



In situ long-term durability analysis of biocomposites in the marine environment

Guilherme Apolinario Testoni

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Guilherme APOLINARIO TESTONI

le 16 décembre 2015

**In situ long-term durability analysis of biocomposites
in the marine environment**

Directeurs de thèse : **Patrick IENNY & Jean-Marc HAUDIN**

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Travaux réalisés au Centre des Matériaux de l'Ecole des mines d'Alès

“Often when pursuing research into green composites we say that we are protecting the environment, that we are working for nature. We may as well stop kidding ourselves – nature will be fine; nature will work out OK and adapt to the changes. It’s humans that will cease to exist if we continue the way we are at present. Some scientists and engineers have realized that they need to take responsibility for the outcome of their work. Researching ways of creating faster machines and bigger toys, without due consideration of the effects on the environment or on people, is irresponsible.”

Caroline Baillie

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Symbols and Abbreviations

MATC	U.S. Environmental Protection Agency's Maximum Achievable Control Technology
OECD	Organisation for Economic Co-operation and Development
RTM	Resin Transfert Moulding
Carbon HS	Carbon High-Strength
Carbon HM	Carbon High-Modulus
UD	Unidirectional
UP	Unsaturated Polyester
DCPD	Dicyclopentadiene
ILSS	Interfacial Shear Strength
IFSS	Interfacial Shear Strength
PE	Polyethylene
PP	Polypropylene
PLA	Polylactic acid or polylactide
PHA	Polyhydroxyalkanoate
PET	Polyethylene terephthalate
LCA	Life cycle assessment
ΔT	Thermal potential
α	Coefficient of thermal expansion
Δc	Variation fo water concentration
η	Coefficient of hydroscopic dilataion
σ	Ultimate stress
A	Plasticising coefficient

T_g	Glass transition temperature
T_{gp}	Polymer's T_g
T_{gw}	Water's T_g
ρ	Density
τ	Shear stress
D	Diffusion coefficient
D_c	Corrected diffusion coefficient
C	Concentration in water
m_∞	Absorbed water mass (or mass fraction) at the equilibrium
m_t	Absorbed water mass (or mass fraction) at time t
e	Thickness of the specimen
l	Samples length
w	Samples width
k	Slope of the linear part of the curve $m_t=f(\sqrt{t}/e)$
n	Number of free water molecules
N	Number of the bonded water molecules
σ	Stress
ϵ	Strain
UTS	Ultimate tensile strength
E	Stiffness
E_d	Modulus of a fully dense material
E_p	Modulus of a porous material
M_s	Weight uptake at saturation
$\tan \delta$	Loss factor
E''	Loss modulus
E'	Storage modulus
RH	Relative humidity
V_f	Fibre volume content
V_m	Matrix volume content

V_p	Porosity volume content
E_f	Fibre modulus
E_m	Matrix modulus
NFRC	Natural fibre reinforced composites
GFRC	Glass fibre reinforced composites
FFRC	Flax fibre reinforced composites
DMA	Dynamic mechanical analysis
DSC	Differential scanning calorimetry
SEM	Scanning electronic microscopie
FTIR	Fourier transform infrared spectroscopy
MPS	Methacryloxypropyltrimethoxysilane
BMA	Butyl methacrylate
S	Styrene
THF	Tetrahydrofuran
LVDT	Linear variable differential transformer
MBR	Minimum bounding rectangl
X	Cross-linking degree
ΔH	Reaction enthalpy
LMWS	Low molecular weight species

Introduction

The increasing number of scientific papers published over the last years on the degradation of fibre reinforced composites properties due to moisture, temperature, fire and UV radiation, demonstrates the strong interest of scientific and industrial communities in this topic [1]. The application of conventional composites, such as glass fibre reinforced composite (GFRC), for marine structures and their mechanisms of water ageing were extensively studied in the literature. Their long-term behaviour was described by several authors with the objective to understand the effect of water ageing on the mechanical and physicochemical properties of these materials.

Over the last decades composite materials have replaced wood and metal in floating structures (such as boat hulls and components of the nautical sport sector) thanks to their low weight, high corrosion resistance and reduced need for maintenance. GFRC has driven the improvement of marine products and is nowadays the most often used material for pleasure boats.

More recently, engineering industries in several sectors, including the marine industry, have been searching to develop new materials to conform to the new environmental policies adopted in Europe and worldwide. Indeed, the increasing environmental consciousness and demands by government authorities have promoted the growing interest in the study and application of bio-based materials to replace the conventional polymer reinforced composites. Vegetal fibres such as flax, hemp, jute, sisal and ramie have received much attention in the last decades not only from the academic community but also from industry due to their challenging mechanical specific properties in comparison to glass fibres. Nowadays, vegetal fibres are gradually replacing glass fibres for reinforcement in polymer composites in many applications, such as surfboards, canoes, tennis racquet where long fibres are used, or internal car products where short fibres are used. The introduction of vegetal fibres in polymer matrices (bio-based or not) can bring advantages or disadvantages with regard to density, mechanical properties, costs and ageing in water environment.

The transition between conventional and new technologies needs to take into account both the environmental and the technical issues. One of the concepts of eco-development described by the international standard ISO 14062:2002 states that “the solutions proposed to society and industrials need to meet better environmental performances and lower environmental footprint through equivalent or superior technical properties and a price suited to the market”. It is important to emphasize here that new eco-designed solutions need to present similar or superior technical properties compared to the conventional ones. Two broad fields of research on biocomposites have been promoted in order to support this change: the improvement of both biocomposites mechanical performances through their processing technique and durability in service.

