EFFECT OF THERMO-HYGROMETRIC EXPOSURE ON FRP, NATURAL STONE AND THEIR ADHESIVE INTERFACE

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Abstract

As well known, the performance of Fiber Reinforced Polymer (FRP) materials as external strengthening technique isstrongly dependent on the bond behavior between FRP and substrate. Several experimental studies have been performed on this topic, however limited attention has still focused on the bond durability. In this paper, the effect of a thermo-hygrometric environment on the interface behavior FRP-calcareous natural stones isinvestigated. Each utilized materials (natural stone, adhesive, FRP sheets) was firstly exposed to the same thermo-hygrometric atmosphere; a relevant decay of mechanical properties has been found for the analyzed substrates (Lecce stone and Neapolitan tuff) while a negligible influence of the exposure has been observed for the composite reinforcements (CFRP and GFRP) . The results regarding the variation of mechanical properties of the resins evidenced that the effect of the performed exposure is strictly correlated to the specificmaterials properties: a relevant degradation or even an improvement of mechanical performances has been,in fact,registered. The bond strength and the kind of failure were both analyzed as a function of the treatment used, as well as the strain and stress distribution at the interface.The kind of failure changed in some cases when passing from unconditioned to conditioned specimens; the bond strength, the maximum bond stress and the interface stiffness were affected by the treatment, manly depending on the adhesive resin deterioration. Finally, on the basis of the provisions given by the CNR-DT 200 R1/2013 document, the possibility of defining design relationships, able to take into account also durability aspects, is discussed.

Keywords: A. Polymer-matrix composites (PMCs),B. Debonding, C. Environmental degradation, D. Mechanical testing, E. Calcareous Stones.

1 Introduction

In the last decades, the use of FRP composites to repair and/or upgrade existing buildings or infrastructures proved to be an effective solution, being able to overcome some of the drawbacks experienced with traditionaltechniques. Many scientific papers have been published exploring the use of FRP on existing concrete structures, the most recent findings being reported in [1-4]. On the other hand, different codes or guidelines are available in several countries [5-11].

The application of FRP on masonry structures, even if considered as a promising solution, received less attention from researchers; only recently the Italian Research Council published a guideline in this field [11]. It is obvious that the assessment of design guidelines of general validity is much more difficult in this context due to the great variability of masonry and construction typologies worldwide as well as the different conservation approaches in the different countries. It is well recognized that the reliability of FRP strengthening based on EBR (Externally Bonded Reinforcement) techniques depends to a large extent on the bond between the reinforcement and the substrate, thus on the ability of stresses transfer at the interface. Generally speaking, masonry walls strengthened by external FRP sheets may undergo to crisis by both local and global failure modes, namely: the cracking of masonry in tension; the crushing of masonry in compression; the shear-sliding of masonry; the failure of the FRP reinforcement; and, finally, the delamination of FRP from masonry substrate [1-4, 11]. This last mechanism is deemed particularly dangerous since it causes a brittle and premature collapse. In order to evaluate the maximum stress that can be transferred before debonding by the reinforcement to the substrate, specific bondtesting and analysis procedures should be performed.

The analysis of the bond between FRP reinforcement and masonry has been the topic of recent research works. The bond behavior and load transfer mechanisms at the FRP-masonry interface were found basically similar to those relative to FRP-concrete joints. Bond tests evidenced, in fact, the occurrence of a risky mechanism of failure due to delamination, even more marked when FRP strips are glued to historic masonry, characterized by poor surface properties [12-25]. Analogously, only few analytical studies are available, especially aimed at defining the bond behavior at the masonry-FRP reinforcement interface and at calibrating a design relationship able to predict failure modes and loads. Such a lack of knowledge is due both to the variability of the masonry supports, which makes difficult to assess general relationships valid for whatever support, and to the absence of homogeneous experimental results for each type of support, due to the intrinsic variability, in texture, characteristics, etc., of the substrate. Some efforts have been recently done in order to describe the bond behavior of FRP reinforcements-clay bricks joints both via experimental tests and numerical analyses [18, 21, 24].

The interface behavior can be also severely affected by environmental or other aggressive agents that could greatly compromise the efficacy and durability of the intervention. It is well recognized that the durability performance of FRP strengthening practice is very difficult to assess, since it depends on the durability of the FPR system used to rehabilitate the structure, thus on the durability of the FRP's components, on the integrity of the FRP/substrate joint and on the durability of the substrate itself.Few studies have been recently devoted to the analysis of the durability of masonry structures strengthened by FRP materials[26-31]. A finite element modeling procedure for analyzing the hygro-thermo-mechanical response of multilayered structures constructed with distinctive permeable materials was developed by incorporating structural stress analysis into the coupled moisture/temperature finite element model [26-29]. The interfacial stresses increased with the increase of the humidity diffusion time and monotonically approached the stress level at the steady-state condition of the humidity diffusion. It was also shown that, by assuming constant humidity transport properties,the analysis resulted in a significant underestimation on the maximum interfacial stresses [26]. The effect of temperature gradient on the moisture distribution resulted in an accumulation of moisture at the interface, and induced interfacial stresses even in the absence of a moisture gradient [28-29].

An experimental investigation on the changes in the bond behavior of FRP strengthened masonry elements due to saturation after water immersion is reported in [30]. Shear bond tests showed that the ductility of the bond behavior increases with immersion time of the tested specimens. The bond strength and stiffness were observed to decrease, while the debonding slip increased. It was observed that the degradation in the bond strength and stiffness diminishes with time and possibly a residual value is obtained after a certain immersion time. A similar degradation was also observed in interfacial fracture energy. The failure mode was cohesive in all the specimens, with the fracture surface inside the brick [30].

