DURABILITY OF FLAX/BIO-EPOXY COMPOSITES INTENDED FOR STRENGTHENING APPLICATIONS IN CONSTRUCTION

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Abstract

Environmentally friendly FRP composites, made of natural fibers and bio-based polymer matrices, may be used as externally bonded reinforcement for civil structures or buildings subjected to moderate outdoor conditions, in replacement of traditional carbon/epoxy systems. However, a major drawback of natural fibers is their sensitivity to moisture which can affect both the mechanical properties of FRP composites and their adhesive bond with concrete. This research aims at studying the influence of hygrothermal ageing on the performances of "green composites" manufactured by hand lay-up process using unidirectional flax fabrics and a bio-based epoxy matrix. The test program consists in subjecting FRP laminates and FRP strengthened concrete slabs to accelerated ageing conditions under various combinations of temperature and humidity, and to natural ageing in outdoor environment as well. Aged laminates are then periodically characterized by tensile tests and interlaminar shear tests, while the bond properties of concrete/composite assemblies are assessed by pull-off tests. Results are discussed in the light of complementary physico-chemical investigations, in order to relate observed performance evolutions to actual microstructural changes or damage processes taking place in the material.

Keywords:

Flax fibers; Bio-based thermosetting matrix; Durability; Accelerated ageing

1 INTRODUCTION

Over the past decades, rehabilitation / strengthening of concrete structures using externally bonded composite materials has become a common practice worldwide, due to its effectiveness and easy installation in the field. This technique usually involves composite materials made of synthetic fibers and oil based polymer matrices, whose manufacturing process is both energy-consuming and polluting. Therefore, due to global concerns towards climate change and reduction of carbon emissions, the development of more eco-friendly material becomes a relevant objective. This consideration has led to the development of bio-composites in which synthetic fibers, generally carbon and glass fibers, are replaced by natural fibers such as flax [1], hemp [2], sisal [3], etc…

On the other hand, with the use of natural fibers, several new durability problems emerge due to the hollow structure and non-homogeneous hydrophilic nature of these fibers, that make bio-composites susceptible to extensive moisture absorption. Multiple studies have proven that mechanical properties of vegetal fiber based composites are strongly affected by water absorption [4-10], but until now there is no clear understanding of the coupling effects of temperature and humidity on the ageing behavior of these materials.

The present study aims at achieving a better understanding of these coupling effects on the mechanical properties of an innovative bio-composite consisting of a bio-based epoxy matrix reinforced by flax fibers.

2 EXPERIMENTAL

2.1 Materials and accelerated ageing conditions

Unidirectional (UD) flax fiber fabrics used in this study were produced by Groupe Depestele, a French natural textile company. The main characteristics of these fabrics are listed in Tab. 1.

The epoxy resin (CHS-EPOXY G520) was supplied by Spolchemie, a Czech chemical company known for its environmentally-friendly products. This resin (30% bio-sourced) was mixed with a 100% bio-sourced amine hardener in stoichiometric proportions.

Composite laminates made of two plies of UD flax fabrics were then manually prepared (hand lay-up technique) by impregnating the fabrics with the previous polymer mix. The resulting Flax Fiber Reinforced Polymer (FFRP) composites had a fiber volume fraction around 16% and were cured in the laboratory conditions (20°C/35-50% RH) for 3 weeks until stabilization of the

polymerization process. In addition to the previous laminates, FFRP reinforced concrete slabs were also prepared for the purpose of adhesive bond characterizations by pull-off tests. Concrete slabs were first prepared using a ready-to-mix commercial mixture of compressive strength 50 MPa at 28 days (see Tab. 2). The slabs were stored for 90 days before strengthening of the upper face with a single ply of UD flax fabric impregnated by the bio-epoxy matrix. As previously, a 3-week cure was achieved prior exposure of the specimens to the various ageing environments.

Tab. 1: Characteristics of the unidirectional flax fabrics LINCORE® FF 200.