The first issue consists in revisiting the techniques employed to develop and process vegetal fibres and biocomposites. Vegetal fibres exhibit very scattered length and cross section shape, just as the corresponding woven fabrics. Initially, the techniques for manufacturing composites were simply transposed from synthetic fibres to vegetal fibres without taking into account their singular features.

Nowadays much attention has been paid to the conditions of storage and processing aiming to optimise the production of performing biocomposite materials.

Indeed, processing composites materials is an important step to create and design structures. In the marine industry, glass-fibre reinforced materials are mainly manufactured using the vacuum infusion technique. This technique has some advantages compared to other manufacturing techniques, including the possibility to produce large-sized composites exhibiting low porosity.

One disadvantage of this technique is that composite thickness is mainly controlled by the arrangement of the fabrics, which means that producing vegetal and glass fibre composites by the same technique could lead to different fibre contents, and therefore different mechanical properties. Most frequently, glass fibres are found to be better dispersed in vacuum infused composites than vegetal fibres, which leads to higher glass fibre contents. The investigation of the influence of processing parameters on the morphological and mechanical properties of biocomposites is an interesting way to improve their mechanical performance.

Another major issue for the industrial application of biocomposites, and the main topic of this study, concerns the durability of these materials especially when exposed to water. Other environmental conditions can lead biocomposites to degradation, such as temperature, mechanical stresses, UV radiation, biological attack, or a combination of these solicitations. Glass fibre composites usually show a good resistance when exposed to long-term water ageing conditions due to the hydrophobic behaviour of the glass fibres [2]. However, the introduction of hydrophilic vegetal fibres can lead to a drastic change of the ageing mechanisms at the composites scale. Water was found to generate larger degradation of mechanical and physicochemical properties of biocomposites than for GFRC [3] [4], and is considered to be one of the main limitations of the use of vegetal fibres in marine applications. One field of research currently in development concerns the improvement of biocomposites durability by the hydrophobic treatment of vegetal fibres [5] in order to enhance their resistance to water sorption. However, their ageing mechanisms are still not well understood. Therefore, it is of major interest to improve the knowledge about the structural modifications of biocomposites in ageing environment related to the evolution of their performance, for single or coupled solicitations.

In this study, the hydro-thermal and mechanical behaviour of a flax fibre reinforced unsaturated polyester composite was characterised and related to the physical and chemical modifications observed during ageing. Then, water was removed from the aged material in order to assess the induced irreversible changes. It is of practical interest here to disassociate the impact of damage in composites behaviour resulting from mechanical loadings or temperature for example, from the intrinsic effects of water within these materials. The phenomena observed at this point will support the understanding of the reversible and irreversible mechanisms of ageing. Then, mechanical solicitations are coupled to hydro-thermal ageing in order to study the effect of coupling on the biocomposites behaviour when exposed to mechanical-hydrothermal ageing.

Besides, in addition to the characterisation of ageing mechanisms and the evolution of mechanical properties of biocomposites during ageing, an objective of this study is to develop a numerical model able to quantify and evaluate the long-term durability of biocomposites. The multi-scale modelling proposed in this study allows predicting water diffusion in FFRP by taking into account the main morphological and statistical features of their microstructure.

Chapter I. Background

The background chapter presents the bibliographic information necessary for the understanding of the work performed. This chapter is divided into five parts:

The first part concerns the application of composite materials for marine structures and the mechanisms of water ageing. Traditional composites (glass fibre reinforced composites) age when exposed to seawater environment. Their long-term behaviour is described in this chapter aiming to understand the effect of water ageing on their mechanical and physicochemical properties.

The second part defines the concepts of biocomposites (polymer matrix, natural fibres) presenting their interest for the development of new materials. An inventory of natural fibres (specifically vegetal bast fibres) will be described.

The third part describes the main mechanisms of ageing and their effects on polymer and composite materials behaviour. They are classified into physical, chemical and mechanical ageing.

The fourth part deals with the ageing mechanisms and degradation of biocomposites in water. The effects of the environmental conditions, which can lead to composites degradation, are described separately for the water uptake, the temperature exposition and the mechanical solicitation. Then, the combined effect of these environmental conditions on the physical and mechanical properties of biocomposites is related.

Finally, the fifth part positions the methodology employed in this study.

The purpose of this chapter is to introduce the traditional composite materials used for marine applications and compare their ageing behaviour to new biocomposite materials. The introduction of natural fibres in polymer matrices (bio-based or not) can bring advantages or disadvantages with regards to density, mechanical properties, costs and ageing in water environment. An exhaustive scientific review will assist in the understanding of the experimental results.

Chapitre I – Contexte et bibliographie

Ce chapitre propose une revue bibliographique et définit le contexte de l'étude présentée dans ce manuscrit. Ces informations constituent une aide à la compréhension des travaux effectués, et sont divisées en cinq parties :

La première partie concerne l'utilisation de matériaux composites pour des structures marines et l'étude du vieillissement subi par ces matériaux en immersion. Le comportement à long terme des composites renforcés par des fibres de verre traditionnellement utilisés dans le secteur marin sera décrit dans ce chapitre, dans l'objectif d'identifier les effets du vieillissement hydrique sur les propriétés mécaniques et physico-chimiques de ces matériaux.

La deuxième partie vise à introduire le concept de biocomposites (matrice polymère, fibre naturelle) et présente leur intérêt pour le développement de nouveaux matériaux. Un inventaire des fibres naturelles (plus spécifiquement des fibres d'origine végétale) sera décrit dans cette partie.

