

Effects of water ageing on the mechanical properties of flax and glass fibre composites: Degradation and reversibility

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Abstract Mechanical properties of flax-fibre reinforced composites (FFRC) are strongly affected by water ageing compared to glass-fibre reinforced composites (GFRC). This study highlights the influence of water absorption during immersion at 30°C on mechanical properties of unsaturated polyester reinforced composites. Flax-fibre composites showed a Fickian absorption behaviour and a water uptake 15 times higher than that of glass-fibre composites. GFRC's tensile modulus and maximum stress were slightly affected by water uptake while FFRC's tensile modulus decreased by 37%, and ultimate stress increased by 34%. A silane-based chemical treatment (1% compared to flax fibres) was applied onto flax fibres. Water uptake was slightly reduced by 9% while tensile modulus at saturation was enhanced by 22% on treated FFRC compared to untreated ones. Moreover, the complete recovery of the tensile modulus after desiccation suggests that ageing was mainly reversible: fibre and matrix plasticizing phenomena occurred during immersion at 30°C. No damage was noticed but composites' initial properties changed with the action of water: further crosslinking of matrix and release of fibre's extractibles into water were observed. Finally, the drying conditions influenced the return to the initial state before ageing insofar the flax fibres partially lost their initial humidity.

1. Introduction

According to the French FIN (Nautical Industries Federation) around 95% of boats, which reach their end-of-life in 2015, are manufactured with glass-fibre reinforced composites (GFRC) mainly unsaturated polyester based composites (Le Duigou et al., 2014). The application of GFRC to ship structures includes hull, decks and structural bulkheads but also framing parts and non-structural bulkheads (Smith, 1990) (Grabovac and Turley, 1993). Marine applications of composites require materials with weak influence of water on diffusivity and mechanical

properties (Davies et al., 1996) (Camino et al., 1997) (Gellert and Turley, 1999) (Bergeret et al., 2001). New environmental legislation and public pressure have promoted the search for bio-based materials to substitute these conventional non-renewable composite components (Le Duigou et al., 2009). Plant fibres, in particular flax, present some advantages comparing with glass fibres, such as low density, specific stiffness and biodegradability (Bledzki and Gassan, 1999), and using natural fibres as alternatives to glass fibres is relatively recent (Mussig, 2010) (Baley et al., 2006). The feasibility of this substitution is the subject of numerous studies (Bledzki and Gassan, 1999) (Pillin et al., 2011) (Shah, 2014) (Faruk et al., 2012) since natural fibres present a strong sensitivity to water which leads to composite degradation (Le Duigou et al., 2009) (Scida et al., 2013) (Dhakal et al., 2007) (Assarar et al., 2010).

Concerning GFRC, Davies et al (Davies et al., 1996) have demonstrated that these composites showed a Fickian diffusion behaviour during immersion at room temperature and that the weight gain was not affected by post-cure treatment. Davies et al. reported also non-Fickian behaviour during immersion at 50°C attributed to water transport through free edges along the fibre/matrix interface (wicking mechanism). Fraga et al. (Fraga et al., 2003) highlighted the plasticizing effect of water in polymer composites and the removing of extractibles during immersion. The resin plasticization (physical modification) was displayed by the glass transition temperature changes but chemical modification (hydrolysis of chain molecules) was not observed neither at 40°C, nor at 80°C. Thus the main reason of the observed weight decrease should be the extraction of monomers or oligomers.

In recent years, biocomposites degradation studies have been performed to characterize long-term influence of water on diffusivity and mechanical properties. Assarar et al. (Assarar et al., 2010) showed that water ageing of flax-fibre composites reinforced composites (FFRC) at room temperature exhibited a Fickian behaviour and a saturated weight gain 12 times higher than that of GFRC. Water ageing of FFRC degraded the Young's modulus (-39%) and the ultimate tensile stress (-15%), but improved the ultimate tensile strain (+63%). Concerning GFRC, both Young's modulus and maximum strain were slightly affected by water (saturated weight gain around 1%). Acoustic emission technique suggested that matrix cracking was the dominant damage mechanism in GFRC and FFRC. However, the 25% ultimate stress decrease in GFRC indicated that other damage mechanisms were taking place.