In a previous paper, the effect of a long term immersion in water on bond durability was analyzed when FRP elements were externally applied to a natural masonry substrate[31]. The obtained results showed that the bond strength reduced up to 26% passing from unconditioned to conditioned specimens, and a more fragile bond behavior was observed. In all cases, the debonding involved the first masonry layers, due to the weakness of the substrate with respect to the reinforcing system, both in standard conditions and after the aging in water. In addition, the water seems have little influence on the stiffness of the interface. The available relationships, provided by the Italian Technical document [11] for evaluating the bond strength in standard conditions, seemed to be still effective in the case of aged specimens, once the decay of the mechanical properties of the utilized materials is considered. Otherwise, an appropriate environmental coefficient should be added for taking into account the reduction of the bond strength.

In the present paper, the effect of the exposure to a thermo-hygrometric environment on the performance and durability of FRP-masonry joint was analyzed and discussed. To this aim, an investigation on the FRP sheet-natural stone bond behavior in standard conditions and after exposure to 40°C and 90% R.H., performed in a climatic chamber, was carried out. Two types of natural stones were employed: "Lecce stone", traditionally employed in masonry constructions of the Salentine Peninsula, and "Neapolitan tuff", in particular "Neapolitan Yellow tuff", characteristic of the volcanic area surrounding Naples. The commercial FRP reinforcements used were made by unidirectional one-layer carbon or glass fibers and an epoxy based matrix, applied to the stone substrate by the hand lay-up technique. Each material employed in the present study (i.e. the stone elements, adhesive and putty, composite sheets) was also exposed to the same thermo-hygrometric environment used for the FRP-stone joints in order to analyze the influence of the treatment performed on any single component. On the basis of the provisions given by the CNR-DT 200 code [11], the possibility to calibrate design relationships, able to take into account also durability aspects, is discussed.

2 Experimental investigation

2.1 Materials

Two types of natural stones, widely used in existing masonry structures of Southern Italy, were selected in the present study: the "Lecce stone" and the "Neapolitan tuff". They are both calcareous stones characterized by high porosity, easy workability, good aesthetic and satisfactory mechanical and physical properties, even if the latter are highly dependent on the quarry location. "Lecce stone" shows a widespread porosity, around 39% [32], and small pore size, while "Neapolitan tuff" displays a porosity of about 50% [33].

Two commercial FRP's, used as reinforcing systems, were analyzed: a Carbon Fiber Reinforced Polymer (CFRP) and a Glass Fiber Reinforced Polymer (GFRP). Both FRP's were manufactured through hand lay-up technique, following the procedure suggested by suppliers. The glass or carbon fiber sheets were thoroughly soaked in an epoxy adhesive, supplied by the same company, removing any excess of the resin by a roller. In each layer, the glass or carbon fibers were disposed in the lengthwise direction. The main properties of the fibers composing the two FRP systems, attained from the relative data sheets, are reported in Table 1.

The specimens of both CFRP and GFRP were manufactured in dimensions and shape according to the code relative to the assessment of tensile properties of composites, as previously reported [34].

The same epoxy adhesive used as matrix for the two FRP's, as well as an epoxy putty used to finish the surface of the substrate where the FRP was applied, were also analyzed in the present study. They are both two-part cold-cured epoxy systems; the putty contains about 60% wt. of an inorganic filler [34], while the adhesive is an unfilled resin. The main characteristics of both epoxy systems, as reported on their data sheets, are shown in Table 2.

In order to evaluate the effect of water on any single component of the strengthening/repairing system, samples of the two epoxy systems, i.e., putty and adhesive, were produced in suitable dimensions. In this way, the limits/deficiencies of each component composing the FRP's were identified, assessing their effects on the performance of the whole system. The two liquid epoxy systems were poured in Teflon molds to produce samples of standard dimensions, shown in Figure 1, to be tested in tensile mode. The cure of the putty and the adhesive wasperformed at ambient temperature up to 45 weeks. Even though the suppliers suggested for the resins curing times at ambient temperature (about 23°C) of about 20-30 days, a much higher curing time was employed, following the results of previous studies performed on similar cold-curing epoxy resins used as adhesives and/or matrices for composites employed in infrastructure applications [38-40]. An appropriate curing time is mostly needed when the influence of environmental or other aggressive agents on the mechanical performance of cold-cured systems is addressed, in order to guarantee the attainment of a "stable" system and to analyze the effects that can be totally attributed to the aging treatment under investigation [34].

For the same reasons, the cure of both FRP systems was performed at ambient temperature up to 44 weeks, i.e. much longer times than those suggested by suppliers (about 30 days).

2.2 Mechanical tests on stones and epoxy systems

The mechanical properties of all the materials employed in the present study were experimentally evaluated, as following described.

The compressive strength of both kinds of stone was determined by compression test on cubes (side of 71 mm), according to the proper standard [41]; the flexural strength of stones was evaluated by three-points bending test on prisms of standard dimensions (20 x 30 x 120 mm^3), according to the code [42].

The tensile characteristics of putty and adhesive resins were evaluated at two different curing times, i.e. 33 and 45 weeks, following the appropriate code [43]. Cured specimens of each system (Figure 1) were tested using a Lloyd Instruments Machine (LR5K), with displacement control, at a cross-head speed of 5 mm/min. Tensile properties (modulus of elasticity and tensile strength) were calculated averaging the results of five experiments, at least. In order to record the strain during each test, two electrical strain gauges were glued for a 6 mm length on each side of the specimens.

2.3 Mechanical tests on adhesively bonded FRP/stone elements

Bond tests were performed in a "double lap shear" configuration, as shown in Figure 2. The reinforcing sheets (dimensions: 80 x 400 mm^2) were bonded at two opposite sides of the ashlars block.

Each stone element (dimensions: 100 x 200 x 250 mm^3) was reinforced with FRP sheets providing a bond length (glued portion) of 150 mm, while a 50 mm length of the sheet was left un-bonded (free portion) in order to limit specimens imperfections [13]. In Figure 3, the scheme of application of FRP layer on each ashlars block is depicted.