La troisième partie décrit les principaux mécanismes de vieillissement et leurs effets sur le comportement des matériaux polymères et composites. Ces mécanismes seront classés selon leur nature physique, chimique et mécanique.

La quatrième partie traite des mécanismes de vieillissement et de la dégradation hydrique des matériaux composites renforcés par des fibres végétales. Les effets des conditions environnementales, qui peuvent entraîner la dégradation des propriétés des biocomposites, sont décrits séparément pour chaque source d'endommagement : diffusion hydrique, exposition aux températures et sollicitations mécaniques. Ensuite, l'effet combiné des sources d'endommagement sur les propriétés physiques et mécaniques des matériaux biocomposites est investigué.

Finalement, la cinquième partie positionne la méthodologie développée dans cette étude.

L'objectif de ce chapitre est de présenter les matériaux traditionnellement utilisés dans le secteur du nautisme et de comparer leur comportement en vieillissement à celui des nouveaux matériaux biocomposites. L'introduction de fibres végétales dans les matrices polymères (biosourcées ou non) peut apporter avantages et inconvénients de par leur densité, propriétés mécaniques, coût et comportement en vieillissement hydrique. La revue bibliographique exhaustive proposée dans ce chapitre aidera la compréhension des résultats expérimentaux.

I-1. Ocean environment

Composite materials have replaced wood and metal in floating structures (such as boating hulls and nautical sport skins) because of their low weight, high corrosion resistance and reduced need for maintenance. Glass fibre composites (GFRC) had driven the improvement of marine products and are nowadays the most often used material for boats. This part introduces the materials used to produce composites for marine applications, mainly its economical and technical aspects. Then the ageing phenomena and evolution of composites properties when immersed in water is addressed in the second part of this subchapter.

I-1.1. Composite structures

Composite materials were first used in the marine industry during the 1960's when glass fibre reinforced composites were employed to build small boats. They present several advantages over metallic materials, such as lightness, mechanical fatigue resistance, simple and dynamic processing, resistance to corrosion and low cost. The estimated worldwide consumption of glass fibre in the marine industry in 2012 was of 190 thousand metric tons (4.6% of the global consumption) and 50 thousand metric tons in Europe (5.6% of the European consumption) (see Figure I-I). The world production of composite materials has been driven by the United States, followed by Germany, Italy and France. Particularly in France, the scientific approach for the conception of marine structures led the country to develop a solid marine industry employing glass fibres but also carbon fibres (often used for competition boats). According to the OECD (Organisation for Economic Co-operation and Development), the French marine industry is the world's leading exporter of sailing boats [6]. The mediterranean region (Languedoc Roussillon, PACA, Corse) generated more than 1.4 billion euros of turnover in 2009/2010, which represents a quarter of the national sales [7]. More than 95% of the pleasure boats fabricated in France are designed using composite materials, mainly glass fibre reinforced composites (GFRC).

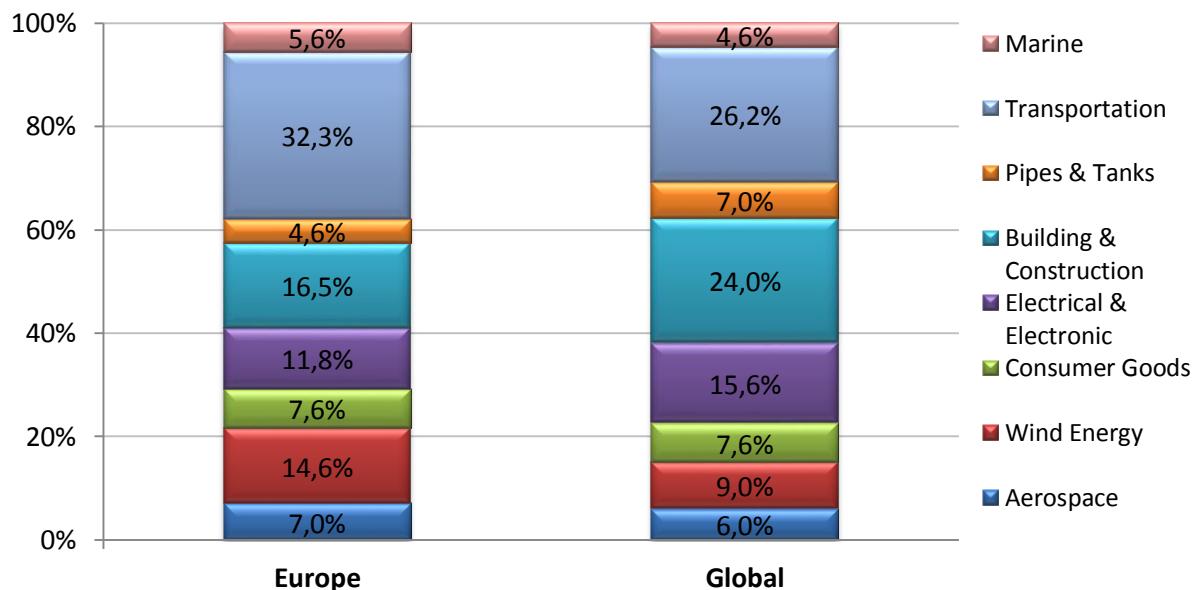
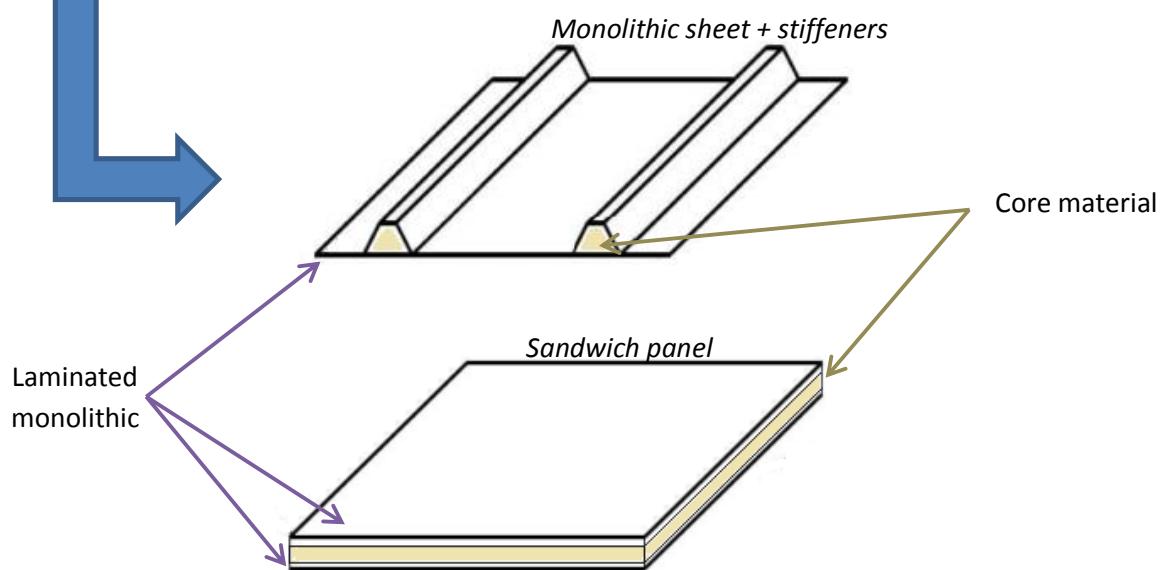


