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Durability of flax / bio-based epoxy composites intended for structural strengthening

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Abstract. Environmentally friendly FRP composites, made of natural fibres 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, funded by the French National Research Agency (ANR Project MICRO), 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. 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. This paper presents the first results of this ongoing program which is scheduled over a period of 2 years. Results are discussed in the light of complementary investigations (water sorption behaviour, microscopic observations and evaluation of the glass transition temperature by differential scanning calorimetry – DSC) in order to relate observed performance evolutions to actual microstructural changes or damage processes taking place in the material.

1 Introduction

Throughout the past few decades, composite materials have been proven effective for the rehabilitation and strengthening of concrete structures because of their high mechanical properties to weight ratio and their resistance to corrosion. However, considering their energy-consuming fabrication process and the increase of global concerns towards climate change and reduction of carbon emissions, the search for more eco-friendly material becomes a relevant objective. This consideration has led to the development of bio-composites as a greener alternative to conventional composites, in which synthetic fibres, such as carbon and glass fibres, are replaced by natural fibres such as flax [1], hemp [2], sisal [3], etc...

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

moisture absorption in the ageing behaviour of these materials.

Therefore, the present study aims at achieving a better understanding of this coupling on the mechanical properties of an innovative bio-composite consisting of a bio-based epoxy matrix reinforced by flax fibres.

2 Experimental

2.1 Materials and accelerated ageing conditions

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

The epoxy resin (CHS-EPOXY G520) was supplied by Spolchemie, a Czech chemical company known for its green environmental-friendly products. This resin (30% bio-sourced) was mixed with an amine hardener (100% bio-sourced) 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 laminates had a fibre volume

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fraction around 16%, and were cured in the laboratory conditions (20°C/35-50% RH) for 3 weeks until stabilization of the polymerization process. These specimens were then divided into 6 series that were placed in climatic chambers or in thermo-regulated water tanks (in the case of 100% RH environments), located either at LMC2 Laboratory in Lyon or at Ifsttar in Paris.

In total, 6 different combinations of temperature and humidity were selected according 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 and humidity). These ageing conditions are named V1 to V6 (see details in Table2).

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, however this paper only displays results collected during the first 6 months considering that the ageing process is still in progress until 2019.

Table 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 construction, in threads/cm | Warp 3.7 Weft 5.1 | UNI EN 1049-2 |
| Weight distribution, in % | 91 9 | - |

Table 2. Ageing conditions considered in the optimized design of experiments

| | T | Humidity | Location |
|----|------|------------------------------|------------------|
| V1 | 20°C | 50% RH (climatic chamber) | Ifsttar |
| V2 | 20°C | 100% RH (immersion in water) | Ifsttar |
| V3 | 60°C | 50% RH (climatic chamber) | Ifsttar |
| V4 | 40°C | 100%RH (immersion in water) | LMC ² |
| V5 | 60°C | 75% RH (climatic chamber) | LMC ² |
| V6 | 60°C | 100% RH (immersion in water) | LMC ² |

In addition to the previous composite laminates, strengthened concrete slabs were also prepared for the purpose of the 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 Table 3). The slabs were stored for 90 days before being strengthened with a single ply of UD flax fabric impregnated by the bio-epoxy matrix. As previously, a 3 week cure was respected prior exposure of the test specimens to the various ageing environments.

2.2 Kinetics of water sorption

In order to evaluate the water sorption kinetics of the Flax Fiber-Reinforced Polymer (FFRP) composite,

square samples of 25 x 25 mm² were cut from a 250 x 250 mm² 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 0.001 g.

Table 3. Composition of the concrete mixture

| Material | Cement CEM III/B | Sand 0/5 | Gravel 10/25 | Water |
|---------------------------------|------------------|----------|--------------|-------|
| Quantity (kg / m ³) | 350 | 865 | 1030 | 145 |

2.3 Determination of the Glass Transition Temperature (T_g)

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 (T_g) was determined from the reversing heat flow thermograms, using the midpoint-by-half-height identification method. 4 analyses were performed for each type ageing condition, to obtain an average 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 fibre sheets) is presented in Figure 1. In addition, glass fibre composite tabs are glued to each extremity of the specimens using an epoxy adhesive. 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.

