 12 - Tensile modulus changes after hygrothermal ageing and natural weathering exposure – UP profile

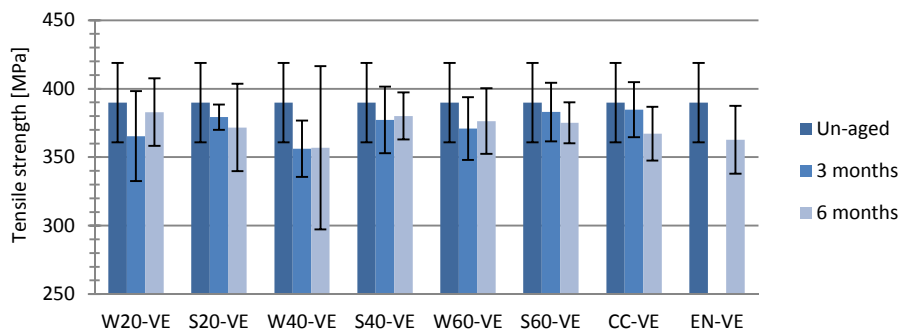


Figure 13 - Tensile strength changes after hygrothermal ageing and natural weathering exposure – VE profile

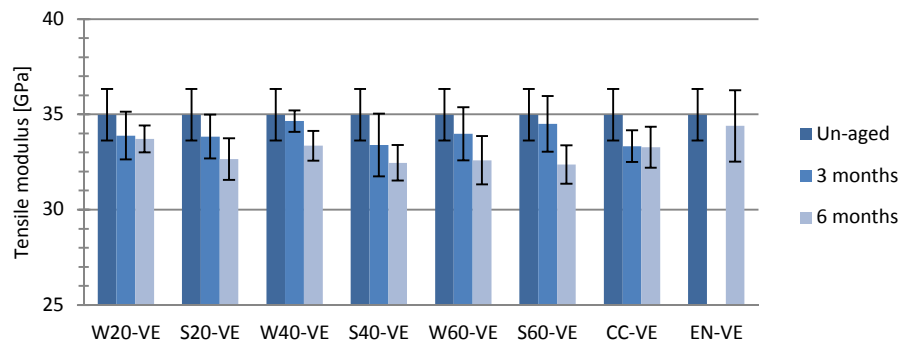


Figure 14 - Tensile modulus changes after hygrothermal ageing and natural weathering exposure – VE profile

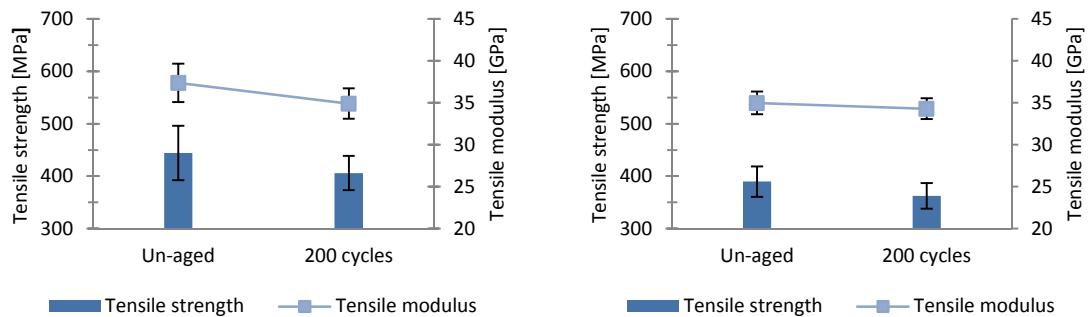


Figure 15 - Tensile strength and modulus after thermal cycles – UP (left) and VE (right) profiles

Exposure to thermal cycles caused slight decreases (under 10 %) in tensile strength and modulus for both profiles. According to Karbhari *et al.* [23], who observed similar losses for VE profiles in this kind of exposure, thermal cycles cause fiber-matrix debonding and matrix microcracking with consequent decreases in tensile properties.

4.5.3 Interlaminar shear strength

Changes in interlaminar shear strength are plotted in figures 16 and 17, for the UP and VE profiles, respectively. Figure 18 shows changes in this property for both profiles after exposure to thermal cycles.

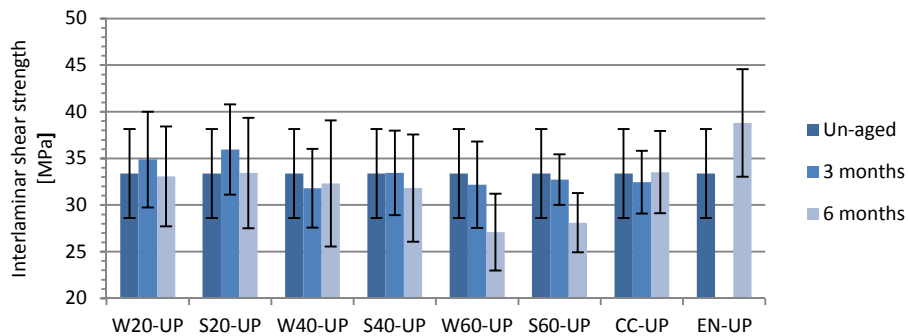


Figure 16 - Interlaminar shear strength changes after hygrothermal ageing and natural weathering exposure – UP profile