Chemical treatments can be used for modifying the surface characteristics of natural fibres. Xie et al. (Xie et al., 2010) showed that a γ -methacryloxypropyltrimethoxysilane (MPS) treatment can offer a good affinity between natural fibres and polyester matrix. Moreover, polysiloxane formed a monolayer on the fibre surface, and then was adsorbed by the hydroxyl groups of fibres. Alix et al. (Alix et al., 2011) showed that weight gain can be slightly reduced by around 1% by treating flax-fibre unsaturated polyester composites with MPS. The silane treatment impact on water sorption of composites could be inter-

preted by an interface effect, which consists in improving the fibre/matrix interface by a crosslinking reaction between methacrylate groups of silane agent and the unsaturated functions of polyester chains.

2. Materials and methods

2.1 *Materials*

2.1.1 *Resin and fibres*

A dicyclopentadiene isophthalic unsaturated polyester resin Enydyne® (Cray Valley –Rouvroy, France) was used. The resin was polymerized with 1.8% w/w of methyl ethyl ketone peroxide Luperox K1S® (Arkema – Colombes, France)

Unidirectional glass fibres were supplied by Chomarat (Le Cheylard, France) for a weight of 416 g/m² (Weft: 408 g/m² / Warp: 8 g/m²). Unidirectional flax fibres were manufactured by Fibre Recherche Developpement (Troyes, France) for a weight of 390 g/m² (Weft: 360 g/m² / Warp: 30 g/m²).

2.1.2 *Chemical treatment*

Glass fibre fabrics were pre-treated by the manufacturer with a silane based sizing. A chemical treatment (1.0 wt.% γ -methacryloxypropyltrimethoxysilane or MPS compared to flax fibres) was set up to flax fibres by immersing the fabrics into an ethanol and water (60/40 wt.%) solution containing MPS. Silane was hydrolysed during 3h at pH 4. Flax fibre fabrics were thereafter dried in an oven at 105 °C during 2h and stored at 23°C and 50% H.R. before processing.

2.1.3 *Vacuum infusion processing of composite sheets*

Composite sheets (300 mm x 250 mm) consisting of 6 layers of glass fabrics for GFRC and 4 layers of flax fabrics for FFRC were vacuum infused with the resin. A vacuum pump was used to maintain impregnated fibres under a constant pressure of 100 mbar during 24 hours (curing at room temperature). Subsequently, a post-curing step took place in an oven at 60°C for 24h to obtain a polyester crosslinking rate of 88%. The thickness of GFRC (respectively FFRC) ranged from 1.8 to 2.1 mm (respectively 2.7 to 3.4 mm). Samples were cut to size of 250 mm x 25 mm using a diamond cutter. Composites of 54% and 32% vol. of fibres were fabricated for GFRC and FFRC respectively. All specimens were stored in a climatic room, at 23°C and 50% H.R., before testing.

2.2 Methods

2.2.1 Water ageing conditions

Six samples were immersed into water for more than 6 months at 30°C, period during which relative weight uptake and tensile modulus were followed respectively by gravimetric and vibration analysis. Ultimate tensile stress and strain were determined by uniaxial tensile tests and the composites fracture surfaces analysed by scanning electron microscopy.

2.2.2 Water uptake, volume and density variations

Ageing tests were performed in a controlled temperature bath with specimens immersed for different periods and taken away from the bath for weight measurements. Composite samples were carefully wiped to remove water from surface, weighed and replaced into the water baths. The water uptake W was determined according to equation (1):

$$W(\%) = ((w_t - w_o)/w_o) \times 100 \quad (1)$$

where w_t (resp. w_o) is the mass of sample at time t (resp. at time $t = 0$ h).