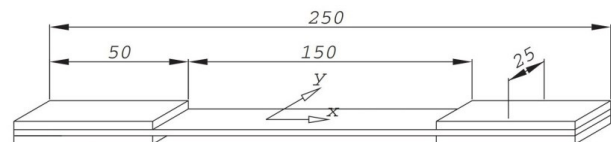


Fig. 1. Geometry of the tensile specimens (dimensions in mm)

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 to further evaluate the pull-off bond strength. The type of failure mode is also an important characteristic.

2.6 Microscopic observations

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 during for achieving a smooth mirror surface. Finally, these polished surfaces were examined using a Zeiss Axio Scope A1 optical microscope.

3 Results and discussions

3.1. Sorption behaviour

Figure 2 shows the mass uptake evolution curves for FFRP composites subjected to the different ageing environments, with the exception of conditions at 20°C/50% RH and 60°C/50% RH for which no mass variation was observed.

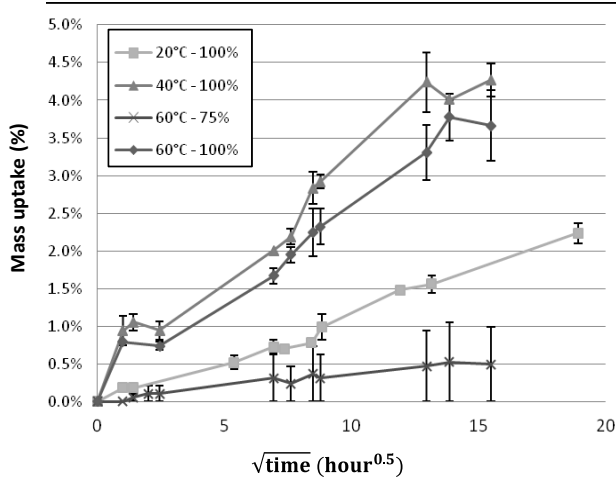


Fig. 2. Evolution of the mass uptake of FFRP composites subjected to the various ageing conditions

Globally, initial parts of the curves are linear, suggesting that water sorption is controlled by a Fickian diffusion process.

Furthermore, as expected, relative humidity and temperature play both major roles in the sorption kinetics, as the slope of the curve increases significantly as one of these two factors is raised. At this stage, one cannot calculate the diffusion coefficients, as water saturation has not been reached. However, large water uptakes (up to 4.5%) were obtained under 100% RH conditions after 12 to 15 days. This result shows that FFRP composites are susceptible to extensive water ingress under wet environments, and water absorption may thus be a leading 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.

3.2. Microstructural changes

Glass transition temperatures (T_g) measured by DSC on the initial FFRP laminate and on specimens subjected to accelerated ageing in the various environments for periods of 3 and 6 months are shown in Figure 3.

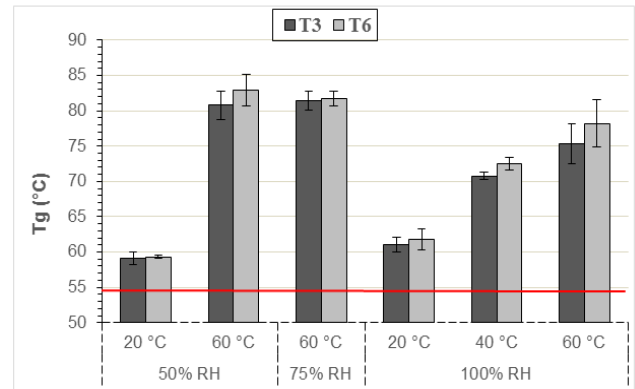


Fig. 3. T_g of the FFRP laminates after exposure for 3 and 6 months (T3 and T6) to the various ageing conditions

Regarding the unaged laminate, which was cured for 3 weeks at room temperature, a T_g of $(54.9 \pm 0.4)^\circ\text{C}$ was obtained (this reference value is depicted by the red line in Figure 3). For this reference material, the polymerization process didn't reach completion and the corresponding samples remained under-cured.

After 3 months exposure at 20°C under moderate humidity (50% RH), a slight increase in T_g was observed, up to 59°C. Between 3 and 6 months, this value didn't evolve any more, suggesting that the polymer network is stabilized in this condition, but still in an under-cured state.