Before the application of FRP sheets, the stone elements were dried at 80°C for 24 – 48 hours in order to eliminate absorbed water, if present. Then, the FRP was applied on the surface to be strengthened through the wet lay-up technique using the different epoxy systems, following the procedure indicated by suppliers. The first resin was a two-part epoxy primer to prepare the substrate to which the FRP will be applied. The putty, used only for Neapolitan tuff elements, was then applied in order to adequately finish the surface of the stone substrate. Finally, the two-part epoxy adhesive was used as either the matrix to manufacture the FRP and the adhesive to join it to the surface to strengthen.

Electrical strain gauges were glued on both sides of each specimen in the load direction, corresponding to the fibers direction of the FRP sheets, as shown in Figure 4. Strain gages were also glued on the free portion region of each FRP layer, to determine the tensile modulus of elasticity of the laminate.

The FRP/stone specimens were, finally, inserted into a steel frame fixed at the clamp on the bottom of universal testing machine (as shown in Figure 2). The free end portions of each sheet was clamped at the top of the crosshead by a special gripping device, able to transmit the tensile load to the composite reinforcement via a steel pin, inserted thorough a drilled hole in the composite sheet. Premature damage in that region was avoided providing an adequate bond of the sheets within two steel plates (size: 150 x 100 x 3 mm^3). The described configuration allows to apply a compressive load on the stone element, while on each of the two opposite FRP layers a tensile load equal to an half of the compressive load is applied (Figure 2). The described tests were carried out under displacement control, with a displacement rate of 0.2 mm/min. More details on the test set-up and procedure can been found in a previous paper [13].

2.4 Exposure to a thermo-hygrometric environment

In order to evaluate the effects of realistic environmental conditions characteristic of Mediterranean regions on the mechanical properties of the investigated materials, mechanical tests on both kinds of stone, on the two (putty and adhesive) epoxy resins and on the FRP/stone specimens were performed after a thermo-hygrometric treatment performed in a climatic chamber (Perani, model UC1000/20), as following described.

The mechanical tests on both natural stones were carried out after a 32-week exposure at 40°C and 90% R.H..

In order to estimate the effects of the aging procedure on epoxy systems, specimens of adhesive and putty, previously cured, were tested in tensile mode after a 32-week conditioning(40°C and 90% R.H).Both the resins, as well as the FRP, were tested after a curing time of 14 weeks.

The adhesively bonded FRP/stone specimens were exposed to the same thermo-hygrometric treatment for shorter times (25 weeks). In Table 3, a summary of the aging tests performed on the FRP/stone elements is illustrated.

3 **Results and discussion**

3.1 Mechanical tests on single components

The mechanical properties of the materials employed in the present studyare summarized in Tables 4 and 5. In these Tables, the materials properties measured in standard conditions are compared to those determined after the thermo-hygrometric treatment.

As clearly noticeable in Table 4, the properties of both stones were drastically affected by the thermo-hygrometric aging. In the case of Lecce stone, in particular, the compressive strength was almost halved with respect to that measured in standard conditions. The compressive strength of Neapolitan tuff was reduced by 20%. The observed mechanical degradation of stones can be explained in terms of their high porosity: the water humidity, easily entering into the stone, causes internal damage due to the additional pressure exerted by the presence of the liquid within the pores of the stone [44]. The noticeable reductions of mechanical performance measured for both types of stone was found also in previous studies, where a decrease in uniaxial compressive strength in presence of water is reported [31,34]. As already observed for the compressive strength, a significant reduction in the flexural strength was obtained after the thermo-hygrometric treatment, this time more marked for the Neapolitan tuff (almost 70%).

In Table 5 the results of the tensile mechanical tests performed on the two resins, i.e. putty and adhesive, cured for 33 and for 45 weeks, are reported. While the tensile strength appears to be scarcely influenced by the curing time, the modulus is still increasing after a 33-week curing time. The latter observation confirms what previously found on similar cold-cured resins [37-40]: even after 33 weeks of curing, the cold-cured systems did not reach a "stable" state, i.e. they are still curing. The putty resin, in particular, containing about 60% of inorganic filler, after a 45-week curing displays an increase in stiffness of about 44% with respect to the same property measured after 33 weeks of curing. Comparing these results with the mechanical characteristics provided by suppliers (Table 2), much higher values for tensile strength were found in the present study for the two systems cured for much longer times with respect to those reported on data sheets (referred to a 7-day curing).This result confirms that, in the case of cold-cured systems, the cure is not concluded in the period generally suggested by suppliers (never longer than 14 days)but it proceeds for much longer times, up to months or years, with a corresponding progressive build-up of mechanical properties [45].

The "in-plane" tensile properties calculated on specimens of CFRP and GFRP, cured for 36 and for 44 weeks, are summarized in Table 5. As already reported in previous studies [34], the increase of the curing time has a very limited effect on the mechanical properties of both composite sheets. The tensile mechanical properties of a single ply composite measured in the fiber direction are, in fact, highly dependent on the properties of the fibers and not influenced by the curing time of the resins; the matrix resin, on the other hand, is mainly responsible for the stress transfer across the fibers. By comparing the mechanical characteristics found for both FRP systems with those reported on their data sheet (Table 1), very similar values of elastic modulus can be noticed irrespective to the curing time, confirming our hypothesis.

Referring to the maximum tensile strength, the values calculated in our study for both CFRP and GFRP are somehow lower (by about 35%) than those reported by suppliers. Finally, the relatively high standard deviation values calculated in the tests and reported in Table 5, especially in the case of both FRP's, can be justified by the manual manufacture of FRP specimens, leading to a not perfectly uniform thickness of the composites (about 1 mm) and, possibly, to the formation of in-homogeneities during the impregnation of fibers.