Composites absorbed water until saturation, and exhibited a diffusion kinetics that can be described by the Fick's law, whose expression for a plane sheet of thickness h is developed in equation (2):

$$\frac{W}{W_m} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-(2n+1)^2 \pi^2 D t}{h^2}\right) \quad (2)$$

where W is the water uptake at time t , W_m is the maximum water uptake, at equilibrium state, D is the diffusion coefficient and h is the composite thickness.

The water uptake varies linearly according to the square root of immersion time in the initial part of the Fick's curve (i.e., $\frac{W}{W_m} < 0.6$), thus leading to the assessment of the diffusion coefficient D from equation (3):

$$D = \left(\frac{k}{4W_m}\right)^2 \pi \quad (3)$$

where k is the slope of the linear part of the curve $W = f(\sqrt{t}/h)$.

2.2.3 Composites drying

After saturation was reached, samples were desiccated at 30°C / 2%RH until weight stabilisation. Then, mechanical properties were determined for dried samples to assess the impact of reversible (physical) and irreversible (chemical) ageing.

2.2.4 Viscoelastic properties measured by vibration analysis

The viscoelastic parameters (elastic modulus and loss factor) of polyester matrix, FFRC and GFRC were determined using vibration analysis. On a general point of view, vibration techniques aim to study the dynamic behaviour of a structure thanks to its natural vibration modes (Corn et al., 2012). This technique is non-destructive and easy to implement, therefore it is well suited for monitoring materials during ageing. For this study, the set-up simulated free boundary conditions by supporting the sample with soft suspensions (Gibson, 2000). The sample, a 250 mm x 25 mm beam, was excited in free vibration by an impulse hammer and its response was monitored by an accelerometer. An additional steel mass (86 g) was clamped at each end of the beam in order to bring down the natural frequency f_1 of its first “traction-compression” mode inside the measurable frequency range (100-9000 Hz). The resonant frequencies of the sample are given by the series of peaks in the frequency response. The software MODAN®, developed by the FEMTO-ST (Franche-Comté University, Besançon, France), was used to extract natural frequencies and damping ratios from the frequency response function (by using a curve fitting technique). Then, the expression of the elastic modulus E was given in equation (4):

$$E = \frac{\rho L^2 f_1^2}{\left(\frac{\beta_1}{\pi}\right)^2} \quad (4)$$

with β_1 being the lowest positive root of equation (5):

$$\beta_1 \cdot \tan \beta_1 = \frac{m}{M} \quad (5)$$

where M is the total added mass (172 g), L and m being respectively the length and the mass of the part of the sample located between these two clamped masses, and ρ its mass density.

Tensile quasi-static measurements were carried out to ensure that dynamic elastic modulus was close to Young’s modulus for these materials.

2.2.5 Uniaxial tensile tests

Ultimate tensile properties were assessed with a MTS testing machine (model Criterion C45.105) equipped with a 100 kN capacity load cell. Samples were loaded at a constant crosshead displacement rate of 1 mm/min at room temperature until breaking according to the standard ISO EN 2747. The reproducibility was evaluated on 5 samples.

2.2.6 Scanning electron microscopy

An Environmental Scanning Electron Microscope (FEI Quanta 200 ESEM) was used to observe biocomposites fracture surfaces obtained from tensile tests before and after immersion into water. Composite samples were observed at different scales: low magnification allows a global fracture view (particularly the relling zone), and high magnification revealed the interface between matrix and fibre and the fibres failure mode.

2.2.7 Differential scanning calorimetry

Thermograms were recorded using a Diamond DSC - PerkinElmer. Polyester resin samples of approximately 20mg were analysed in aluminium pans submitted to temperature ramps from 25°C up to 220°C at a heating rate of 10°C/min. The cross-linking degree (X) was estimated from post-curing peak using equation (6):

$$X = \frac{\Delta H_{total} - \Delta H_{peak}}{\Delta H_{total}} \times 100 \quad (6)$$

with ΔH_{total} the total reaction enthalpy and ΔH_{peak} the residual enthalpy of the polymerized resin.