Exposures for 3 months at 60°C under moderate or intermediate humidity (50% and 75% RH) led to a large increase in T_g up to 82°C, which was assigned to a post-curing process of the polymer matrix. Indeed, this elevated ageing temperature facilitates the diffusion of unreacted monomers and promotes further cross linking of the thermoset network. Between 3 and 6 months in the same conditions, no additional significant evolution of T_g was noticed, suggesting that the network had reached equilibrium (and was possibly fully cured).

Regarding samples immersed at 100% RH for 3 months, T_g was found to increase as the ageing temperature was raised from 20 to 60°C, due to the same post-cure effect. Nevertheless, for a given temperature of 60°C, T_g of immersed samples remained significantly lower compared to that of specimens exposed to moderate or intermediate humidity level (50% and 75% RH) at the same temperature. This result suggests that, under wet environment, the evolution of T_g may be controlled by both the post-cure process and the plasticization by water, which have opposite effects [14-15].

3.3. Tensile properties of FFRP composites

Figures 4 to 6 reports the tensile properties (strength, modulus and ultimate strain, respectively) that were determined for the unaged FFRP samples and for specimens subjected to ageing periods of 3 and 6 months in the various environments. As mentioned before, this is an inter-laboratory study, and half of the exposure (V1 to V3) and mechanical tests were carried out at Ifsttar, while the other half was performed at LMC2 Laboratory (V4 to V6). Small differences were found on average property values and dispersions obtained for unaged specimens in the two laboratories (Figs 4.a, 5.a and 6.a), since different operators were involved in the tests. Therefore, in order to have a comparable referential, residual tensile properties of aged specimens obtained in each laboratory were normalized by the initial values determined in the same laboratory.

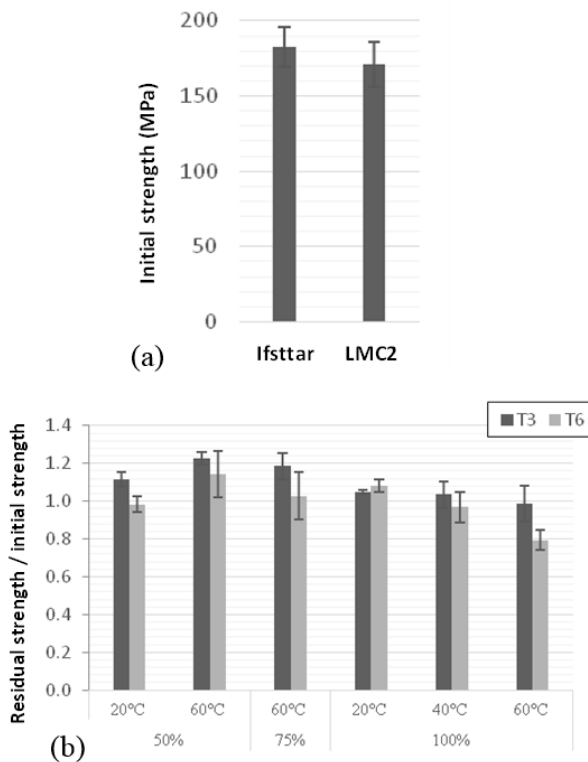


Fig. 4. Tensile strength of FFRP composites - (a) initial values obtained in the 2 laboratories for unaged specimens and (b) residual strengths of specimens that were exposed to the various ageing conditions for 3 and 6 months (T3 and T6).

Regarding the tensile strength (Fig. 4), FFRP composites didn't show any degradation after 3 months ageing, and significant increases were even observed for specimens exposed to 50% and 75% RH, especially at the temperature of 60°C, which was explained by the post-curing process of the bio epoxy matrix as previously evidenced by DSC experiments. Between 3 and 6 months ageing, a global decrease in the effective tensile strength was noticed for all specimens. Nevertheless, only the specimen exposed to 60°C/100% RH decreased its strength significantly below the initial value (reduction of 20%, approximately). This may be explained by the extensive water absorption process

observed in this specific condition, as shown previously in Figure 2

Regarding the evolution of the tensile Young's modulus (Fig. 5.b), the increase in humidity is found to degrade significantly the longitudinal stiffness of the FFRP laminates over ageing. This effect is accompanied by an increase in ultimate strain, as shown in Figure 6. These phenomena can be assigned to the plasticization effect induced by water on the bio-epoxy matrix, and to degradations / swelling of the fibre/matrix interfacial regions as well.