Characteristics	Value		Standard Method
Nominal weight, in g/m^2	200 ± 4%		UNI 5114
Thickness, in μm	250 ± 15%		UNI EN ISO 5084
Nominal structure, in threads/cm	<u>Warp</u> 3.7	<u>Weft</u> 5.1	UNI EN 1049-2
Weight distribution, in %	91	9	-

Tab. 2: Composition of the concrete mixture used for the preparation of concrete slabs

Material	Cement CEM I 52,5 N	Sand 0/4	Gravel 4/20	Water
Quantity (kg / m^3)	350	1030	860	140

All these specimens (FFRP laminates and reinforced slabs) were then divided into 7 series that were placed in various environments, corresponding to either accelerated ageing conditions or outdoor weathering conditions (see Tab. 3).

Tab. 3: Ageing conditions considered in the optimized design of experiments (both for FFRP laminates and FFRP reinforced concrete slabs)

	T	Humidity
V1	20°C	50% RH (climatic chamber)
V2	20°C	100% RH (immersion in water)
V3	60°C	50% RH (climatic chamber)
V4	40°C	100%RH (immersion in water)
V5	60°C	75% RH (climatic chamber)
V6	60°C	100% RH (immersion in water)
VN		Outdoor exposure in Lyon, France

Regarding accelerated ageing conditions, 6 different combinations of temperature and humidity were selected according to a design of experiments based on Hoke's matrix (simplification of a factorial matrix with 3 levels per factor, where the factors in our case are the temperature (T) and humidity). These accelerated ageing conditions are named V1 to V6, and were applied using either climatic chambers, or immersion in thermo-regulated water tanks in the case of 100% RH environments. Besides, the last series of specimens was exposed to weathering conditions in an outdoor storage site located in Lyon area in France. This exposure condition is named VN in the following.

Within the framework of the French National Research Agency (ANR) project called MICRO, it is planned to conduct this durability study over a period of 2 years for accelerated ageing tests, and up to 5 years for outdoor exposure tests. This paper presents the first results collected during the first year of the project.

2.2 Kinetics of water sorption

In order to evaluate the water sorption kinetics of the FFRP composites, square samples of 25 x 25 mm^2 were cut from a 250 x 250 mm^2 laminate plate. These samples were also subjected to the various accelerated ageing environments, and were periodically weighted with a Sartorius CP 4235 balance of precision 10^{-3} g.

2.3 Determination of the Glass Transition Temperature (Tg)

In order to assess the impact of accelerated ageing on the microstructure of the polymer matrix, characterizations by differential scanning calorimetry (DSC) were performed on small samples (~10 mg) of aged FFRP specimens. These analyses were carried out with a Discovery DSC 250 apparatus from TA Instruments, using a ramp of temperature from -10 to 180°C at a heating rate of 2°C/min, and a superimposed temperature modulation (amplitude of 1.5° with a period of 60s). The glass transition temperature (Tg) was determined from the reversing heat flow thermograms, using the midpoint-by-half-height identification method. 4 analyses were performed per type of ageing condition to determine a mean Tg value and a standard deviation.

2.4 Tensile testing procedure

Direct tensile tests were carried out according to ISO 527 standard [11] and French AFGC guidelines [12]. The geometry of test specimens (which are made of 2 layers of flax fiber fabrics) is presented in Fig. 1. Glass fiber composite tabs are glued to each extremity of the specimens using an epoxy adhesive, in order to improve the grip during tensile tests. An Instron 5969 universal testing machine, equipped with a non-contact AVE extensometer, was used to apply the loading speed of 1 mm/min as advised in the standard method.
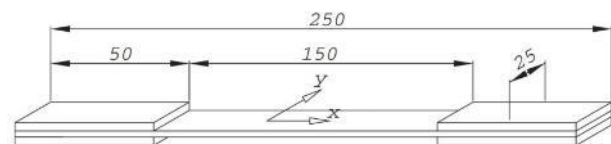

Fig. 1: Geometry of the tensile specimens (dimensions in mm).

