Durability of an epoxy adhesive and a CFRP laminate under different exposure conditions

Pedro Fernandes[1], Patrícia Silva[2], Luís Correia[3] and José Sena-Cruz[4]

[1] ISISE, University of Minho, Guimarães, Portugal, pfernandes@civil.uminho.pt
[2] ISISE, University of Minho, Guimarães, Portugal, patricia.silva@civil.uminho.pt
[3] ISISE, University of Minho, Guimarães, Portugal, lcorreia@civil.uminho.pt
[4] ISISE, University of Minho, Guimarães, Portugal, jsena@civil.uminho.pt

ABSTRACT: In many of the retrofitted structures, carbon fibre reinforced polymer (CFRP) laminates bonded with epoxy adhesives are used. In the last decades the developed extensive research was mostly devoted to the short-term structural performance of strengthened structural elements and rarely considered the full structure's life time. The assessment of the full structure's life time requires the evaluation of the durability of the involved materials. The present work aims to contribute for the knowledge on the durability of a specific CFRP laminate strip and an epoxy adhesive widely used in this context. For that purpose an experimental program was carried out to assess the degradation on their tensile properties due to five distinct environments: (i) thermal cycles; (ii) freeze-thaw cycles; (iii) immersion in pure water; (iv) immersion in salt water; and, (v) wet-dry cycles with salt water. The obtained results indicate that the immersion in pure water was the most critical environment for the adhesive specimens, with a reduction on the strength of 38% after 2 years of exposure. Results also showed that the CFRP samples had negligible losses on their tensile properties.

1 INTRODUCTION

Nowadays, the use of fibre reinforced polymer (FRP) materials on the strengthening of existing structures is a viable alternative to conventional materials like steel and concrete. In general, these materials can be designated according to the type of fibres (carbon, glass, aramid or basalt), the form (strips, sheets or rods) and the system ("wet lay-up" or "pre-cured"). The "pre-cured" systems use prefabricated FRP which are normally best suitable for straight surfaces, whereas the "wet lay-up" systems can be used on plane and convex surfaces due to the flexibility of its composing fabrics or sheets (Fib Bulletin 14, 2001).

Several FRP strengthening techniques have been developed over the last three decades, being the external bonded reinforcement (EBR) and the near surface mounted (NSM) the two most commonly used methods. In the latter technique the FRP material is applied into grooves opened in the concrete cover, while in the EBR the FRP is glued to the external surface of the elements to be strengthened. Due to its lower density, high tensile capacity and stiffness the Carbon FRP (CFRP) is the most used FRP material for the case of concrete structures. The bond between the concrete surface and the FRP is an important factor for the success and efficiency of the strengthening. Structural epoxy adhesives are commonly used as bonding agent as they provide the required shear load path between both materials. Several studies show that this composite system of CFRP bonded with epoxy adhesive can improve the ultimate carrying capacity and the serviceability of the reinforced concrete (RC) elements (Sena-Cruz *et al.*, 2011; Michels *et al.*, 2013; Correia *et al.*, 2014).

When exposed to environmental degradation, the evolution of the mechanical properties of CFRP/epoxy adhesive systems must be known since they play a critical role on the viability and service life of the strengthening solution. In spite of that only a few studies can be found in the literature regarding this issue, e.g. (Silva *et al.*, 2014a; Silva *et al.*, 2014b; Myers *et al.*, 2014).

The present work aims at contributing to the existing knowledge on durability of a CFRP and an epoxy adhesive. For that purpose, a wide experimental program of tensile tests was carried out with a CFRP laminate strip and an epoxy specimens previously subjected to one of the following five environmental actions: (i) thermal cycles, (ii) freeze-thaw cycles, (iii) immersion on tap water, (iv) immersion on salt water (3.5% of chlorides), and (v) wet-dry cycles on salt water (3.5% of chlorides). Additionally, reference specimens (lab environment), without any ageing action were also tested. Depending on the environmental action, the exposure period of time lasted in between 120 to 720 days.

2 EXPERIMENTAL PROGRAM

2.1 Epoxy adhesive and CFRP laminate

The present work details the experimental program conducted with aim of identifying the influence of five different environmental actions on the tensile properties of a CFRP laminate strips and an epoxy adhesive widely used in the structural rehabilitation industry.