On the other hand, the effect of temperature seems to depend on the level of relative humidity. At low RH values, the tensile modulus is found to increase over ageing as the temperature is raised, but contrariwise, at 100% RH (immersed samples), the modulus decreases when the temperature rises. These trends may relate to the relative effects of post-cure and plasticization phenomena, as post-cure seems predominant at low RH and high temperature, while plasticization becomes dominant at high RH and high temperature. This is consistent with previous observations from the same team in the case of conventional carbon fibre reinforced composites (Benzarti et al. and Quiertant et al. [14-15]) and is also supported by DSC analyses.

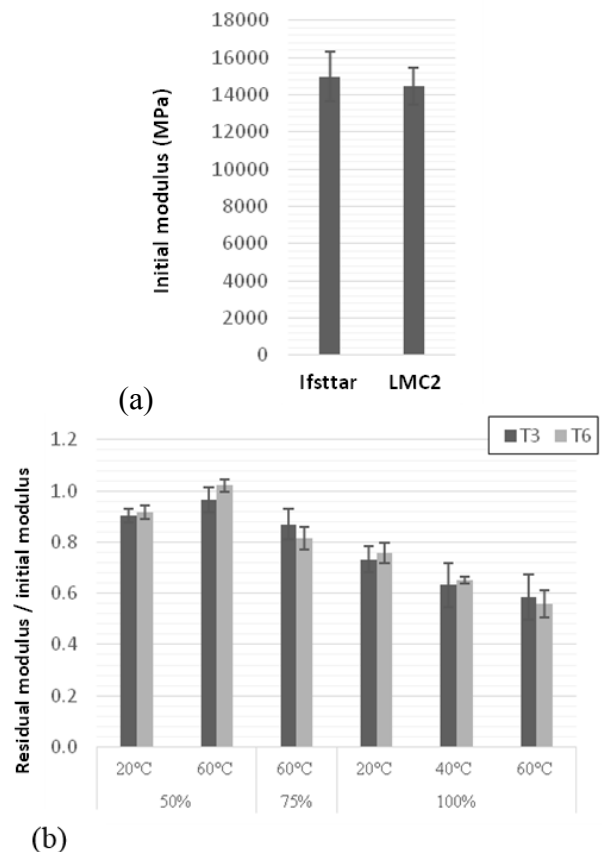


Fig. 5. Tensile modulus of FFRP composites - (a) value of unaged specimens obtained in the 2 laboratories and (b) normalized values of specimens exposed to the various ageing conditions for 3 and 6 months (T3 and T6).

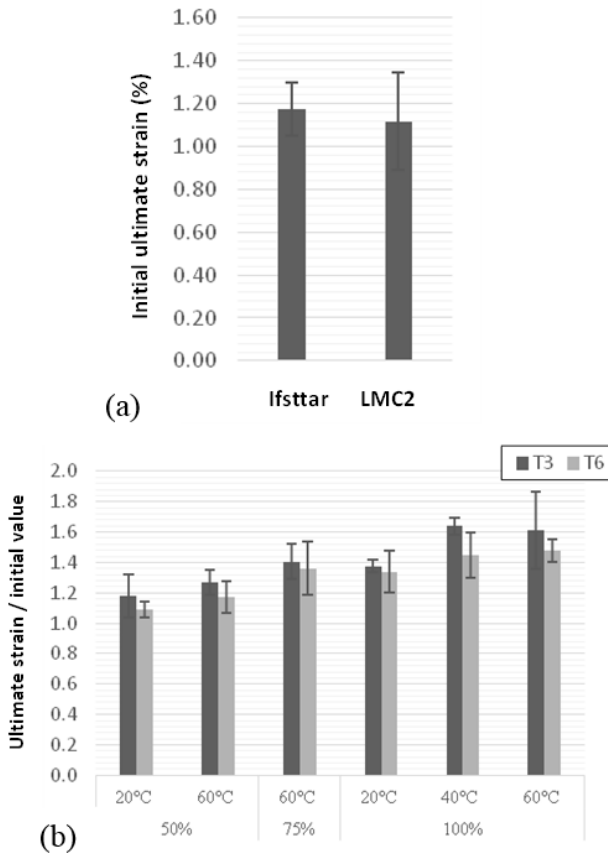


Fig. 6. Ultimate Tensile strain of FFRP composites - (a) initial values of unaged specimens obtained in the 2 laboratories and (b) normalized values of samples exposed to the various ageing conditions for 3 and 6 months (T3 and T6).