Figure I-I Estimated worldwide consumption of glass fibre in 2012 per region and sector [8]

The manufacturing of pleasure boats employs sandwich or monolithic composites to produce large lightweight structures. Monolithic composites in particular are obtained by stacking fibre fabric plies and impregnating the fabrics with a thermoset resin. After the resin is cured, a thin laminated low-weight sheet is obtained. Certain nautical parts are produced using monolithic laminated composites. However, the thickness of monolithic composites ($\approx 5\text{mm}$) leads to a low flexural resistance and some stiffeners are often used to reinforce the structure (see Figure I-II). Stiffeners are usually a foam/composite assembly bonded or laminated to the monolithic sheets [9].

Another solution to improve composites flexural resistance is the assembly of sandwich composite materials. It is often an association of a low-density core (honey-comb, PVC foam, balsa, etc...) coated with a laminated monolithic composite to increase the inertia of the structure. The sandwich material presents the advantage to resist different types of loading due to its stratified structure: the monolithic skin provides a tensile/compression resistance while the shear stress is supported by the core. However, to meet requirements of lightness, the monolithic skin is usually very thin, which makes this type of structure sensitive to punching damage.



*Figure I-II Image of a catamaran boat hull and a schematic representation of composite panels.
(adapted from [9])*

The composites designed for marine applications are fabricated mainly by two processing techniques: the cast moulding contact (open mould technique) and the vacuum infusion technique (closed mould technique). Other variants of these two processing techniques can be employed, such as the simultaneous projection and the resin transfer moulding (RTM).

The major part of the composite materials for marine applications is fabricated by the contact moulding technique. It is a cheap and easy-processing technique that allows producing larger as well as small components. This technique consists in stacking the fibres (mat or fabrics) on a mould and impregnating them with a catalysed resin system. The resin can be applied by hand lay-up or spray lay-up. The hand lay-up technique consists in the compaction of each impregnated ply using a roller that expels partially the air from the composites structure and provides a good impregnation of fibres. The spray lay-up consists in spraying the resin onto the fibres that are placed by hand. The disadvantages of these processing techniques are their low production rate (up to 500 units per year), variable thickness, low fibre content (usually between 25% and 40% in volume), and the lack of a good surface finish on one side. In addition the high styrene emission during processing causes health problems to workers and impacts the environment.

The implementation of closed-mould techniques, such as RTM and vacuum infusion, was an alternative employed by the nautical industry to gain in competitiveness and reduce the styrene emission during processing. The manufacturers of reinforced plastic composites were required to reduce their air pollutant emissions under the implementation of the U.S. Environmental Protection Agency's Maximum Achievable Control Technology (MATC) standards in 2006. This agency requires manufacturers to capture and control 95% of their styrene emissions [10]. In France, the French agency for food, environmental and occupational health safety (ANSES) recommended a limit of exposure in the workplace for the purpose of preventing the possible neurotoxic and respiratory system irritation effects caused by the styrene exposure [11].

Closed moulding of boating decks for example, grew from 5% in 2000 to around 25% in 2005, according to a study published by the JEC Group (Paris, France) in 2006 [12]. The same study predicted that closed mould would be used for more than 60% of marine composites in 2015.

The advantages of closed mould techniques are the improvement of the fibre content (usually between 40% and 60% in volume) by the application of important pressure during processing and the homogenisation of the composites thickness. The inconvenient of these techniques is the high price of tooling (for RTM technique) and consumables (for vacuum infusion), and a higher sensitivity to defects than the open-mould techniques. Despite the cost, the better mechanical properties and lower styrene emission is leading the marine industry to add closed mould techniques, mainly vacuum infusion, to produce pleasure boat components.