3. Results and discussion

Fig.1 describes the water uptake of GFRC and FFRC compared to polyester resin as a function of ageing time. It can be observed that flax fibres tended to accelerate diffusion process while glass fibre acted like a barrier to water absorption in composite (compared to non-reinforced polyester). Moreover, the water uptake obeyed a Fickian behaviour with a saturation weight gain 15 times higher for FFRC than for GFRC. Assarar et al. (Assarar et al., 2010) showed a saturated weight gain 12 times higher for flax/epoxy composites than for glass/epoxy composites (samples immersed into a water bath at room temperature). Finally it was shown that the flax fibre treatment slowed down water diffusion in composite and led to a slight reduction of 9% on weight gain compared to untreated FFRC.

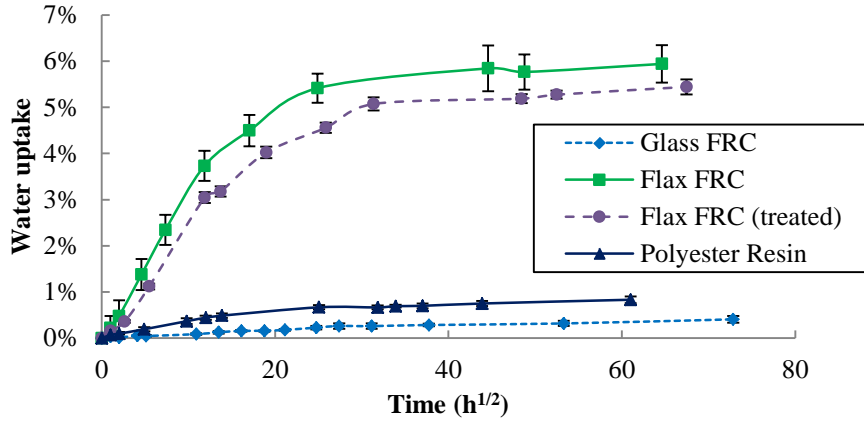


Fig.1 Water uptake as a function of ageing time for polyester resin, glass and flax-fibre composites (untreated and silane treated flax fibre) immersed in water at 30°C.

Table 1 shows the values of the modulus (E_0) and damping (a_0) before ageing, while **Fig.2** displays the relative modulus evolution of GFRC and FFRC compared to polyester resin as a function of ageing time. The relative modulus value is the modulus of the aged sample divided by the modulus of the unaged one (E_0).

Table 1 GFRC, FFRC and polyester resin modulus and damping before ageing.

References	Initial	
	E_0 (GPa)	a_0 (%)
Polyester resin	3.25 ± 0.64	1.25 ± 0.18
GFRC	34.88 ± 1.16	0.24 ± 0.01
FFRC	20.26 ± 1.16	1.00 ± 0.06
FFRC (treated)	20.44 ± 0.74	0.99 ± 0.04

On one hand no change in modulus was observed for GFRC while a slight decrease was obtained for polyester resin. On the other hand a 37% decrease with ageing time was depicted for FFRC which was lowered (-22%) when flax fibre fabrics were treated. It is well known that water diffusion induces both plasticization that leads to a decrease in mechanical properties and post-crosslinking (because of higher macromolecular chain mobility) that leads to higher mechanical properties (Azwa et al., 2013). These two phenomena were in competition during ageing (**Fig.3**). The polyester resin post-crosslinking had been verified by differential scanning calorimetry: the crosslinking rate increased from 88% before immersion to 96% at saturation (**Fig.3-a**). Nevertheless a decrease in modulus was shown, thus denoting that plasticization was predominant. The plasticizing effect for matrix was shown on **Fig.3-b**. For GFRC both phenomena induced equivalent effects. For FFRC the water uptake was so important that only plasticization was observed. The fibre plasticizing effect can be highlighted by monitoring the damping ratio of the materials during ageing.