2.5 Pull-off testing procedure

Pull-off tests were carried out according to EN 1542 standard [13] and AFGC guidelines [12]. The single layer of FFRP composite reinforcing each concrete slab was first drilled using a cylindrical core drill of diameter 50 mm, until reaching a depth of 4 mm within the concrete substrate. A cylindrical steel disc of diameter 50 mm was then glued to the drilled zone using an epoxy adhesive. Finally, a tensile loading was applied

to the disc at constant speed of 0.05 MPa/sec using a Proceq DY-216 dynamometer, until failure occurred. This allowed to determine the peak load, and further calculate the pull-off bond strength. The type of failure mode is also an important characteristic of the test.

2.6 Microscopic observations and X-ray tomography

Cross-sections of the aged FFRP composite specimens were polished using a Struers LaboForce 100 device equipped with adequate series of grinding discs. Diamond spray was also used in order to smooth mirror surfaces. Finally, these polished surfaces were examined using a Zeiss Axio Scope A1 optical microscope.

Additional investigations were carried out by X-ray tomography on aged composite specimens, in order to evidence possible microstructural damages (cracks, interfacial debonding,…).

3 RESULTS AND DISCUSSIONS

3.1 Sorption behaviour

Fig. 2 shows mass uptake evolution curves over 12 months for FFRP laminates subjected to the different ageing environments, with the exception of conditions at 20°C-50% RH, 60°C-50% RH and outdoor exposure for which no significant mass change was observed.

Although sorption curves show initial linear evolutions, they do not reach a plateau at longer times and rather follow an asymptotic trend. This feature suggests that sorption process is not controlled by pure Fickian diffusion. Furthermore, as expected, humidity and temperature levels both play major roles in the sorption kinetics, as the initial slope of the curve increases significantly when one of these two factors is raised. Besides, large water uptakes are obtained with 100% RH conditions (up to 7.4% mass gain at 60°C after 12 months ageing). This result shows that FFRPs are prone to extensive water ingress when exposed to moist or wet environments. Water absorption may thus be a driving factor in the degradation of the mechanical performances of both the laminate and its adhesive bond with concrete during wet ageing. This point will be investigated in the next sections.
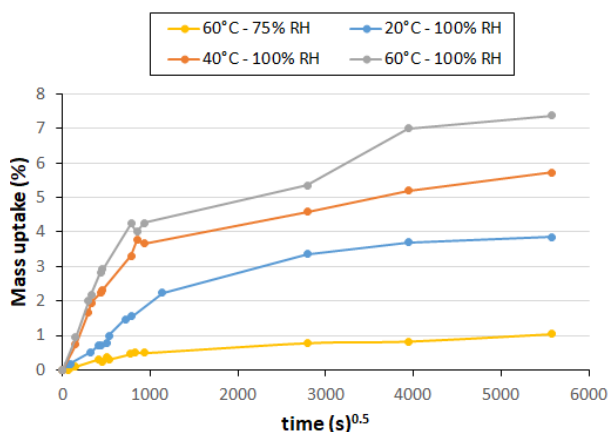

Fig. 2: Mass uptake versus (time)$^{0.5}$ for FFRP laminates subjected to the various ageing conditions.

3.2 Microstructural changes

Fig. 3. reports values of the glass transition temperature (Tg) measured by DSC on FFRP laminates aged in the various environments for periods of 3, 6 and 12 months.

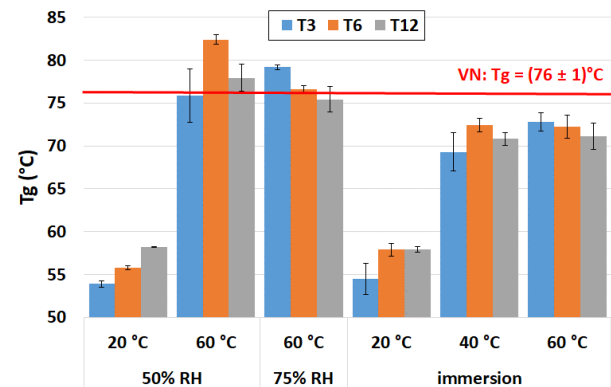Tg of the specimen exposed to weathering conditions (VN) for 12 months is depicted by the red line.