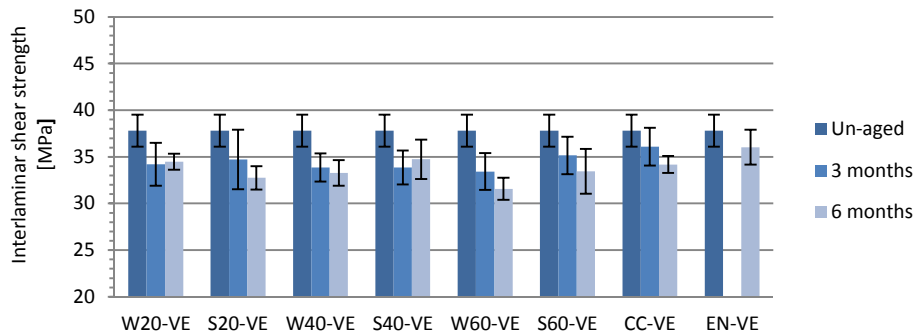


Figure 17 – Interlaminar shear strength changes after hygrothermal ageing and natural weathering exposure – VE profile

Results for the UP profile present relatively high scatter. However, a degradation trend is visible for the immersion in demineralized and salt water solution at 60 °C, which suggests irreversible damage may have occurred on the matrix or the interphase region. A maximum loss of 19 % was registered for a 6 months exposure to demineralized water at that temperature. Regarding the VE profile, losses were observed in all exposure environments, although maximum losses were smaller compared to the UP profile. This suggests that irreversible degradation occurred at some extent on all ageing

conditions for the VE profile. A maximum decrease of 17 % was observed for the VE profile, for the immersion in demineralized water at 60 °C.

Thermal cycles originated contradictory results on both profiles, with an increase of 15 % for the UP profile (although associated to high scatter) and a slight decrease for the VE profile on this property.

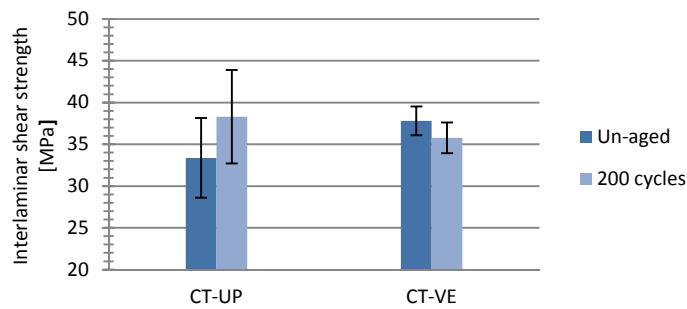


Figure 18 - Interlaminar shear properties after thermal cycles – UP (left) and VE (right) profiles

5 Conclusions

The defined goals for this study were successfully accomplished, leading to the determination of physical, mechanical and aesthetical variations experienced by GFRP pultruded profiles made of unsaturated polyester and vinylester resins when subjected to different ageing conditions.

Drying of test specimens prior to the exposure periods resulted in a general neutralization of post-curing effects in what concerns mechanical testing. However, this kind of effects was observed for the dynamic mechanical analysis, with significant increases in glass transition temperature, especially for the UP profile.

In what concerns sorption behaviour, the UP profile showed significantly higher mass uptake when compared to the VE profile, although it experienced severe mass loss for the 40 °C and 60 °C immersions, which may be due to hydrolysis. Saturation level seemed to be achieved for the UP profile during the exposure period.

Mechanical testing results showed that for most exposure conditions property decreases were higher for the UP profile. Overall, property losses increased with time and temperature of immersion.

For the UP profile, flexural and tensile strengths were the most affected mechanical

properties, with losses up to 30 % in flexural and tensile strengths for the 60 °C immersions. Exposure to continuous condensation led to a significant decrease in tensile strength for this material, which suggests that high moisture sorption led to irreversible damage on the fiber and interphase levels. The VE profile showed a maximum loss of 18 % in flexural strength, corresponding to immersion in salt solution at 60 °C. Regarding tensile strength, this composite showed decreases under 10 %.

Interlaminar shear strength showed greater decreases for the VE profile in most exposure environments. A maximum loss of 17 % for immersion in demineralized water at 60 °C was registered. For this exposure condition, the UP profile exhibited a decrease of 19 % in this property. Results indicate that irreversible damage to the matrix and interphase may have occurred.

Exposure to natural weathering resulted mainly in aesthetical degradation, with no relevant mechanical losses having been registered. Severe colour degradation was observed for the VE profile after a 6 months exposure, with smaller changes occurring for the UP profile. Regarding gloss values, both profiles exhibited significant decreases, although once again the VE profile experienced greater losses.

Thermal cycles resulted in increases in flexural properties for both profiles, which may be due to matrix stiffening. Losses around 8 % in tensile properties of both profiles may result from fiber-matrix debonding and matrix microcracking.