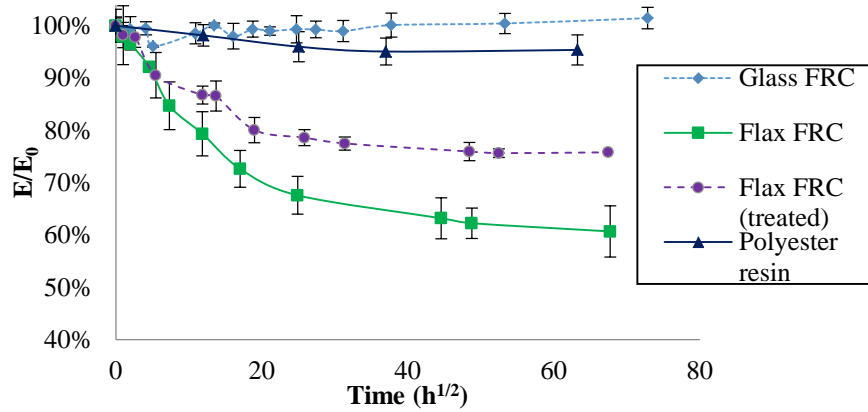


Fig.2 Relative modulus evolution as a function of ageing time for polyester resin, glass and flax-fibre composites (untreated and silane treated flax fibre) immersed in water at 30°C.

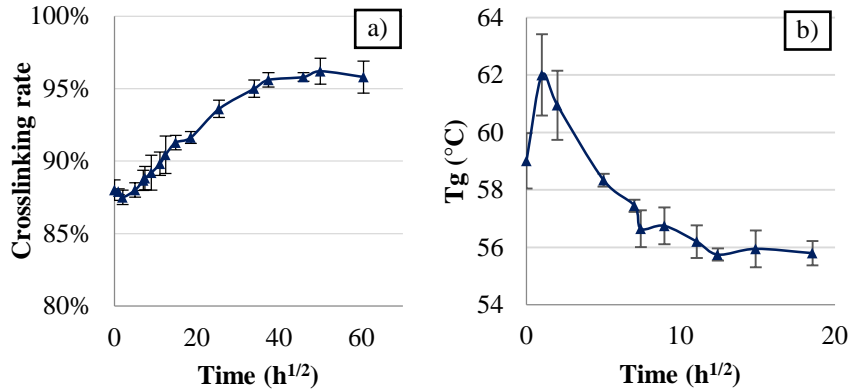


Fig.3 Crosslinking rate (a) and T_g evolution (b) as a function of ageing time for polyester resin immersed in water at 30°C.

Fig.4 corresponds to the damping of the polyester resin, GFRC and FFRC as a function of ageing time. The increase of FFRC's damping during immersion confirmed that viscoelastic properties changed with water uptake. This increase was quite less important for treated flax fibre fabrics. This change was due to the flax fibre plasticization in the presence of water (Joffe et al., 2003). GFRC's damping remained constant along the time confirming the hydrophobic behaviour of glass fibres. The polyester plasticization in water was also observed by following the glass transition temperature during ageing (by differential scanning calorimetry): polyester's T_g decreased from 60°C to 55°C for 1600h in water (**Fig.3-b**) which is in agreement with other work (Fayolle and Verdu, 2005).

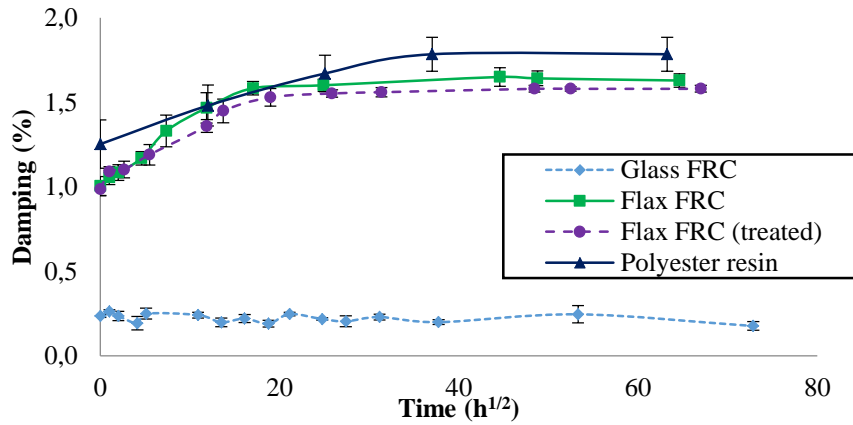


Fig.4 Damping ratio as a function of ageing time for polyester resin, glass and flax-fibre composites (untreated and silane treated flax fibre) immersed in water at 30°C.