In Table 5 the effect of the thermo-hygrometric treatment performed on mechanical properties of resins and FRP's, is shown. As already underlined, the resins and the FRP's were cured for 14 weeks before their exposure to a temperate-moist atmosphere, i.e. an appreciable higher curing time than that suggested by suppliers (i.e. 20-30 days). The total time (curing plus exposure) was, then, 46 weeks from their manufacture. In such a way, we were able to compare the mechanical behavior of all the materials after the same time but spent in different atmospheres, i.e. solely laboratory or laboratory plus temperate-moist atmosphere.

Analyzing first the effect of the thermo-hygrometric treatment on the putty resin, its tensile strength remains fairly constant, considering the high standard deviation values, while an appreciable increase in tensile modulus is noticed, almost doubled with respect to un-exposed specimens. These results would be in contrast to what generally recognized, i.e. the water ingress is likely to produce a decrease in mechanical properties due to plasticization effects [39,46]. On the other hand, in the present study the exposure to humidity is accompanied by a thermal stage. It has been already observed that the curing process of putty resin continues well beyond 33 weeks. In addition, as reported in a previous study [34], the glass transition temperature (Tg) measured on this system after a 45-week curing is around 37°C and it drops to 34°C upon immersion in water, due to plasticization of entering water. The same plasticization can also occur when the system is exposed to a humid atmosphere, as in the present study: thus, the putty can undergo to a similar decrease in Tg. In such conditions, the Tg of the not-fully cured resin is appreciably lower than the temperature selected in the thermo-hygrometric treatment, i.e. 40°C, and the curing process of the resin can continue at an increased rate (since it is a kinetic driven process) [39]. The expected decrease in mechanical properties due to moisture, therefore, is counteracted by the continuation of curing, taking place during the thermal stage, producing a general increase of mechanical properties, mainly in stiffness, of the putty resin.

Referring to the adhesive, a different behavior was registered in Table 5, i.e. an appreciable decrease (around 70%) in tensile strength after the exposure to a temperate-moist atmosphere. The tensile modulus of the adhesive resin, on the other hand, seems to be almost unaffected by the same treatment. The Tg of the adhesive resin measured after a 45-week curing is appreciably higher (i.e. about 52°C) than the temperature used for the thermo-hygrometric treatment [34]. This would imply that the curing process can occur also in adhesive resin during the thermal stage but at a very low rate. Therefore, the plasticization due to the humid atmosphere in this case would prevail on the tensile strength, leading to an appreciable decrease in this property. The tensile modulus, on the other hand, was probably equally influenced by the advancement of curing and the plasticization of moisture, resulting almost unaffected by the temperate-moist atmosphere.

Finally, referring to CFRP and GFRP specimens, their tensile strength seems only slightly affected by the thermo-hygrometric treatment performed, bearing in mind the high standard deviation values measured in the tests. The decrease in strength is higher in the case of glass fibers reinforcement, being glass fibers more susceptible to aging. The tensile modulus of both FRP's is almost unaffected by the same treatment. As reported in [31], the presence of moisture/water has only limited effects on the tensile mechanical properties of unidirectional single-ply composites, when measured in the fibers direction.

3.2 Bond test

The influence of the thermo-hygrometric treatment on the bond between FRP sheets and natural stones, i.e. Lecce Stone and Neapolitan tuff, is analyzed and discussed in the following sections. The comparison between unconditioned and conditioned samples allows to highlight interesting aspects related also to the kinds of substrate and reinforcement used.

3.2.1 Failure modes

For samples tested under standard conditions the bond failure occurred by debonding of the FRP reinforcement with the detachment of a stone layer (Figure 5); this kind of cohesive crisis (within the substrate) is due to the poor mechanical properties of the substrate itself. In particular, for the specimens made by Lecce Stone, the delamination involved the detachment of a very thin layer of the substrate, irrespective of the kind of sheet; regarding the Neapolitan tuff specimens, the delamination took place crushing a thick stone layer. This last failure mode is mainly due to the specific properties of the stone (Figure 5); in fact, the high porosity of the tested Neapolitan tuff allowed a more extensive impregnation ofthe resin, thus causing the failure to shift beneath a deeper layer of the substrate [13].

For conditioned samples is not possible to identify a common trend as regard the type of bond failure, as better specified in the following.

After 25 weeks of exposure at 40°C and 90% humidity atmosphere performed in a climatic chamber, Lecce Stone specimens reinforced with CFRP showed a mixed failure (Figures 6a and 6b), partly adhesive and partly cohesive within the substrate, whereas for the unconditioned specimens the failure mode was always cohesive. This is consistent with a substantial deterioration of the employedadhesive due to humid ageing [47].

Referring to the Lecce stone samples reinforced with GFRP, in one case the bond failure was cohesive as for unconditioned specimens(Figure 6c). In the other case, the failure finally occurred within the reinforcement, with cracks parallel to the fibers, as shown in Figure 6d. However, a cohesive delamination was contemporary observed near the loaded end, as also confirmed by the analysis of the bond stress versus slip curves, discussed below.

Debonding between GFRP and Neapolitan tuff took place inside the stone, as observed in standard conditions.For both samples of Neapolitan tuff reinforced with CFRP, an evident cracking within the sheet, at the matrix-fiber interface, caused the crisis (Figure 6e), displayinga different behavior with respect to unconditioned samples, shown in Figure 6f. The intra-laminar crisis of the CFRP sheet could be related to the degradation of the mechanical properties of the adhesive involving a decay of the fiber-matrix bond; however, the effect of possible imperfections should be also considered, as normally expected for hand lay-up technique used to apply of the reinforcement.