3.4. Adhesive bond properties

Figure 7.a displays the initial values of pull-off strengths that were obtained for the unaged specimens in the 2 laboratories. A slight difference was obtained between initial values determined at IFSTTAR (4.09 ± 0.25) MPa and at LMC2 (3.73 ± 0.36) MPa. It was attributed to the fact that 2 different operators were involved in the sample preparation and test procedure. Therefore, similar to previous tensile tests, results of pull-off tests obtained in each laboratory for aged specimens were normalized by the initial value obtained in the same laboratory.

Figure 7.b displays the residual bond strengths of specimens exposed to the various environments for periods of 3 and 6 months. A significant decrease in bond strength was observed for all specimens, with the exception of those stored at 20°C/50% RH. Moreover, samples exposed to 100% relative humidity were the most affected, with 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. 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 after ageing (both in concrete and by partial peeling of the composite, as shown in Figure 8). This change in

failure mode and the reduction in bond strength are both attributed to a weakening of physico-chemical bonds at the concrete/composite interface in presence of water.

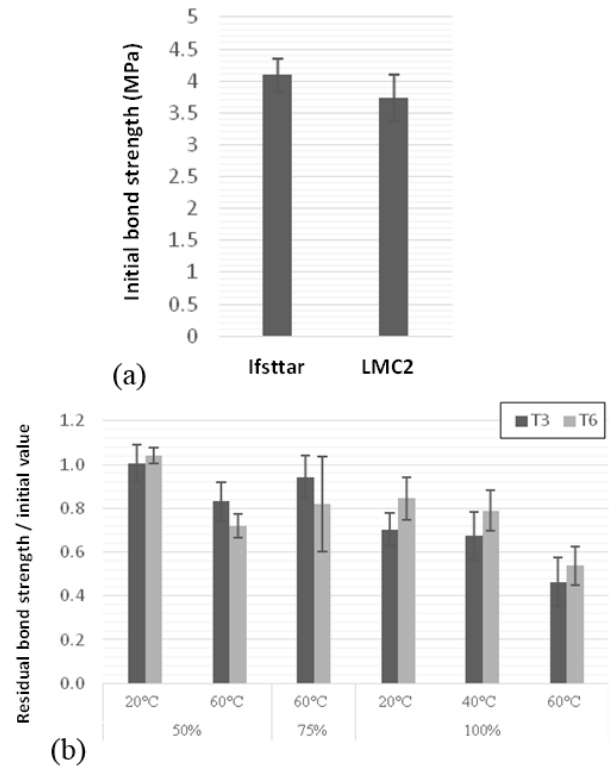


Fig. 7. Bond strength between FFRP composites and concrete - (a) initial values of unaged specimens obtained in the 2 laboratories and (b) normalized values of samples exposed to the various ageing conditions for 3 and 6 months (T3 and T6).



Fig. 8. Failure modes after pull-off tests - (a) initial cohesive concrete failure for unaged specimens and (b) typical mixed failure for specimens subjected to wet ageing at 100% RH.

3.5. Microscopic observations

Figure 9 displays several images obtained by optical microscopy, showing polished cross-sections of FFRP laminates that had been exposed to the various ageing environments for periods of 3 months.

Two main features are revealed by these images:

- A variation of the apparent section of flax fibers can be noticed, depending upon the ageing conditions. An increase in the fiber cross-section is observed for laminates subjected to 20°C/100% compared to those subjected to 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 result is not clearly explained at this stage of the study, but suggests that for FFRP composites immersed at high temperature, the extensive sorption process evidenced in Figure 2 mainly results from water absorption by the polymer matrix / interfacial areas and not by the fibers, since the section of these latter is reduced after ageing.
- Besides, a change of color of the flax fibers is observed for FFRP laminates exposed to high temperatures.

Complementary observations are currently being performed by Scanning Electron Microscopy (MEB), in order to provide a better understanding of the previous phenomena.

4 Conclusions

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). At this stage of the test program, changes in the tensile properties and bond strength have been determined after 3 and 6 months ageing in these environments. Additional characterizations were also carried out to evaluate the water sorption behaviour and microstructural changes in aged laminates.