When saturation was reached, ultimate tensile tests were performed on composites and the fracture surfaces analysed by ESEM (**Fig.5**). The presence of unbounded zones (**Fig.5-A**) after water immersion suggested that debonding took place at the interface between matrix and fibres. This debonding can lead to fibre slippage, which was highlighted by a longer relling length (**Fig.5-B**). Finally, the fibre ductile fracture behaviour after immersion (**Fig.5-C**) confirmed that fibre plasticization was related to the presence of water within composites.

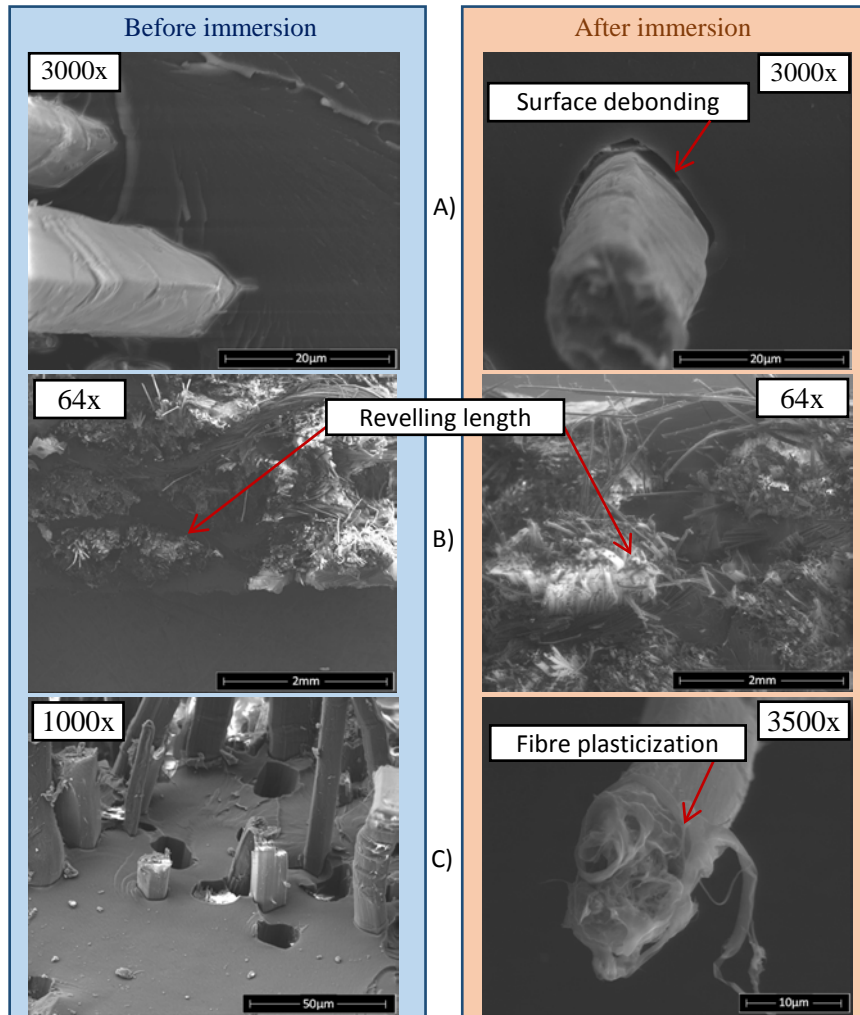


Fig.5 Fracture surface analysis of untreated FFRC before ageing and after ageing at saturation (immersion in water at 30°C).