The CFRP strip studied has a rectangular cross section with 10 mm of width and 1.4 mm of thickness and normally is delivered in rolls of 100 m of length. This CFRP strip is produced by S&P Clever Reinforcement Ibérica Lda., has the trademark CFK 150/2000, and consists of unidirectional carbon fibres held together by an epoxy vinyl ester resin matrix. According to the supplier, the expected modulus of elasticity of the CFRP laminate should be higher than 165 GPa and the tensile strength higher than 2000 MPa.

The S&P Resin 220 epoxy adhesive used in this work is produced by the same supplier of the CFRP laminate. This epoxy is a solvent-free, thixotropic, grey two-component (resin and hardener) with a mixing ratio of 4:1 and it was specially developed for bonding the S&P CFK laminates. The adhesive’s technical datasheet indicates an expected Young modulus higher than 7.1 GPa. Finally, this epoxy adhesive is available on units of 5 kg and 15 kg.

2.2 Description of the experimental program

The present experimental program was composed of 72 samples of epoxy adhesive and 60 samples of CFRP laminate strip. The samples were grouped into six series as shown in Table 1. For each series, composed of six specimens, different environmental action was induced for a period of time that lasted from 120 days to 720 days.

Series S0 were used as reference series (ADH_REF720, FRP_REF), being kept in lab controlled environment during 2 years (temperature around 22ºC and relative humidity close to 55%). For the case of the epoxy adhesive material, one additional series (ADH_REF) was tested at the very beginning of the experimental program. The effect of thermal action was studied with series S1 and S2, through thermal (TC) and freeze-thaw (FT) cycles, respectively. Two sub-series were defined: specimens aged during 120 days and during 240 days, respectively (TC120 and FT120) and (TC240 and FT240). For both series each single cycle lasted a 24 hours of duration. In S1 series, the program of thermal cycling was based on EN 13687-3:2002 standard and the applied temperatures ranged between –15ºC and +60ºC (with plateau that lasted 12.5 and 10 hours for these two extreme temperature values). The freeze-thaw cycles were subjected to temperatures from –18ºC to +20ºC (CEN/TS 12390-9:2006 standard) and water immersion (when the temperature was positive). As it is shown on Table 1, another three distinct environmental actions were considered: immersed in pure water at 20ºC (series S3 - PW); immersed in water at 20ºC with 3.5% chlorides (series S4 - CW); and submitted to wet-dry cycles with water at 20ºC with 3.5% chlorides (series S5 - WD). For these series half the specimens were submitted to these actions during 360 days, whereas the other half continued this aging tests up to 720 days.

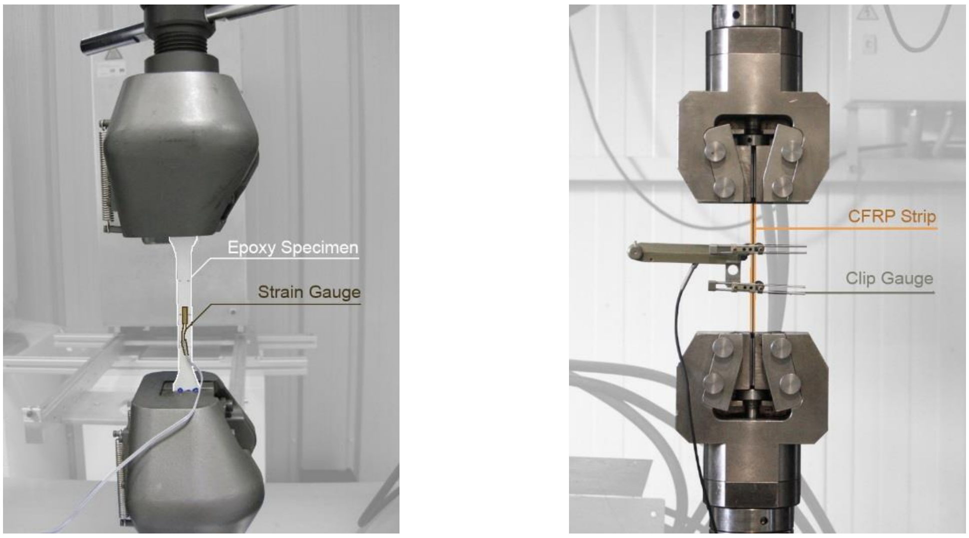
Each series is labelled with a generic denomination: X_YZ, where X is the specimen material type (ADH – epoxy adhesive; FRP – CFRP laminate strip), Y indicates the environment action (REF – lab environment, TC – thermal cycles, FT – freeze-thaw cycles, PW– pure water, CW – chlorides water, WD – wet-dry cycles) and Z is number of days that the specimens were submitted to the corresponding environmental action.