I-1.2. Composite materials for marine applications

The industry of pleasure boats frequently employs thermoset resins (unsaturated polyester, epoxies, vinyl ester) reinforced by glass fibres to produce composite materials. The performance of these composites depends on the characteristic of its components but also on their interaction, which is related to the concept of the fibre-matrix interface. It is interesting here to present the overall properties and characteristics of each element and the role of the interface on composites before studying their behaviour when immersed in water.

I-1.2.1 Glass fibres

Glass fibres (primarily E-glass) are used for reinforcement in over 95% of the total volume of composites for marine applications (long fibres, rovings, mat, etc.) [13] because of its cost, good strength characteristics and workability [14]. Additionally, glass fibre exhibit weak sensitivity to water absorption, which is an important characteristic of a material employed for marine application. The glass fibres are usually treated by a compatibilising or sizing treatment in order to improve the fibres-matrix adhesion. The main properties of glass fibres compared to other synthetic fibres are shown in the Table I-I.

Table I-I The main properties of glass fibres compared to aramid and carbon fibres [14][15].

Fibre	Diameter µm	Density g/cm³	Longitudinal modulus GPa	Poisson's ratio	Stress at break GPa	Strain at break %
E-Glass	15 - 20	2.52 – 2.60	72 - 77	0.20 - 0.25	2.1 - 3.4	2.8 - 3.5
Kevlar	12	1.45 – 1.49	124 - 135	0.40	2.8 - 3.5	1.9 - 2.5
Carbon HS	7	1.75 – 1.80	200 - 260	0.30	2.5 - 4.5	1.0 - 1.8
Carbon HM	5 - 6	1.80 – 1.95	350 - 600	0.35	2.2 - 4.0	0.5 - 1.2

The properties of the fibres but also their architecture (woven or mat product) are important parameters to be taken into account when designing composites. The choice of the organisation of the fibres is a key factor to produce easy-processing and resistant composites that will withstand external loadings during service. The fibres organisation can be classified according to their architecture (see Figure I-III):

- The mats patterns present fibres randomly disposed in the fibre-plane. They present some advantages such as easy processing and possibility to produce complex geometries that possess identical properties in the plane. However, mat reinforcement often leads to low fibre content composites presenting inferior mechanical properties compared to composites reinforced by fibre fabrics.
- The unidirectional fibres (UD) present all the fibres oriented in the same direction conferring good axial properties to composites. Their application is limited because of its difficulty to be correctly oriented during composites assembly and by the fact that UD composites present a low resistance on the perpendicular direction of fibres.
- The fibre fabrics consist of two-thread warp and weft systems. The individual threads are crossed in a certain kind of weave, usually in orthogonally cross-weaving. The most used weavings are taffeta, twill and satin. Other configurations such as multi axial fabrics are also used by the marine industry.

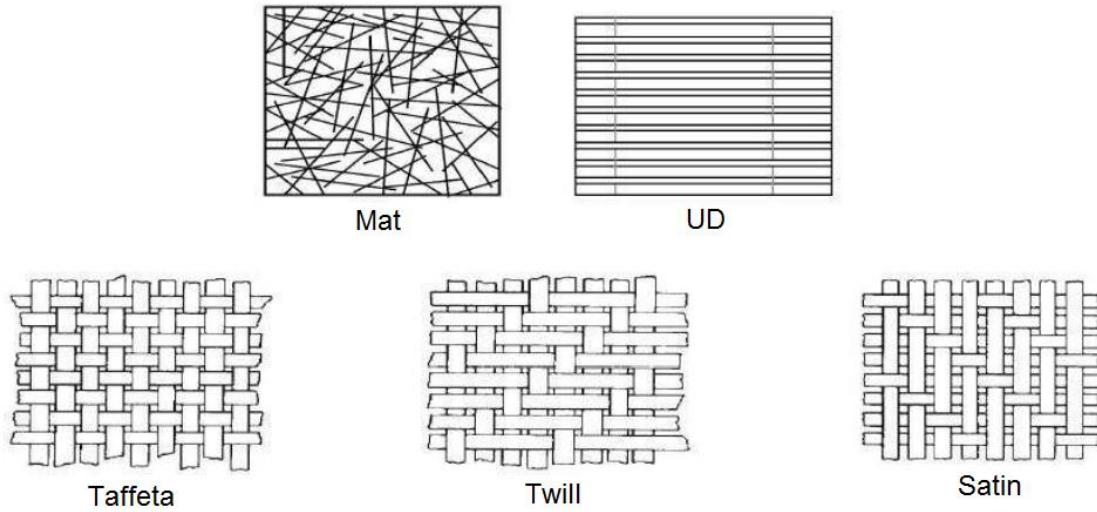


Figure I-III The most used fibre weavings [9].

I-1.2.2 Thermoset resins

Resin systems were especially developed for marine applications consisting in a work on formulation, additives, catalysis and cure conditions. In almost all cases, marine constructors have based their composite structures production on polyester resin, with trends to vinyl ester resin and epoxy for structurally demanding projects and highly engineered products.

The advantages and disadvantages of these resins are presented in Table I-II. Between the three resins, the polyester based systems are the most used for marine applications because of their long-term resistance, thermal stability, good processability and acceptable mechanical properties. Two types of polyester resin are commonly used for marine applications: orthophthalic and isophthalic unsaturated polyesters. The orthophthalic resins are the original group of polyesters developed but are less employed than isophthalic resins because of their limited thermal stability, chemical resistance and processability characteristics. The isophthalic resins presents better mechanical properties, better chemical resistance and better resistance to water permeation, which has prompted many constructors to use isophthalic resins as gel coat or barrier coat in marine laminates [14].