The different bond failures observed for conditioned samples might be mainly due to the different thicknesses of resin at the interface stone/sheet, as explained in the following.In the epoxy adhesives the water moves to the interface according to Fick's law [34-37]and both the amount of absorbed water and the rate of absorption depend on formulation variables, such as theepoxy resin and curing agent types employed;the environmental variables, such as temperature and relative humidityand the curing conditions are also influential [36, 37]. At the interface, since it is difficult to directly measure the moisture content, in a recent research a numerical simulation of moisture diffusion has been performedin the case of concrete specimens reinforced by FRP;the governing equation utilized for mass diffusion is basically an extension of Fick’s equation, accounting for non-uniform values of diffusivity and solubility in multiple constituent materials [36, 37]. The weakening of the interface due to the presence of moisture led to a significant reduction in fracture toughness indicating that moisture had a detrimental effect on the FRP-concrete interfacewhile causing a shift in the failure mode from stone delamination in dry specimens to concrete-epoxy interface separation in wet specimens [36,37].

In the present work the materials are the same as those used in Sciolti et al.2010 foranalyzing the effect of immersion in water on bond between FRP and stone substrate as well as on the mechanical performances of each utilized material; in that case a saturation time of 24 weeks and diffusion coefficients equal to $10^{-10} \mathrm{cm}^2 / \mathrm{s}$ have been found for the epoxy systems [34]. In the same work the samples were conditioned in a climatic chamber at temperature and humidity of 40°C and 90% R.H, respectively; however, on the basis of results reported in [35] saturation time of about of 24 week is stillexpectedfor the resin.Themore complex behaviour at the interface with respect to that of thehomogeneous materials [36,37] makes reliable the hypothesis that a longer period (over 25 weeks)is neededfor the interface degradation in most of the analyzed cases.

In addition the diffusion coefficient is inversely proportional to the thickness, therefore for blocks with a larger thickness of the resin, the water takes longer time to reach the interface.

Among tested samples, those made in Neapolitan tuff reinforced by GFRP had the greatest thickness of resin while the Lecce Stone reinforced with CFRP presented the lowest resin's thickness. In fact only for the Lecce Stone reinforced with CFRP there was a shift in the failure mode, from delamination in dry specimens to epoxy/stone interface separation in wet specimens, with a significant reduction in fracture toughness, this confirms a weakening of the interface due to the presence of moisture [36,37]. For the remaining samples, water probably did not have time to reach the interface, therefore in some cases the sheet broke parallel to the fibers while in others a cohesive failure, occurred.

3.2.2 *Bond strength, maximum bond stress and optimal length*

In Table 6, the experimental results recorded for each sample are shown as well as the average values measured on similar samples for which the same type of failure has been observed. The table reports the stiffness of the sheet, the time of exposure, the bond strength, $F_{\max}$, the maximum shear stress at the adhesive-stone interface, $\tau_{\max}$, the optimal bond length, L_o, and the types of failure.

The shear stress at the adhesive-stone interface has been evaluated imposing the translational equilibrium condition of the sheet ,

$$\tau(x) = t_s \cdot E_s \cdot \frac{\varepsilon_{th} - \varepsilon_2}{x_2} , \qquad (1)$$

where:

ε_{th} theoretical strain values function applied load at the interface, P_s, and elastic modulus E_s;

ε_2 strain values obtained from strain gages “2” or “12”, figure 4;

x_2 position of strain gages “2” (or “12”) measured from the loaded end of the sheet, figure 4;

t_s thickness of the sheet;

E_s elastic modulus of the sheet, determined on the basis of strain values registered on the unglued length, as reported in more detail in previous works [12,13].

The optimal bond length refers to the length of the sheet where stresses are effectively transferred at the interface under service condition, namely before the delamination process starts. Such a length is measured from the loaded end to the distance corresponding to negligible strain values; its determination has been performed here considering as negligible the strain values equal to $1/500 \cdot \varepsilon_0$, being ε_0 the strain at the unglued sheet, and at load levels less than $50\% F_{\max}$. With regard to the maximum shear stress and the optimal bond length, the corresponding average values evaluated for both the applied sheets are reported in Table 6 for each specimen.

The ultimate load has been determined by halving the applied load, in the hypothesis of symmetric behavior at the two opposite sides of the specimen.

Analyzing the results reported in Table 6 it can be observed that, for Lecce Stone samples under standard conditions, the maximum shear stress changed depending on the stiffness of the reinforcement. For samples reinforced by GFRP, the maximum shear stress ($\tau_{\max} = 3.8\,MPa$) is lower than that observed for the samples reinforced with carbon sheets ($\tau_{\max} = 6.3\,MPa$) of about 40%. Theexposed Lecce Stone samples didnot show significant variations in the maximum shear stress by varying the type of reinforcement ($\tau_{\max} = 3.9\,MPa$ in the case of CFRP sheet, $\tau_{\max} = 3.6\,MPa$ in the case of GFRP reinforcement). This result can be justified by the circumstance that the hygro-thermal treatment didnot affect the Lecce Stone samples reinforced by GFRP (the maximum shear stress varied of about 7%) while a relevant influence was noticed for samples of Lecce Stone reinforced by carbon tapes (the maximum shear stress varied of about 40%). As already observed analyzing the failure mode only for the samples reinforced with CFRP, the conditioning treatment caused a significant degradation of the interface, due to the smaller thickness of resin. The adhesive interface suffered, therefore, the effects of the conditioning in agreement with results obtained for materials (Table 5).

For Lecce Stone specimens reinforced with glass sheet, limited variations were observed between conditioned and unconditioned samples also in terms of bond strength (variation about 14%) and optimal bond length (variation of about 11%). As regard to the Lecce Stone reinforced with carbon sheet, little variations have been registered over aging time for the bond strength and the optimal bond length, 19% and 5%, respectively. However, an evolution of the failure mode was registered from cohesive failure towards a mixed failure,as previously explained. A similar result is reported in Karbhari and Gosh,Tuakta C and Büyüköztürk, and in Benzarti et al., for bond between concrete and FRP [36, 37, 47,48].