Table 1. Experimental program

Series	**Environmental action**	**Epoxy adhesive**	**CFRP laminate**
S0	Lab environment	ADH_REF ADH_REF720	FRP_REF
S1	Thermal cycles	ADH_TC120 ADH_TC240	FRP_TC120 FRP_TC240
S2	Freeze-thaw cycles	ADH_FT120 ADH_FT240	FRP_FT120 FRP_FT240
S3	Specimens immersed in pure water at 20ºC	ADH_PW360 ADH_PW720	FRP_PW360 FRP_PW720
S4	Specimens immersed in water at 20ºC with 3.5% of chlorides	ADH_CW360 ADH_CW720	FRP_CW360 FRP_CW720
S5	Specimens submitted to wet/dry cycles with water at 20ºC with 3.5% of chlorides	ADH_WD360 ADH_WD720	FRP_WD360 FRP_WD720

2.3 Specimen's geometry, preparation and test setup

The tensile properties of the epoxy adhesive and CFRP laminate strip materials were assessed following the ISO 527-2:1993 and ISO 527-5:1997, respectively, after being submitted to the aging action. For the case of the epoxy adhesive special moulds were used to cast the specimens, whereas for the case of the CFRP laminate samples were cut with the proper dimensions. The epoxy samples were tested on a universal testing machine under displacement control of 1 mm/min. The applied load was measured with a 50 kN load cell (1/1000±5% precision). The Young modulus and ultimate strain was assessed through either by using a 50 mm clip gauge or a TML BFLA-5-3-3L strain gauge (see Figure 1a). The CFRP samples were also tested using a universal testing machine under displacement control of 2 mm/min. During these tensile tests, the applied load was measured with a 200 kN load cell and the strains were measured through the use of a 50 mm clip gauge (see Figure 1b).



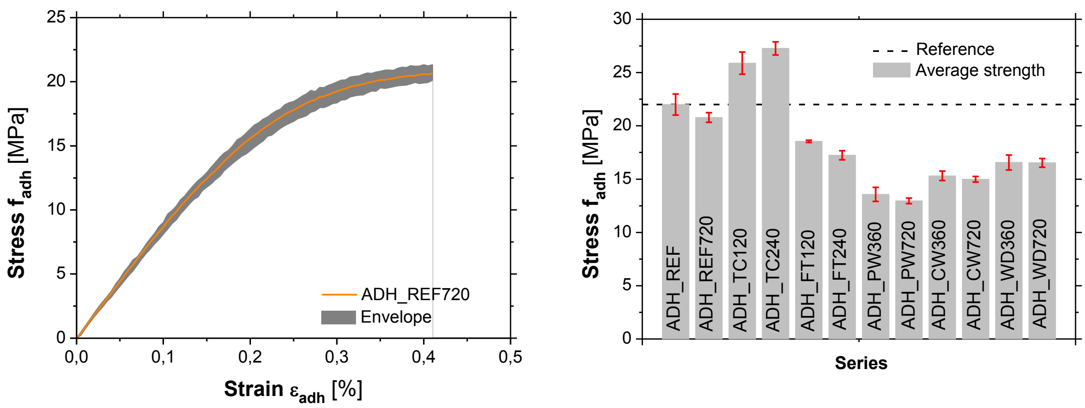
(a) (b)

Figure 1. Overview of the test setup of the: (a) epoxy adhesive; (b) CFRP laminate strip.

3 RESULTS

3.1 Epoxy adhesive

Figure 2a shows a typical stress-strain response obtained in the tensile tests with the epoxy adhesive. The average values of the main parameters obtained (tensile strength, Young modulus and ultimate strain) from the tensile tests are presented in Table 2. From these results the following three major observations can be pointed out: (i) an increase on the ultimate tensile stress and Young modulus for the series ADH_TC120 and ADH_TC240; (ii) a decrease on the tensile strength and modulus of elasticity for the freeze-thaw cycles samples; and, lastly, (iii) an generalized decrease on the tensile stress and elastic modulus for series S3, S4 and S5.



(a) (b)

Figure 2. Epoxy adhesive: (a) typical stress-strain curve; (b) Tensile strength obtained in each series.