Table I-II Principal advantages and disadvantages of the laminating resins [16]

Resin	Advantages	Disadvantages
Unsaturated polyester and Vinyl ester	<ul style="list-style-type: none"> - Good adhesion on glass fibres (with sizing treatment) - Easy preparation and crosslinking at low temperatures - Relatively good chemical resistance - Low price 	<ul style="list-style-type: none"> - Significant retraction during polymerisation (5 to 10%) - Hydrolysis (mainly for polyester) - Low storage life (around 6 months)
Epoxides	<ul style="list-style-type: none"> - Good mechanical and thermal properties - Low retraction during polymerisation (1 to 2%) - Good chemical resistance - Excellent adhesion to fibres and metals 	<ul style="list-style-type: none"> - Longer polymerisation duration than polyester - An optimum crosslinking rate is necessary (post-crosslinking treatment) - High price

A special unsaturated polyester resin based on an organic component, the dicyclopentadiene (DCPD), was developed aiming to limit the emission of styrene and improve the fibres impregnation. The specificity of this resin is its low pre-polymer molecular weight in styrene which confers certain interesting characteristics: lower styrene content than standard polyesters (30-35% compared to 40-45% of standard polyesters); better fibres impregnation due to a lower viscosity; optimised polymerisation cycle which leads to shorter demoulding time. The DCPD unsaturated polyester are currently used by the marine industry, especially for the production of pleasure boats.

Despite the advantages of unsaturated polyester resins to produce marine composites, they present two disadvantages from a chemical point of view:

- Their ester functions suffer from hydrolytic attack and;
- Their styrene bonds are sensitive to oxidants and solvents.

The hydrolytic degradation of polyester unsaturated groups when exposed during long time to water ageing is a non-negligible aspect to take into account when employing this resin for marine composites [17], [18]. Indeed polyester composites are usually protected from water ageing by a gel-coat layer specially developed for marine applications.

I-1.2.3 The role of the fibre-matrix interface

a. Definitions

The interface plays an important role on the performance of composite materials. It is at the interface that polymer and fibres interactions takes place, affected by the thermodynamic compatibility, or adhesion, between them. Before approaching the interface aspects of glass/polyester composites, it is important to define some notions about adhesion and bonding surface.

A bonding surface can be defined as a discontinuous and thermodynamically unstable site where materials can interact physically or chemically. The term adhesion is a term that describes the contact between two bonding surfaces held between them. In composites, it refers to the efficacy in the transfer of mechanical loadings from resin to fibres. It is a physico-chemical concept that involves the interaction of bonding surfaces and their affinity. The adhesion between two components of composite materials is the result of physical and/or chemical factors:

- The **mechanical anchoring** is a physical interaction between two surfaces created by an increase in the contact area between two materials. The rugosity and porosity at the interface is at the origin of this mechanism;
- The **physico-chemical bondings** (ionic, covalent, metallic, Van der Waals, etc...) are related to the chemical nature of components and can be improved by compatibilisation treatments.

b. Mechanical characterisation

The interfacial or interlaminar shear strength (IFSS or ILSS) is a mechanical property of composite materials that take into account the fibre-matrix interface. This property can be characterised by macro and micromechanical tests. Macro analyses are realised on composites while mainly micro tests employ unitary fibres impregnated into a block or polymer matrix.

The macromechanical tests are often realised using unidirectionally oriented composites in different set-up configurations depending on the angle of loading. The latter is determined in a manner that no other mechanism is engaged than interface resistance. The most common are the $\pm 45^\circ$ tensile test (standard ISO 14129:1997) and 90° tensile test (standard ISO 527-4:1997) also called transverse tensile test. Other testing configurations, such as 3 points bending tests (standard ISO 14130:1997) with a low distance between supports to introduce a shearing solicitation or a double notched tensile tests (standard ASTM D3846:2008), aims to qualify the interlaminar shear strength (ILSS) of composites.

The micromechanical tests consist in mechanically loading a fibre impregnated in a block of polymer matrix. The most used micromechanical testing are the single-fibre pull-out test [19], the microdroplet test [20] and the fragmentation tests [21]. These tests aim to measure the Interfacial shear strength (IFSS).

c. Interfacial shear resistance of glass fibre composites

Glass fibres are often treated to promote adhesion between fibres and the specific matrix for which it is formulated [22]. The optimisation of the fibre-matrix interface leads to an increase in the composites mechanical properties, mainly the ultimate properties [23]. Indeed the load transfer from matrix to fibres is optimum at high deformation levels and the resistance to fracture depends on two main parameters: the nature of fibres and the interface shear resistance.

In the Handbook of composites, Lubin [24] shows an increase in the mechanical properties of glass fibre unsaturated polyester composites with the sizing treatment of glass fibres. The fibres treatment led to a significant increase in compression and flexural resistance, but the effect was less pronounced for the tensile strength. This result confirms that longitudinal tensile and flexural ultimate properties are little influenced by the quality of the fibre/matrix interface, while the transverse tensile and flexural ultimate properties integrate the quality of the stress transfer at the fibre/matrix interface [25].

As reported before, the adhesion between two components of composite materials is the result of physical and/or chemical factors. The fibres treatment involves chemical adhesion while the composites porosity involves physical interactions. Thomason [26] confirmed the dependency of the interfacial shear strength (short beam shear tests – ASTM D-2344) on the void content of glass/epoxy composites . A loss of 2-10 MPa per 1% voids, depending on fibre-matrix combination, was reported for composites produced by pultrusion technique.