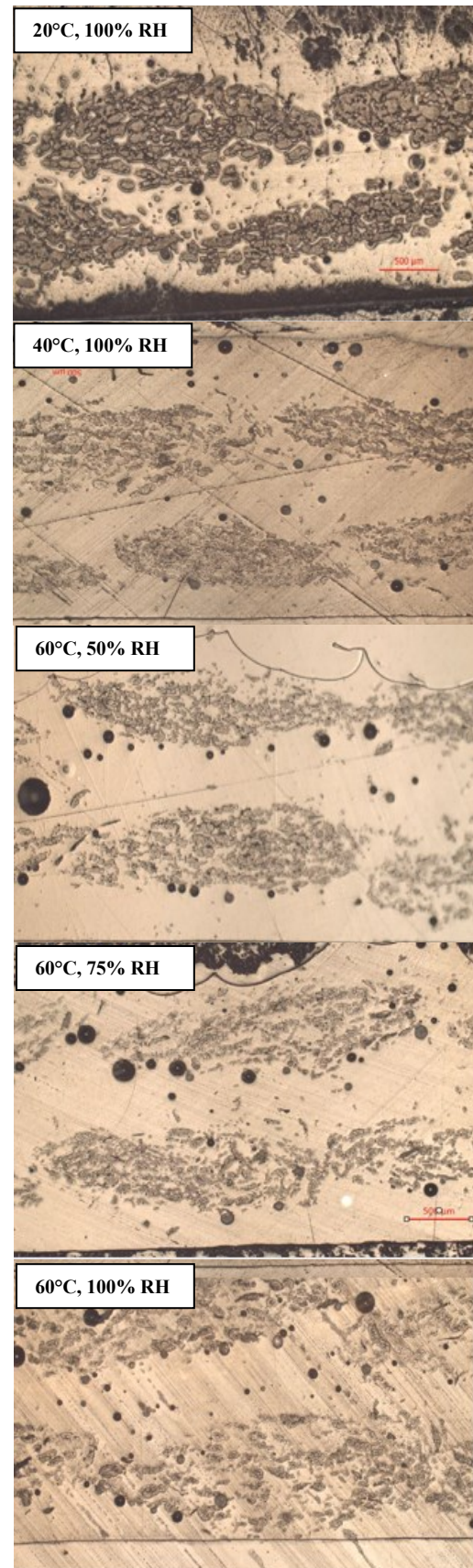
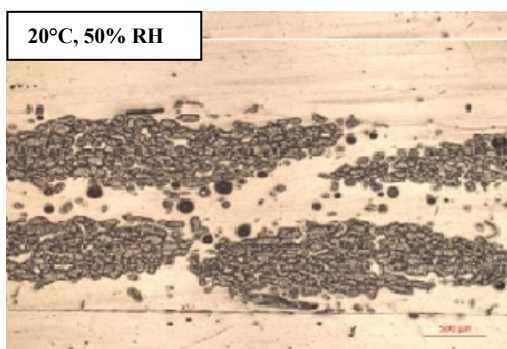


Fig. 9. Microscopic observations of polished cross-sections of FFRP laminates subjected to various ageing conditions for 3 months

Water sorption kinetics was directly linked to the level of relative humidity of the ageing environment and was also accelerated by temperature. Micrographic observations showed significant swelling of the flax fibers for specimens immersed at 20°C, but contrarily, a reduction of the fiber section was noticed after immersion at 40 and 60°C, suggesting that water sorption occurs mainly within the bio-epoxy matrix and interfacial areas in this case.

Tensile tests revealed limited effects of ageing on the effective strength: a slight increase was observed at elevated temperature (60°C) and moderate/intermediate humidity (50 and 75% RH), due to a post-cure effect of the polymer matrix as confirmed by DSC analyses. Besides, wet ageing had a negligible effect on strength, with the exception of samples immersed at 60°C which exhibited a strength reduction of about 20%.

Differently, the longitudinal Young's modulus of laminates was significantly affected under wet environments: immersed samples showed substantial degradation of their modulus over time (up to 40% loss for samples subjected to 60°C and 100% RH which had the highest water uptakes). This draws a direct correlation between the water uptake and the rigidity of the FFRP laminate, due to extensive plasticization of the bio-polymer matrix and possible degradation at the fiber/matrix interface.

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

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