Fig. 3: Tg of FFRP laminates after exposure from 3 to 12 months (T3 to T12) in the various ageing conditions. Red line corresponds to Tg level after 12 months outdoor exposure (VN).

Reference Tg value measured for the unaged laminate cured for 3 weeks at room temperature was 55.0 ± 0.5°C. Such a low Tg is characteristic of an under-cured state of the polymer matrix, in which the polymerization process didn't reach completion.

From Fig. 3, it is found that Tg of the specimen aged at 20°C under moderate humidity (50% RH) increases slowly over time, without overpassing 58°C after 12 months. This is due to the very slow reaction kinetics of residual monomers at this temperature. A similar trend is observed at 20°C under immersion, for the same reason.

Exposure to 60°C under moderate humidity (50% RH) leads first to a very large increase in Tg during the first 6 months (up to 82°C), followed by a slight decrease over the next 6 months. The first increase can be assigned to the post-curing process of the polymer matrix, as the elevated temperature facilitates the diffusion of unreacted monomers and promotes further crosslinking of the thermoset network. In the second stage, the decay may result from oxidation induced degradation (to be confirmed by FTIR analyses).

Ageing at 60°C and 75°C leads also to a sharp increase in Tg during the first 3 months, followed by a decay after 6 and 12 months, which may relate to the effect of humidity through a plasticization process. Oxidation-induced degradation may also be involved at long ageing times.

Regarding samples immersed in water (100% RH) at elevated temperatures (40 and 60°C), an initial Tg increase is also observed during the first 3 months due to post-cure (the higher the ageing temperature, the higher this Tg increase). However, such an increase remains limited compared to that obtained at 60°C under moderate or intermediate humidity levels (50 and 75% RH). This result suggests that, under wet environment, the evolution of Tg may be controlled by both the post-cure process and the plasticization by water, which have opposite effects on Tg [14-16]. At longer times (12 months at 40°C and 6 months at 60°C), a decreasing variation of Tg is observed again, suggesting that plasticization effect becomes predominant.

A very interesting feature is that Tg measured on specimens exposed for 12 months to outdoor conditions is about 76°C (very close to Tg value obtained after 12

months at 60°C-50% RH and 60°C-75% RH), suggesting that outdoor temperature variations have achieved significant post-cure of the polymer matrix.

In order to investigate further the microstructural alterations induced by hygrothermal ageing, observations were made on polished cross-sections of aged FFRP laminates using optical microscopy.

Fig. 4 displays pictures of specimens aged for 3 months in the various environments. Two main features are revealed by these images:

- First, a variation of the apparent section of flax fibers can be noticed, depending on the ageing conditions. An increase in the fiber section is observed for laminates subjected to 20°C in immersion compared to those stored at 20°C-50% RH, which can be assigned to the swelling of flax fibers induced by water absorption. Differently, specimens exposed to elevated temperatures show reduced fiber sections compared to those stored at 20°C, whatever the level of relative humidity. This may result from a modification of the fiber structure, which is not clearly identified at this stage (collapse of the internal hollow structure, extraction of soluble components?). Nevertheless, it suggests that for FFRP composites immersed at high temperature, the extensive sorption process evidenced in Fig. 2 results from water absorption by the polymer matrix and interfacial areas, and not by the fibers themselves.

- Besides, lightening and change of colour of the flax fibers (which turns to light honey colour) are observed for FFRP laminates exposed to high temperatures.