Analyzing the results for Neapolitan tuff reinforced with carbon sheet, reported in Table 6, it can be observed that after conditioning, the bond strength, F_{max}, decreases by about 42% compared to that recorded for unconditioned samples. The maximum shear stress at the adhesive-stone interface and the optimal bond length do not change significantly, with differences of respectively 1% and 2%. The significant change recorded for the maximum load is related to the different failure modes (cohesive or intralaminar).

For samples with Neapolitan tuff reinforced with GFRP it can be noted that the stay in a climatic chamber was not influentialwith respect to the bond strength value, the optimal bond length and the maximum shear stress; the percentage variation being: 15%, 3% and 23%, respectively. In this case, the performed treatment has a little effect most likely because the exposure time in the climatic chamber was not enough to diffuse the water in the resin up to the interface.

Furthermore, from the analysis of values reported in Table 6, an interesting result can be observed comparing the bond properties of specimens made with different stones and reinforced with the same kind of composite sheet. Besides the mechanical properties, also the physical properties, depending on the microstructure of the stone, have a relevant influence on the bond performance. In particular, the Lecce Stone shows higher mechanical characteristics with respect to Neapolitan tuff,due to a lower porosity. For this reason, the layer of substrate involved by adhesive impregnation is different and thicker for Neapolitan tuff. An increased interface deformability improves the fracture energy and the interface ductility involving a higher ultimate load. On the basis of this consideration it can be understood the high value of the bond strength found for Neapolitan tuff if compared to that measured for Lecce Stone, even if the mechanical properties of the material in the first case (Neapolitan tuff) are lower. Instead, the peak bond stress decreases with the mechanical properties of the substrate, as generally expected.

3.2.3 Interface deformability end bond stress-slip curves

The Figures 7, 8, 9 and 10 show the comparison in terms of deformation-position and bond stress- slip curves for conditioned and unconditioned samples. In particular, for the samples in Lecce Stone reinforced with carbon sheet, the Figure 7 shows the deformation recorded along the sheet at a load level equal to 4kN, corresponding to a load less than 50% of the maximum load. The strain values recorded on both sides of similar samples are drawn.

The elastic modulus used for data processing is obtained as the average of those recorded for unconditioned specimens [13], since the stiffness of the sheet was not affected by the treatment.

Analyzing the Figure 7 it can be noticed that, up to a distance of about 50mm from the loaded end, the deformations referred to the conditioned samples are higher than those of samples left in standard conditions; this confirms that the system CFRP-Lecce Stone is more deformable after conditioning.However, the effect is not such as to influence the optimal bond length value. In fact, for all samples strains become negligible at a distance of about 100mm. The greater deformability of the interface detected for conditioned samples can be found also observing the bond stress-slip curve, reported in Figure 8.

For both types of samples (conditioned and unconditioned) the results show that the behavior at the interface is characterized by the following steps: at the first stage an elastic behavior is observed and a perfect bond exists between sheet and stone; after the attainment of the peak in bond stress, a softening branch follows,ending with a residual bond stress due to the friction contribution. In the first stage, the curves of conditioned specimens have a slope of 127 MPa / mm while for the unconditioned samples the slope is 148 MPa / mm, with a stiffness reduction of about 16%. The slope of the curve is equal to the ratio Ga/s, where Ga is the shear modulus and s is the thickness of adhesive (resin layer between the reinforcement and the substrate). As the analyzed curves (Figure 8) refer to stone elements reinforced with CFRP and having an equal resin thickness, the different recorded slope of the bond stress-slip curves can be justified by the deterioration of the adhesive layer, as already underlined. The area under the $\tau - s$ curve is equal to the fracture energy, relevant in the determination of the bond strength. The reduction of the fracture energy after conditioning justifies the decay of the maximum load (about 20%) for conditioned samples.

For the Lecce Stone samples reinforced by GFRP and for all Neapolitan tuff samples, the bond stress – slip curves (Figure 9) showa similar slope at the elastic stage comparing conditioned and unconditioned samples, confirming that the interface stiffness was not affected by the imposed treatment. Also after the peak bond stress the curves path of conditioned and unconditioned samples appears similar; the post-peak curve is not reported for samples failed by intralaminar cracking.

The Figure 10 shows the deformation recorded along the sheet for all tested samples, at load values equal to 3 kN and 4.5 kN, which are less than the 50% of the maximum load. The analysis of these graphs evidences again a negligible difference comparing the behavior of conditioned and unconditioned samples, confirming the results discussed above.

4 Theoretical simulations

4.1 Strains at the interface

Starting from the Volkersen theory [49], an analytical model has been utilized to evaluate the shear stress at the interface FRP-substrate. The following assumptions are considered:

1. Materials are homogeneous, isotropic and elastic linear.
2. The thickness of the different elements (stone, sheet, glue) is constant along the bond line.
3. The width of the sheet is constant along the bond line.
4. The peeling normal stresses are negligible.

Referring to a small element of the system stone-sheet, dx length, and taking into account the constitutive law of materials, the equilibrium and compatibility conditions allow to define the bond stress distribution along the composite sheet.

In particular, the validity of Hooke's generalized law is assumed and, referring to a unit width, the equations (2) can be obtained:

$$\tau(x)=G_a\gamma(x)=G_a\frac{u(x)-v(x)}{t_a} \tag{2}$$

If imposing equilibrium condition, it can be obtained:

$$\frac{d^2\tau(x)}{dx^2}-\omega^2\tau(x)=0 \tag{3}$$

with

$$\omega=\left[\frac{b_sG_a}{t_a}\left(\frac{1}{E_st_sb_s}-\frac{2}{E_bt_bb_b}\right)\right]^{1/2} \tag{4}$$

After some mathematical calculations, the strain is obtained:

$$\varepsilon_s(x)=\left(\left(\frac{E_bt_bb_b}{E_bt_bb_b-2E_st_sb_s}\right)\left(\frac{E_bt_bb_b-2E_st_sb_s}{E_st_sb_sE_bt_bb_b}\right)P_s\,exp(-\omega x)\right)=\frac{P_s}{E_st_sb_s}exp(-\omega x) \tag{5}$$

where:

P_s = applied load at the interface; L = sheet length; $b_s=80mm$, sheet width; E_s =sheet elastic modulus; $t_s=0.165mm$ and $t_s=0.230mm$, sheet thickness for the CFRP and GFRP, respectively; G_a = adhesive shear modulus; t_a = adhesive thickness; E_b , t_b ,elastic modulus, thickness and width of the stone block; u = displacement of the sheet; v = displacement of the stone block, $\gamma(x)$ = shear strain for the adhesive.