Furthermore, it seems to be difficult to compare results from different shear tests. The absolute values of glass fibre composites shear strength can range from 10 to 90 MPa depending on the sizing treatment applied to glass fibres and the type of testing (pull out, fragmentation, transversal tensile, $\pm 45^\circ$ tensile test, etc...).

I-1.3. Composites in water

The design of composites with respect to long-term durability has been largely based on in-service experience [27]. A large amount of experimental-based-data were published on the influence of water on the properties of glass fibre reinforced composites properties [28][2][29]. The study of the mechanisms involved in degradation takes into account the role of the polymer matrix, but also those of fibres and interface on the composites ageing behaviour. The water diffusion in glass fibre composites leads to physical and chemical degradation.

I-1.3.1 Diffusion and water sorption of composites

The progression of the water molecules within the composite material is governed by their interaction with the fibre and the polymer chains (mainly by hydrogen bonds). These hydrogen bonds are created and broken continuously during water molecules progress throughout the polymer structure and the diffusion kinetics of water is influenced in this way by the water/polymer interaction [30]. In light of this, the diffusion is defined as a process in which water molecules moves from a region of higher concentration to one of lower concentration. The water penetrates from the surface to the bulk of the composite until equilibrium is reached [31]. The diffusion kinetics (i.e. the movement of water into the composite) are characterised by the diffusion coefficient and can be described by the laws of diffusion.

Different analytical approaches allow modelling the diffusion behaviour of water into a polymer. The most often used mechanisms are the Fick's law and the Langmuir's mechanism. Both models assume the reversibility of the absorption.

a. *Fick's law*

The Fick law is one of the most common and simple model to represent the diffusion process where water molecules are free to move in the polymer network [32]. This model can be described by two main parameters: the diffusivity, which is the rate of water sorption into the polymer, and the solubility that is the maximum quantity of water absorbed by the composite assuming that no damage was introduced during water exposure. Since the diffusivity is assumed constant (independent of moisture content or mechanical state), the unidirectional Fick's local diffusion is described by the following differential equation (Equation I-I) [33]:

$$\frac{dc}{dt} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Equation I-I}$$

where c local concentration in solvent;
 x current position on the x-axis (in m);
 D diffusion coefficient (or diffusivity) (in $\text{m}^2 \cdot \text{s}^{-1}$).

This differential equation can be integrated to define the diffusion behaviour of water in polymer composites if certain conditions are verified: the composites water uptake at saturation is weak, the testing temperature far from the polymer glass transition temperature and there is a lack of strong interaction between water and the polymer. For a plane composite sheet of thickness e with uniform initial distribution and equal initial surface concentration, the water absorption is proportional to the square root of time (represented in Figure I-IV) and can be calculated by Equation I-II:

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(\frac{-\pi^2 D t (2n+1)^2}{e^2}\right) \quad \text{Equation I-II}$$

where m_∞ is the absorbed water mass (or mass fraction) at the equilibrium;
 m_t is the absorbed water mass (or mass fraction) at time t ;
 e is the thickness of the specimen.

The absorbed water mass varies linearly according to the square root of water exposure time $m_t=f(\sqrt{t})$ when $m_t/m_\infty \leq 0.5$ and the diffusion coefficient can be determined by Equation I-III:

$$D = \frac{\pi}{(4m_\infty)^2} \left(\frac{m_t e}{\sqrt{t}} \right)^2 = \pi \left(\frac{k}{4m_\infty} \right)^2 \quad \text{Equation I-III}$$

where the coefficient k is the slope of the linear part of the curve $m_t=f(\sqrt{t}/e)$

However, a corrected factor is needed to take into account the finite dimensions of the rectangular specimens:

$$D_c = D \left(1 + \frac{e}{l} + \frac{e}{w} \right)^{-2} \quad \text{Equation I-IV}$$

where l is the samples length;
 w is the samples width.

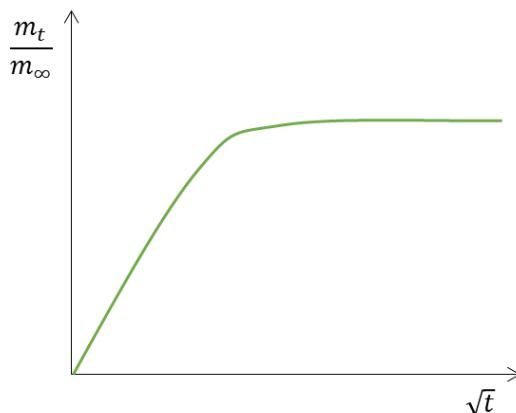


Figure I-IV Kinetics of absorption according to the Fick's law

b. Langmuir mechanism

Carter and Kibler [34] proposed an analytical model based on the Langmuir mechanism to describe the different interactions between water and a polymer. The authors divided the water molecules in two populations: the first is free to move and is called “free water molecules” while the molecules of the second phase are bonded to the polymer network due to reversible chemical reactions and are called “bonded water molecules”. A free water molecule could become a bonded one and reciprocally a bonded molecule could be free with a frequency α and β respectively. The presence of bonded water molecules in a polymer is generally linked to the creation of strong water/polymer bonds (such as covalent bonds in the case of hydrolysis reactions [35]) or to the presence of microporosities [36]. The Langmuir local diffusion model is described by the following differential equations (Equation I-V) and (Equation I-VI):