Complementary observations are currently being carried out by Scanning Electron Microscopy (MEB), in order to get better understanding of these phenomena.
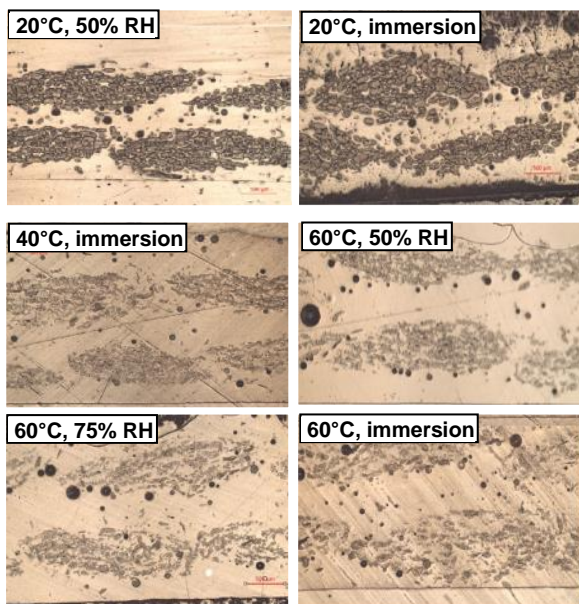

20°C, 50% RH | **20°C, immersion**

40°C, immersion | **60°C, 50% RH**

60°C, 75% RH | **60°C, immersion**

Fig. 4: Microscopic observations of polished cross-sections of FFRP laminates after being subjected to various ageing conditions for 3 months.

Fig. 5 presents a picture obtained by X-ray tomography of the cross section of a FFRP laminate aged at 60°C in immersion for 3 months. Cracks are clearly visible in the matrix located within the fiber bundles, which may result from swelling of the polymer matrix, or from the

"shrinkage" of the fibers as previously noticed. These cracks are not observed for specimens stored at 50% and 75% RH.
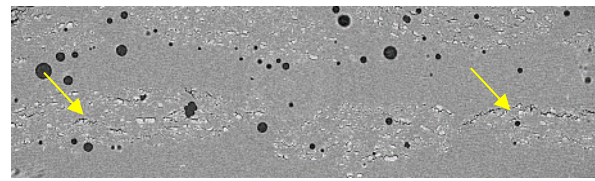

Fig. 5: X-ray-tomography picture of the cross section of the laminate aged for 3 months at 60°C in immersion.

3.3 Tensile properties of FFRP composites

Tensile tests were first carried out on unaged FFRP coupons, providing reference values of 180 MPa and 15 GPa for the effective tensile strength and modulus, respectively.

Characterizations were then performed on aged specimens, and residual properties were normalized by previous reference values.

Fig. 4 and Fig. 5 report the normalized residual tensile properties (residual strength and modulus, respectively) obtained for FFRP laminates subjected to ageing periods up to 12 months in the various environments.
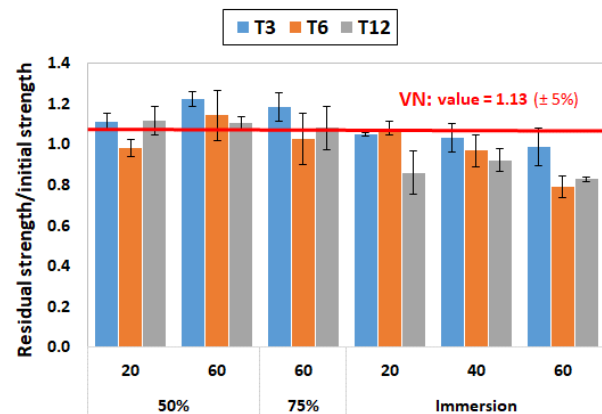

Fig. 4: Normalized residual strengths of specimens that were exposed to the various ageing conditions for periods up to 12 months. (T3, T6 and T12). The red line shows the value of the specimen exposed to weathering conditions (VN) for 12 months.
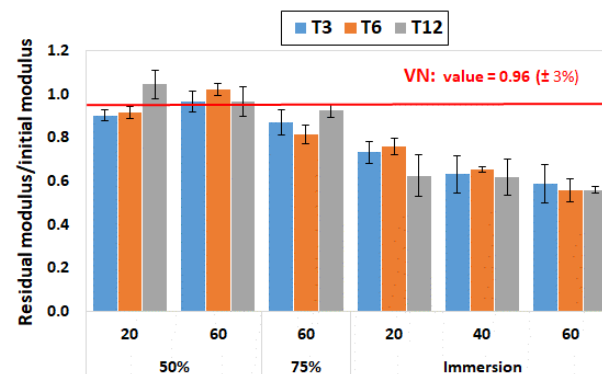

Fig. 5: Normalized residual modulus of specimens that were exposed to the various ageing conditions for periods up to 12 months (T3, T6 and T12). The red line shows the value of the specimen exposed to weathering conditions (VN) for 12 months.