The tensile strength increased 18% and 24% on ADH_TC120 and ADH_TC240 (series S1), respectively, when compared with the ADH_REF (see Figure 2b). Although the technical data sheet of the adhesive does not have any information regarding the curing and post-curing process. Moussa *et al.* (2012) reported that, depending on the type of resin, it might be common the existence of a post-curing phase which improves the mechanical properties of the epoxy. This process starts when temperatures higher than the temperature of the first curing are achieved.

On the series S2 (freeze-thaw cycles) the expected tendency was observed, i.e. a degradation on the mechanical properties was observed with the aging. In fact, e.g. the maximum tensile strength on specimens with 120 and 240 days of ageing decreased 15% and 21%, respectively. The effect of the duration of the aging action also played an important factor on the mechanical properties variation, being greater on the specimens that aged for longer periods. Finally, it should be referred for this series a post-curing phase was not occurred since the applied temperatures ranged between –18ºC and +20ºC.

Table 2. Tensile strength, Young modulus and ultimate strain obtained in the tests with the epoxy adhesive (average values)

Series	Tensile strength (f_{Adh}) [MPa]	Young modulus (E_{Adh}) [GPa]	Ultimate strain (ε_{Adh}) [%]
ADH_REF	22.00 (4.52%)	7.15 (3.71%)	0.36 (15.22%)
ADH_REF720	20.79 (2.16%)	6.66 (3.41%)	0.43 (6.10%)
ADH_TC120	25.88 (4.02%)	7.50 (3.15%)	0.39 (10.76%)
ADH_TC240	27.27 (2.28%)	7.64 (4.66%)	0.43 (5.27%)
ADH_FT120	18.55 (0.55%)	5.93 (1.36%)	0.48 (6.12%)
ADH_FT240	17.24 (2.45%)	5.54 (1.75%)	0.45 (11.78%)
ADH_PW360	13.57 (4.89%)	4.10 (3.01%)	0.55 (23.78%)
ADH_PW720	12.96 (2.06%)	3.52 (3.31%)	0.75 (14.07%)
ADH_CW360	15.31 (2.86%)	4.72 (3.47%)	0.50 (10.57%)
ADH_CW720	14.99 (1.73%)	4.36 (1.45%)	0.68 (11.39%)
ADH_WD360	16.57 (4.24%)	5.43 (2.76%)	0.39 (18.20%)
ADH_WD720	16.53 (2.45%)	5.20 (3.24%)	0.51 (13.55%)

Note: the values between parentheses are the corresponding coefficients of variation (CoV).

The remaining three series (S3, S4 and S5) presented the higher degradation ratios, when compared with series S1 and S2. As previously stated, time can be a major factor on the evolution of the mechanical properties. Because these specimens were aged for longer periods of time, all comparisons have been made to the ADH_REF720 (kept in lab environment for 720 days). Results show that specimens immersed on pure water (series S3) had the greatest degradation ratio (-34% and -38% for ADH_PW360 and ADH_PW720, respectively).

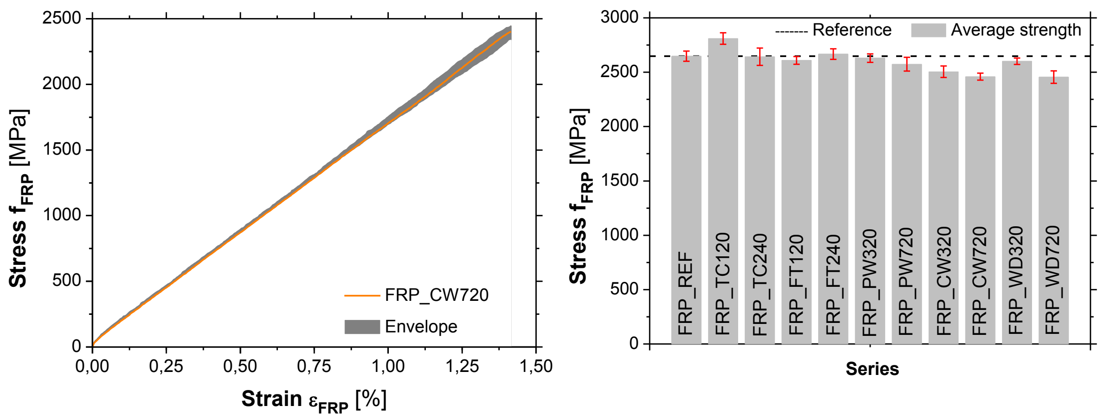
Epoxy adhesives absorb water (moisture) and, as a consequence, they plasticize, increasing their volume and their mechanical properties are enfeebled: namely the stiffness, the tension strength and the glass transition temperature (Cabral-Fonseca *et al.*, 2012; El Yagoubi *et al.*, 2014). El Yagoubi *et al.* (2014) explains that the hydrolysis phenomena observed on materials subjected to wet-dry cycles, is characterized by a chemical reaction at the molecular level that destroys the molecular chains. Series S4 and S5 appear to have a lower degradation ratio in comparison with specimens immersed in pure water (series S3). This fact can be related with the salts (chlorides) do not penetrate in the epoxy adhesive, developing a semipermeable membrane. As a consequence of that, the degradation can be decelerated (Jones, 1999).