Fig.6 exhibits the mechanical properties of composites at initial state (before immersion), at saturation, and after drying. The results confirmed that GFRC modulus was not affected by the ageing performed in this work. The slight decrease in ultimate stress at saturation could be explained by interfacial debonding induced by differential swelling between fibres and matrix (Gautier et al., 1999). Concerning FFRC, both mechanical properties were affected by water sorption: modulus decreased by 37% and ultimate stress increased for about 34%. A similar evolution for stress was reported in other studies (Dhakal et al., 2007). Dhakal et al. attributed the increase in wet ultimate tensile stress (compared to dry samples),

to the fact that water caused swelling of the fibres and could fill the gap between fibre and matrix, which could lead to an increase in ultimate properties. In this work, as shown in Fig.5, no gaps were observed before immersion and the increase of ultimate stress was probably due to an improved frictional effect caused by fibres swelling (Le Duigou et al., 2012). When flax fibres were treated, the decrease in Young's modulus and the increase in ultimate stress were less important. These results are in agreement with the expected behaviour for a composite which absorbs less water than the untreated ones.

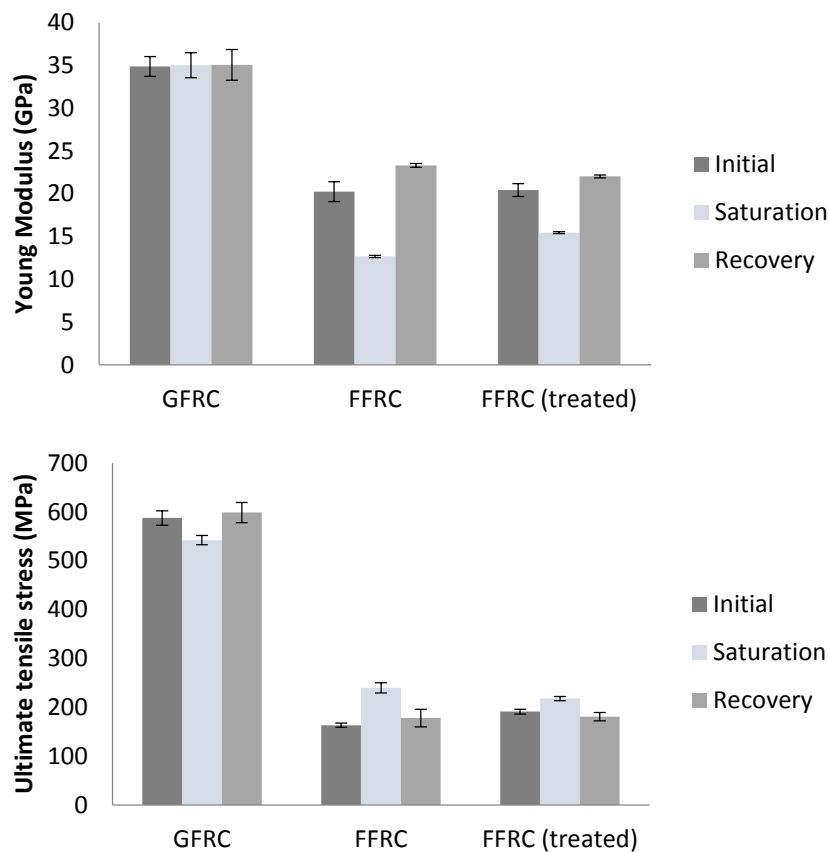


Fig.6 Mechanical properties (Young's modulus and ultimate tensile stress) of glass and flax-fibre composites (untreated and silane treated flax fibre) before immersion, at saturation and after drying.