Regarding the tensile strength (Fig. 4), FFRP composites didn't show any degradation after 3 months ageing, and a significant increase was even observed for specimens exposed to the temperature of 60°C at 50% and 75% RH, which was explained by the post-curing process of the bio epoxy matrix as previously evidenced by DSC analyses. Between 3 and 12 months ageing, specimens immersed in water show a 20% reduction of their residual strength, with a kinetics that is dependent on ageing temperature (the higher the temperature, the higher the degradation kinetics). This feature can be correlated to the water sorption kinetics, which is also temperature dependent as shown previously in section 3.1.

Specimens exposed to outdoor conditions for 12 months exhibit a slight increase in tensile strength compared to the reference, probably due to the post-cure effect evidenced by DSC.

Regarding the evolution of the tensile Young's modulus (Fig. 5), the increase in humidity is found to degrade significantly the longitudinal stiffness of the FFRP laminates over ageing. This effect is usually accompanied by an increase in ultimate elongation. For immersed specimens, the drop of modulus can reach up to 40% after 12 months at 60°C-100% RH. Such phenomena can be assigned to a plasticization effect induced by water on the polymer matrix, and to degradations (cracks) occurring within the matrix and at fiber/matrix interfaces due to swelling of the polymer and alteration of the fiber sections, as shown previously in Figs. 4 and 5.

An interesting point is that natural ageing (12 months exposure to outdoor conditions) does not affect the stiffness of the FFRP laminate significantly, differently from what is observed with accelerated ageing tests, especially under immersion. This result suggests that immersion conditions are very severe compared to natural ageing.

3.4 Adhesive bond properties

Adhesive bond properties were assessed by pull-off tests. In a preliminary stage, reference properties were determined on unaged FFRP strengthened concrete slabs, giving an average value of 4.09 ± 0.25 MPa for the pull-off strength and a typical cohesive concrete failure (Fig. 7.a).

Residual pull-off strength determined on specimens aged in the various accelerated conditions over periods from 3 to 12 months (T3 to T12) are then displayed in Fig. 6. Values are normalized by the reference value, *i.e.* the mean pull-off strength of unaged specimens.

A significant decrease in bond strength was observed for all specimens, with the exception of those stored at 20°C-50% RH. Moreover, samples directly immersed in water were the most affected, with a reduction up to 50% in the case of samples subjected to 60°C-100% RH, which is also consistent with the large water uptake evidenced for FFRP composites in these conditions (Fig. 2). Such a degradation of the bond strength under wet conditions was accompanied by a change in failure mode, from an initial cohesive concrete failure towards a mixed failure mode (Fig. 7b) or FRP debonding mode (Fig. 7c) after ageing. This change in failure mode and the reduction in bond strength can both be attributed to a weakening of physico-chemical bonds at the concrete /composite interface in presence of water.

Here again, a very interesting feature is that specimens aged under natural weathering conditions (VN) for 12 months show only limited reduction of their pull-off

strength (~14%), together with a mixed failure mode similar to that presented in Fig. 7.b. This suggests once more that natural ageing might be less severe compared to accelerated ageing by immersion in water.
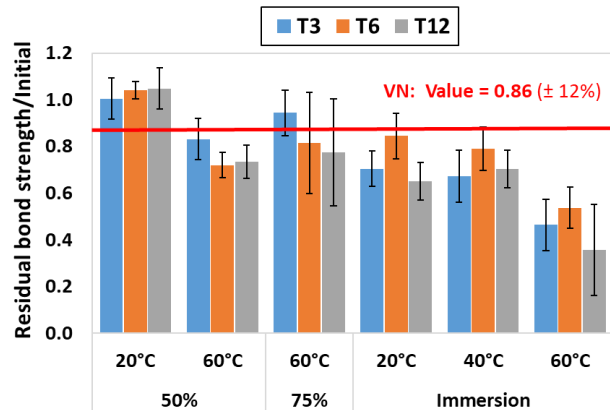