In essence, the mechanical properties of the epoxy adhesive are degraded due to the presence of water. An exception was observed on series S1, where a post-curing phase might be responsible for the increase on the mechanical properties.

3.2 CFRP laminate

A typical stress-strain curve is depicted on Figure 3a (series FRP_CW720), whereas Table 3 presents the obtained tensile strength, Young modulus and ultimate strain for all the tested samples. In a general way, the CFRP specimens seemed to have endure the ageing tests without greater losses on their mechanical properties (see Figure 3b). Results show a maximum decrease of tensile strength equal to 7% on the FRP_CW720 and FRP_WD720 series (when compared with the FRP_REF series). A reduction on the ultimate strain (in between 5% and 6%) was also observed in the same specimens. The specimens immersed on pure water for 720 days had a reduction of 3% of the tensile strength. The thermal cycles and freeze-thaw cycles seemed to maintain the initial stiffness, maximum strength and ultimate strain.

Although the 7% strength loss on series S4 and S5 seemed small and even negligible, this result suggests that chlorides exposure (complete immersed or exposed to wet-dry cycles) may be detrimental to strengthening system with carbon FRP laminates.



(a) (b)

Figure 3. CFRP laminate strip: (a) typical stress-strain curve; (b) Tensile strength obtained in each series.

4 CONCLUSIONS

An experimental program was carried out to assess the evolution of the mechanical properties of two common materials used on the strengthening of RC structures: an epoxy adhesive and a CFRP laminate strip. From the obtained results the following main conclusions can be pointed out: (i) the CFRP specimens presented negligible losses on their tensile properties; (ii) the thermal cycles might have caused a post-curing phase that could explain the increase on the epoxy specimens strength and stiffness; (iii) a reduction on the maximum stress and elastic modulus was observed on epoxy specimens due to the presence of water (from series S3, S4 and S5); and (iv) epoxy material seemed to be more susceptible to the degradation phenomenon with immersed in pure water.

Table 3. Tensile strength, Young modulus and ultimate strain obtained in the tests with the CFRP laminate strips (average values).

Series	Tensile Strength (f_{FRP}) [MPa]	Young Modulus (E_{FRP}) [GPa]	Ultimate strain ($\varepsilon_{FRP,u}$) [%]
FRP_REF	2648.26 (1.76%)	169.48 (2.50%)	1.563 (1.80%)
FRP_TC120	2809.86 (1.89%)	169.56 (2.62%)	1.648 (3.54%)
FRP_TC240	2642.79 (3.04%)	169.42 (2.37%)	1.560 (2.03%)
FRP_FT120	2609.14 (1.37%)	166.05 (1.79%)	1.572 (2.64%)
FRP_FT240	2666.74 (1.82%)	169.66 (2.08%)	1.573 (3.56%)
FRP_PW360	2629.58 (1.48%)	166.48 (2.87%)	1.582 (2.65%)
FRP_PW720	2573.58 (2.46%)	165.44 (2.46%)	1.557 (4.20%)
FRP_CW360	2504.52 (2.13%)	170.13 (2.69%)	1.482 (3.53%)
FRP_CW720	2459.38 (1.31%)	167.30 (0.68%)	1.467 (1.19%)
FRP_WD360	2601.36 (1.12%)	165.08 (5.05%)	1.580 (6.25%)
FRP_WD720	2455.77 (2.34%)	166.12 (0.82%)	1.479 (2.97%)

Note: the values between parentheses are the corresponding coefficients of variation (CoV).