After desiccation, FFRC tensile modulus had increased compared to initial modulus. Two phenomena could explain that result: (i) further matrix crosslinking (observed through DSC analysis) (ii) lower moisture content compared to initial state. Indeed, composites reached a dried mass 2% lower than initial state before

immersion (see **Fig.7**). The weight loss after desiccation could be explained by two factors: (i) the fibres get drier than at the initial state and (ii) the extractibles (small cell-walls components) were removed during immersion which was observed by scanning electron microscope analysis (see **Fig.8**). Furthermore, glass-fibre and treated flax-fibre composites showed ultimate tensile stress that had not changed compared to initial values. Pavlidou and Paspaspyrides. (Pavlidou and Paspaspyrides, 2003) reported that fibre-resin bond was reversible on redrying wet specimens because silane coupling agent bonds were easily hydrolysed in the presence of water. In the case of untreated flax fibre composites, interlaminar shear tests are being carried out in order to verify the interfacial adhesion between fibre and matrix after drying.

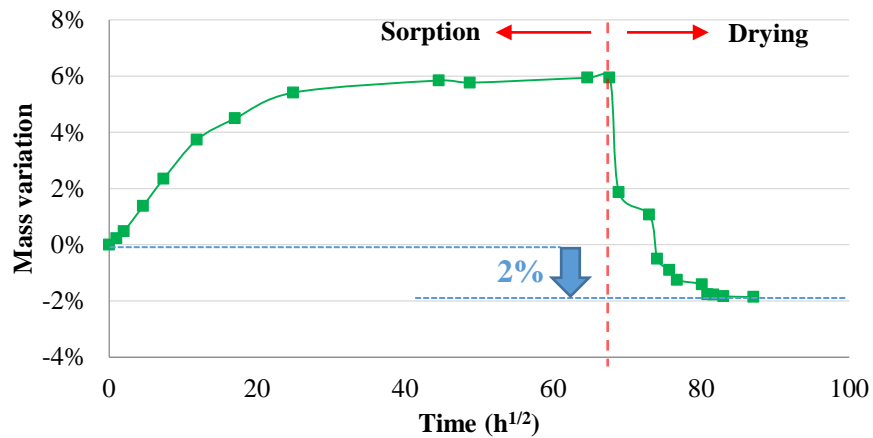


Fig.7 Mass variation of flax fibre reinforced composites during sorption and drying at 30°C.

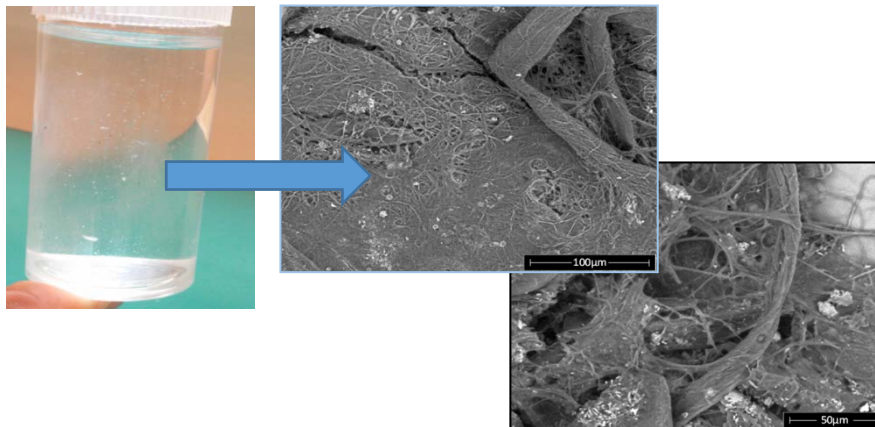


Fig.8 Extractibles (small cell-walls components) removed during immersion observed by analysing the ageing water using an electronic microscope.

4. Conclusions

This study showed that composite's water uptake in immersion at 30°C was mainly controlled by natural fibres and reversible phenomena like fibre and matrix plasticizing took place were observed. The composite's stiffness decreased and damping increased during ageing, highlighting the plasticizing effect of flax fibres. Thus the biocomposite's ultimate tensile stress increased at saturation. No damage was noticed but irreversible phenomena such as further matrix crosslinking and release of extractibles took place during ageing. It was noted that the modifications of biocomposites during immersion were complex to study: physico-chemical plus mechanical modifications are important factors that need to be taken into account simultaneously.

5. References

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