The study of reversibility showed that the irreversible portion of degradation increases with time and temperature of exposure for both materials, with higher losses registered for the most aggressive environments. Glass transition temperature did not present irreversible degradation for the exposure periods, which in the case of hygrothermal ageing suggests that plasticization effects were successfully reverted.

A more accurate method to determine the influence of the drying process and study the reversibility of the degradation is suggested. This could be done by conducting parallel testing in both dry and wet specimens subjected to the same ageing conditions.

6 References

- [1] J. R. Correia, “*Glass fibre reinforced polymer (GFRP) pultruded profiles. Structural behaviour of GFRP-concrete hybrid beams (in Portuguese)*”, Master’s Thesis, Instituto Superior Técnico, Universidade Técnica de Lisboa, 2004.
- [2] J. R. Correia, “*Polymeric matrix composites*”, in “*Science and Engineering of Construction Materials (in Portuguese)*” (Editors: F. Margarido and M. C. Gonçalves), IST Press, Lisboa, 2012.
- [3] J. R. Correia, “*GFRP Pultruded Profiles in Civil Engineering: hybrid solutions, bonded connections and fire behaviour*”, PhD Thesis in Civil Engineering, Instituto Superior Técnico, Universidade Técnica de Lisboa, 2008.
- [4] V. M. Karbhari, J. W. Chin, D. Hunston, B. Benmokrane, T. Jusja, R. Morgan, J. J. Lesko, U. Sorathia, D. Reynaud, “*Gap Analysis for Durability of Fiber Reinforced Polymer Composites in Civil Infrastructure*”, Civil Engineer Research Foundation, American Society of Civil Engineers, 2001.
- [5] ASTM D5229, “*Standard Test Method for Moisture Absorption properties and Equilibrium Conditioning of Polymer Matrix Composite Materials*”, American Society for Testing and Materials, 2004.
- [6] ISO 1172, “*Textile-glass-reinforced plastics – Prepegs, moulding compounds and laminates – Determination of the textile-glass and mineral-filler content – Calcination methods*”, International Organization for Standardization, 1996.
- [7] ASTM E1252, “*Standard Practice for General Techniques for Obtaining Infrared Spectra for Qualitative Analysis*”, American Society for Testing and Materials, 2007.
- [8] ISO 1183, “*Plastics – Methods for determining the density and relative density of non-cellular plastics*”, International Organization for Standardization, 1987.
- [9] ISO 6721, “*Plastics – Determination of dynamic mechanical properties – Part 1: General Principles*”, International Organization for Standardization, 1994.
- [10] ISO 6721, “*Plastics – Determination of dynamic mechanical properties – Part 5: Flexural vibration – non-resonance method*”, International Organization for Standardization, 2007.
- [11] ISO 7724-1, “*Paints and varnishes – Colorimetry – Part 1: Principles*”, International Organization for Standardization, 1997.
- [12] ISO 7724-2, “*Paints and varnishes – Colorimetry – Part 2: Colour Measurement*”, International Organization for Standardization, 1997.
- [13] ISO 2813, “*Paints and varnishes – Determination of specular gloss of non-metallic paint films at 20°, 60° and 85°*”, International Organization for Standardization, 1994.
- [14] ISO 14125, “*Fibre-reinforced plastic composites – Determination of flexural properties*”, International Organization for Standardization, 1998.
- [15] ISO 527-1, “*Plastics – determination of tensile properties – Part 1: General Principles*”, International Organization for Standardization, 1993.
- [16] ISO 527-4, “*Plastics – determination of tensile properties – Part 4: Test conditions for isotropic and orthotropic fibre-reinforced plastic composites*”, International Organization for Standardization, 1997.

- [17] ASTM D2344, “*Standard Test Method for Short-Beam Strength of Polymer Matrix Composite Materials and Their Laminates*”, American Society for Testing and Materials, 2000.
- [18] ISO 14130, “*Fibre-reinforced plastic composites – Determination of apparent laminar shear strength by short-beam method*”, International Organization for Standardization, 1997.
- [19] J. W. Chin, T. Nguyen, K. Aouadi, “*Effects of Environmental Exposure on Fiber Reinforced Plastic (FRP) Materials Used in Construction*”, Journal of Composites Technology and Research, vol. 19, 1997, 205-213.
- [20] W. Chu, V. M. Karbhari, “*Effect of Water Sorption on Performance of Pultruded E-glass/Vinylester Composites*”, Journal of Materials in Civil Engineering, vol. 17, 2005, 63-71.
- [21] B. E. Bogner, P. P. Borja, “*Strength retention of pultruded composites after exposure to ultra-violet (UV) light*”, BP Amoco Research Center, Napperville – Illinois EUA.
- [22] P. K. Dutta, D. Hui, “*Low-temperature and freeze-thaw durability of thick composites*”, Composites: Part B, vol. 27B, 1996, 371-379.
- [23] V. M. Karbhari, J. Rivera, J. Zhang, “*Low-temperature hygrothermal degradation of ambient cured E-glass/vinylester composites*”, Journal of Applied Polymer Science, vol. 86, 2002, 2255-2260.