5 ACKNOWLEDGEMENT

This work is supported by FEDER funds through the Operational Program for Competitiveness Factors - COMPETE and National Funds through FCT - Portuguese Foundation for Science and Technology under the project FRPreDur - PTDC/ECM-EST/2424/2012. The authors also like to thank the S&P Clever Reinforcement Ibérica Lda. Company that has been involved supporting and contributing the development of this study. The first, second and third authors wish also to acknowledge the grants SFRH/BD/80338/2011, SFRH/BD/89768/2012 and SFRH/BD/98309/2013, respectively, provided by FCT.

REFERENCES

BSI, 2002, BS EN 13687-3. Products and systems for the protection and repair of concrete structures. Test methods. Determination of thermal compatibility. Thermal cycling without de-icing salt impact. British Standard Institution (BSI): 12pp. London, England.

BSI, 2006, DD CEN/TS 12390-9. Testing hardened concrete. Freeze-thaw resistance. Scaling. British Standard Institution (BSI): 12pp. London, England

Cabral-Fonseca, S., J. R. Correia, M. P. Rodrigues, and F. Branco, 2012, Artificial Accelerated Ageing of GFRP Pultruded Profiles Made of Polyester and Vinylester Resins: Characterisation of Physical–Chemical and Mechanical Damage. Strain. 48, 162-173.

El Yagoubi, J., G. Lubineau, S. Saghir, J. Verdu, and A. Askari, 2014, Thermomechanical and hygroelastic properties of an epoxy system under humid and cold-warm cycling conditions. Polymer Degradation and Stability, 99, 146-155.

FIB, 2001, Fib Bulletin 14. Externally bonded FRP reinforcement for RC structures. Fédération internationale du béton (fib): 138 pp. Lausanne, Switzerland

ISO, 1997, 527-5:1997. Plastics - Determination of tensile properties - Part 5: Test conditions for unidirectional fibre-reinforced plastic composites. ISO - International Organization for Standardization, Genève, 11 pp.

ISO, 1993, 527-2 1993. Plastics – Determination of tensile properties – Part 2: Test conditions for moulding and extrusion plastics. International Organization for Standardization (ISO): 5pp. Genève, Switzerland.

Jones F.R., 1999, Durability of reinforced plastics in liquid environments. Reinforced Plastics Durability, 70-110.

Myers, J. J., and N. P. Muncy, 2014, Long term in-situ bond behavior of externally bonded fiber reinforced polymer laminates subjected to environmental conditioning. 7th International Conference on Fiber Reinforced Polymer (FRP) Composites in Civil Engineering (CICE 2014), Vancouver, Canada.

Sena-Cruz, J., J. A. O. Barros, M. R. F. Coelho, and L. F. F. T. Silva, 2012, Efficiency of different techniques in flexural strengthening of RC beams under monotonic and fatigue loading. Construction and Building Materials, 29, 175-182, 4.

Michels, J., J. Sena-Cruz, C. Czaderski, and M. Motavalli, 2013, Structural Strengthening with Prestressed CFRP Strips with Gradient Anchorage. Journal of Composites for Construction, 17, 651-661.

Correia, L., T. Teixeira, J. Sena-Cruz, and J. Michels, (2014) Flexural strengthening of RC slabs with prestressed CFRP strips using different anchorage systems, presented at the 7th International Conference on Fiber Reinforced Polymer (FRP) Composites in Civil Engineering (CICE 2014), Vancouver, Canadá.

Moussa, O., A. P. Vassilopoulos, J. de Castro, and T. Keller, 2012, Time–temperature dependence of thermomechanical recovery of cold-curing structural adhesives. International Journal of Adhesion and Adhesives, 35, 94-101.

Silva, P., P. Fernandes, J. Sena-Cruz, M. Azenha, and J. Barros, 2014a, Creep behavior and durability of concrete elements strengthened with NSM CFRP strips. 7th International Conference on Fiber Reinforced Polymer (FRP) Composites in Civil Engineering (CICE 2014), Vancouver, Canada.

Silva, P., P. Fernandes, J. Sena-Cruz, M. Azenha, and J. Barros, 2014a, Behaviour of concrete elements strengthened with near surface mounted CFRP strips under thermal cycles. 7th International Conference on Fiber Reinforced Polymer (FRP) Composites in Civil Engineering (CICE 2014), Vancouver, Canada.

S&P, 2013, Technical Data Sheet. S&P Resin 220 epoxy adhesive. S&P Clever Reinforcement: 3pp.

S&P, 2014, Technical Data Sheet. S&P CFRP – Laminates. S&P slot-applied laminates. S&P Clever Reinforcement: 6pp.