The values of mechanical properties reported in Table 4 and Table 5 have beenused.

The theoretical relationship for the sheet deformations versus positionis of exponential type, $\varepsilon(x) = a\,exp(-\omega x)$, the coefficients a, ω can be calibrated by experimental data. In Figure 11, the sheet deformation versus position is reported for the samples in Lecce Stone reinforced by CFRP. Experimental and theoretical curves are compared for both conditioned and unconditioned specimens, at load value of 4 kN. Once again, analyzing the calibrated curves, it can be noted that the exposed system becomes more deformable. For the conditioned samples,in fact,ω is equal to 0.1362 / mm while for the unconditioned samples ω is equal to 0.1157/mm, with a minimum variation of approximately 15%.Moreover, being $a = \frac{P_s}{E_s t_s b_s}$ inversely proportional to the stiffness of the sheet,it is confirmed that the conditioning does not induce significant changes to this parameter,resulting almost constant irrespective to the treatment.

4.2 Bond stress-slip law

The bond stress-slip law $\tau - s$,provided by the CNR-DT 200 code [11] is bi-linear, as shown in Figure 12. The bond stress-slip law has been calibrated on the basis of experimental results obtained by performed push-off tests.

where:

$f_b = \frac{2\Gamma_{Fm}}{s_u}$ maximum bond stress (6)

s_u interface slip corresponding to full debonding (7)

Γ_{Fm} average specific fracture energy (8)

$K_1 = \frac{c_1}{t_a/G_a + t_b/G_b}$ slope of the ascending branch (9)

Where G_a, G_b represent shear modules of adhesive and masonry stone, respectively, t_a is the nominal thickness of the adhesive and t_b is the effective depth of masonry stone.

The calibrated coefficients, the maximum bond stress, the ultimate slip, the average specific fracture energy and the slope of the ascending branch are reported in Table 7. In the Figure 13, the calibrated bond stress-slip curve for Lecce Stone reinforced with CFRP are reported as well as the experimental points. From Figure 13 it can be seen that theoretical curve fits properlythe experimental points in the elastic range (ascending branch of the curves), while for the softening branch a different trend is observed. In particular, even if a linear softening law could be still adopted, its extension is limited with respect to that proposed by the CNR-DT 200 Bulletin [11]. Such occurrence evidences the fragile behavior of the masonry–FRP interface which does not allow to detect the post pick path without adopting suitable measures for the test set-up [19].

The calibration of the bond stress-slip law has been given only for specimens of Lecce Stone reinforced by CFRP, since only for the latter stone the post peak results can be considered significant. For specimens of Neapolitan tuff, in fact, the optimal bond length is of the same order of magnitude of the used bond length.As well known, reliable results for the softening branch of the bond stress-slip law can be obtained adopting a higher bond length:this aspect will be the subject of future experimental works.

4.3 The bond strength

The bond strength varies depending on the mechanical properties of the stone and of FRP reinforcement [11]:a decay of the bond capacity is,therefore,expected when a mechanical degradation of the materials occurs. Some available codes and guidelines [7, 11] suggest the introduction of environmental coefficients in order to take into account the material degradation; however, these environmental coefficients are not considered when determining the bond strength. In other cases [5] the protection of the strengthened structural element is only advised.

In order to evaluate the influence of thetreatment performedon the bond capacity, the relationships provided by the CNR-DT 200Bulletin [11,25] are comparedwith the experimental results found in the present study.

When the stiffness of the masonry stone support is much greater compared to the stiffness of the FRP system and the bond length is longer or equal to the optimal bond length, the maximum value of the transferred force, F_{max}, shall be expressed as follows [11]:

$$F_{max} = b_s \sqrt{2 t_s E_s \Gamma_F} \tag{10}$$

where: b_s, t_s, E_s, represent FRP width, thickness and Young modulus of elasticity in the direction of the applied force, respectively, and Γ_F is the specific fracture energy, given as:

$$\Gamma_F = k_b k_G \sqrt{f_{cm} f_{ctm}} \tag{11}$$

In Equation (11),

$k_b = \sqrt{\frac{3 - b_s/b_b}{1 + b_s/b_b}}$ is the geometrical factor, k_G is an experimentally determined coefficient, f_{cm} is the average experimental compressive strength of the calcareous stone, f_{ctm} is the average tensile strength of the calcareous stone and it is calculated as $f_{ctm} = 0.1 \cdot f_{cm}$ [20].

From Equations (10) and (11), the bond strength, $F_{\max}$, can be evaluated as:

$$F_{\max} = b_s \sqrt{2 t_s E_s k_b k_G \sqrt{f_{cm} f_{ctm}}} \qquad (12)$$

The maximum theoretical transferred forcewas calculated introducing in Equation (12) the mean value of k_{Gm} , as reported in [11, 20], and the materials properties referred to standard conditions (reported in Table 8). The analysis includes the results obtained in a previous research work [31], referred to samples of*Lecce Stone* reinforced by CFRP and tested after immersion in water (labeledas"C_ls_I" in Table 8); the corresponding samples tested under standard conditions are marked as "C_ls"in the same Table.