Fig. 6: Normalized residual bond strength between FFRPs and concrete after exposure to the various ageing conditions for periods up to 12 months. The red line shows the value of the specimen exposed to weathering conditions (VN) for 12 months.
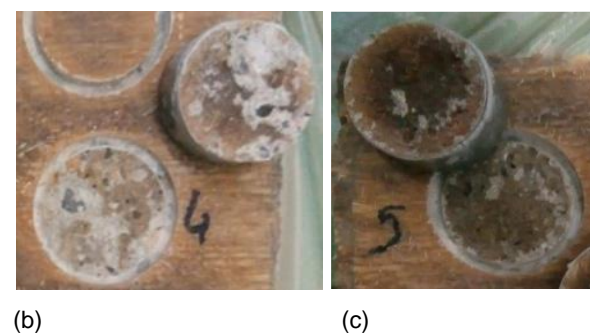

Fig. 7: Failure modes after pull-off tests - (a) initial cohesive concrete failure on unaged specimens, (b) typical mixed failure and (c) composite debonding obtained for specimens subjected to wet ageing.

4 SUMMARY

This paper has presented the first results of a durability study conducted on FFRP laminates and FFRP strengthened concrete slabs subjected to various accelerated ageing conditions (6 different combinations of temperature and relative humidity), and to outdoor weathering conditions as well. At this stage of the test program, changes in the tensile properties and bond strength have been monitored over 12 months. Additional characterizations were also carried out to evaluate the water sorption behavior and microstructural changes occurring in aged laminates during ageing.

Water sorption kinetics was linked to the humidity level of the ageing environment and was also found to be accelerated by temperature. Micrographic observations showed significant swelling of the flax fibers for specimens immersed at 20°C compared to reference samples, but contrarily, a reduction of the fiber section was noticed after immersion at 40 and 60°C, suggesting an alteration of the internal structure of flax fibers. Anyway, large water ingress observed under immersion at elevated temperature was assigned to the sorption process within the bio-epoxy matrix and interfacial areas, and to micro-cracking of the matrix entrapped in fiber bundles, as revealed by X-ray tomography.

Tensile tests showed that ageing under moderate humidity levels (50% or 75%) induces only little effects on tensile properties. A slight increase in strength was even observed at 60°C-50% RH and 60°C-75%, due to a post-cure effect of the polymer matrix, as confirmed by DSC analyses. Differently, specimens immersed in water for long periods experienced significant drop of strength and modulus. The largest reductions were obtained after 12 months immersion at 60°C, with a decreases of 20% and 50% in strength and modulus, respectively. These effects were correlated both to the water ingress leading to extensive plasticization of the bio-polymer matrix, and also to the development of micro-cracks within the matrix.

Finally, a degradation of the bond strength was observed for FFRP reinforced slabs exposed to high RH levels (75% RH and immersion), with a change in the failure modes from a cohesive concrete failure to a mixed failure (concrete + partial peeling of the composite) or a debonding of the composite laminate. This result suggested a weakening of physico-chemical bonds at the concrete/FFRP interface.

A very important result highlighted by this study is that exposure to natural weathering conditions up to 12 months had little effects on tensile properties of FFRP laminates, and only limited effects on adhesive bond properties between the laminate and the concrete substrate (14% reduction on the pull-off strength). In addition, it is to note that cure of the polymer matrix has been almost completed in the outdoor environment, due to natural temperature variations. In the end, natural ageing may be less severe than accelerated ageing in wet environments. Nevertheless, outdoor exposure tests are still being continued for the next four years to confirm this trend in the long term.

5 ACKNOWLEDGMENTS

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