As noticed above, the bond strength and the stiffnessdid not show significant variations for Lecce stone samples reinforced with CFRP (C_LS and C_LS_U)or GFRP (G_LS; G_LS_U).Therefore, as proposed in [11],a unique coefficient was used irrespective to the type of reinforcement, namely $k_{Gm} = 0.022$ [11, 20]. The specimens tested afterimmersion in water were also includedas part of the same sample considering that the referred technical document of CNRprovides aunique coefficient for *Lecce stone* with compressive strength in the range 2-24 MPa.

Also for samples in Neapolitan tuff the performed conditioningdid not have a significant effect.Therefore, a unique coefficient can be again considered, $k_{Gm} = 0.172$ [20].

In Figure 14, the maximum theoretical and experimental values of the transferred load are reported for Lecce stone and Neapolitan tuff specimens reinforced with CFRP or GFRP.The $F_{\max}$valuesreported in [20] are also shown, as they were used for calibrating the coefficients provided in [11]. Analyzing the results in the figure itcanbe noted that in all cases experimental values can be satisfactory predictedby theoretical curve proposedby the CNR-DT 200 bulletin [11].It is interesting to underline that the revised relationships proposed in [11] are able to predict the bond strength also when considering the treatment performed (immersion in water and exposure to a thermo-hygrometric atmosphere); this constitutes a relevant improvement with respect to the previous version of the same technical document [50].

5 Conclusion

The effect of a thermo-hygrometric exposure, 40 °C and 90% humidity, on FRP, natural stone and their adhesive interface has been investigated; .

on the basis of results obtained the following considerations can be remarked:

The mechanical properties of the utilized natural stones are significantly affected by the exposure conditions , in fact a reduction in compressive strength and flexural strength has been found, up to70% for Neapolitan tuff.

The combination of temperature and humidity exposure caused a decrease or even an increase of the resin mechanical properties depending on the curing time and the Tg value. In particular, for the putty resin an increase of stiffness has been found while for the adhesive resin a significant decrease of the tensile strength (almost 70%) has been recorded.

The exposure conditions affected the bond failure mainly due to the adhesive resin degradation. When the moisture diffusion involved the bond-line (as in the case of Lecce stone specimens reinforced by CFRP), a mixed failure occurred (adhesive and cohesive within the substrate). In addition the bond strength and the maximum bond stress were reduced by about 20% and 40%, respectively. For other specimens (Neapolitan tuff reinforced by CFRP) the presence of defects within the composite, expected for the hand layup technique, combined with the adhesive resin degradation caused the premature tensile crisis of the FRP reinforcement, due to the debonding at the interface fibers-adhesive. On the other hand, a cohesive failure within the substrate occurred in all unexposed specimens.

The bond stress – slip curves show similar trend comparing aged and un-aged specimens, unless for Lecce stone specimens reinforced with CFRP. In the latter case, the interface deterioration after exposure was confirmed by a reduction of the initial stiffness, of about 16%. The higher interface deformability after exposure was also found by calibrating the theoretical law giving the strain variation along the sheet. The available relationship, provided by the revised version of the technical document assessed by Italian CNR [11] for evaluating the bond strength in standard conditions, seems still effective in the case of aged specimens. However, further experimental investigation on bond durability are suggested in order to confirm the reliability of obtained results.

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Figure captions

Figure 1: Sketch of the specimen of epoxy systems (putty and adhesive) employed for tensile tests. Sciolti M S et al.

Figure 2: “Double face shear test”test set-up.Sciolti M S et al.

Figure 3: Geometrical details of stones and FRP reinforcement.Sciolti M S et al.

Figure 4: Scheme of electrical strain gauges applied on each FRP laminate. Sciolti M S et al.

Figure 5: Typical bond failures for Lecce Stone (a) and Neapolitan tuff (b) specimens. Sciolti M S et al.

Figure6: Failure mode ofconditioned and unconditioned specimens. Sciolti M S et al.

Figure7: Strains values along the sheet at 4kN load value for the conditioned and unconditioned specimens in Lecce Stone reinforced with carbon sheet. Sciolti M S et al.

Figure8: Experimental bond stress – slip curves at loaded ends for conditioned and unconditionedLecce Stone specimens reinforced with CFRP. Sciolti M S et al.

Figure9: Experimental bond stress – slip curves at loaded ends for conditioned and unconditioned specimens of; a) Lecce Stone -GFRP; b) Neapolitan tuff - CFRP, c) Neapolitan tuff – GFRP. Sciolti M S et al.

Figure10: Strains values along the sheet at different load levels for conditioned and unconditionedspecimens of; a) Lecce Stone - CFRP; b) Lecce Stone -GFRP; c) Neapolitan tuff - CFRP, d) Neapolitan tuff – GFRP. Sciolti M S et al.

Figure11: Experimental and theoretical strain versuspositioncurves for Lecce Stone specimens reinforced with CFRP at 4 kN load value. Sciolti M S et al.

Figure12: $\tau - s$ relationship provided by the CNR-DT 200 Bulletin. Sciolti M S et al.

Figure13: $\tau - s$ relationship provided by the CNR-DT 200 Bulletin calibrated for conditioned and unconditionedLecce stone reinforced with CFRP systems. Sciolti M S et al.

Figure14: Comparison between experimental and theoretical bond strength values. (a) Lecce stone, (b) Neapolitan tuff. Sciolti M S et al.

Table captions

Table 1.Main characteristics of FRP's (from supplier's data sheet).

Table 2. Main characteristics of epoxy systems(from supplier's data sheet).

Table 3.Summary of the tests performed on the adhesively bonded FRP/stone specimens exposed to the thermo-hygrometric treatment.

Table 4.Mechanical properties of the stones.

Table 5.Mechanical properties of thereinforcing systems.

Table 6.Experimental results of bond test

Table 7.Calibrated coefficients for conditioned and unconditioned Lecce stone specimens reinforced with FRP.

Table 8.Values used to determine the maximum theoretical value of the transferred load.