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2} - \frac{\partial N}{\partial t} \quad \text{Equation I-V}$$

$$\frac{\partial N}{\partial t} = \alpha n - \beta N \quad \text{Equation I-VI}$$

where n number of free water molecules ;
 N number of the bonded water molecules;

The Langmuir model is able to represent a wider class of polymer diffusion phenomena than Fick's model. In the case of a plane composite sheet of thickness h exposed to the same initial conditions at $t=0$, the total mass absorbed by the composite material at a time t is presented in Figure I-V and can be described by Equation I-VII:

$$\frac{m_t}{m_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2(r_n^+ + r_n^-)} \left[r_n^+ \left(1 - \frac{r_n^-}{\beta + \gamma} \right) e^{-r_n^- t} - r_n^- \left(1 - \frac{r_n^+}{\beta + \gamma} \right) e^{-r_n^+ t} \right] \quad \text{Equation I-VII}$$

The coefficient of diffusion can be described by Equation I-VIII:

$$D = \frac{h^2 k}{\pi^2} \quad \text{Equation I-VIII}$$

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

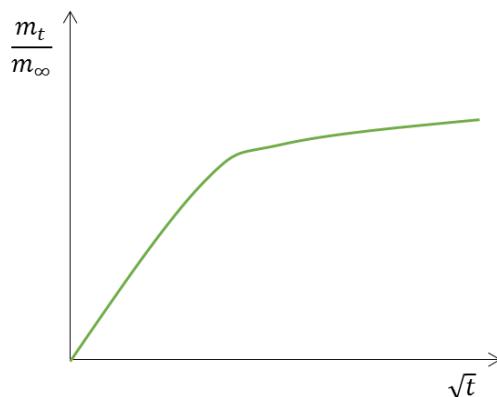


Figure I-V Kinetics of diffusion according to the Langmuir model.

I-1.3.2 The ageing of glass fibre composites

The chemical degradation of glass fibre composites generally involves the hydrolysis of polymer matrix (especially for polyesters), matrix cracking and the degradation of matrix-fibre interface [37]. Even if the glass fibre can be degraded during ageing, this mechanism occurs on a smaller scale [38].

The physical ageing of GFRC involves the plasticisation and the swelling of polymer matrix [39]. The latter can lead to a degradation of the interface such as fibre debonding and delamination phenomena [40].

Davies et al [28] investigated the water uptake behaviour of glass-epoxy composites immersed in water. It was reported that GFRC show a Fickian diffusion behaviour during immersion at room temperature (see Figure I-VI), and a non-Fickian behaviour during immersion at 50°C. The non-Fickian behaviour is attributed to water transport through free edges along the fibre/matrix interface (wicking mechanism). The kinetics of water diffusion was found the same for glass fibre reinforced composites immersed in distilled and saline water at room temperature, but weight gain at saturation was higher for distilled water (1.7% compared to 1.2% for saline water). The explanation is that salt crystals can act as a barrier by blocking the paths through which water diffuses into the material [41].

The authors also highlight that the water diffusion kinetic is not affected by post-cure treatment but a slight difference on weight gain is observed for long times.

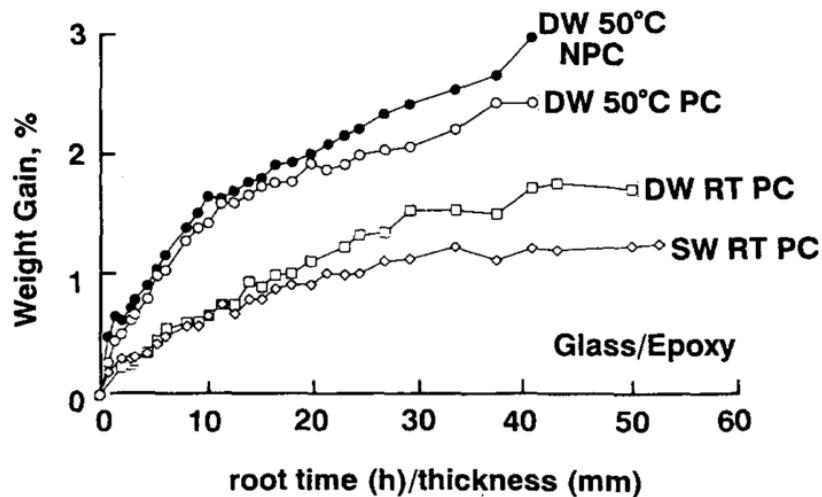


Figure I-VI Weight gain of only cured (NPC) and post-cured (PC) glass fibre reinforced epoxy composites immersed in distilled (DW) and saline water (SW) at room temperature (RT) and 50°C [28]

A non-Fickian behaviour was also observed by Gellert and Turley on a glass/polyester composite immersed in seawater at 30°C [29]. Water sorption of glass fibre composites presented a continuous uptake behaviour rather than a plateau at long immersion times, indicating that additional mechanisms than matrix sorption takes place during ageing (see Figure I-VII). The GFRC plate and cast resin plate curves correspond to experimental results for the water uptake of the composite and the non-reinforced polyester resin respectively. The matrix in GFRC curve is plotted to illustrate the effect of fibres and interfaces on uptake of GFRC, the uptake data were normalised by taking into account that no fibre was present. Up to about 100 days of ageing, the water uptake of composite samples was dominated by water diffusion through the polyester matrix. Beyond this time the divergence of the attributed uptake of the matrix in the composite suggests a second stage of uptake where other

mechanisms, possibly related to the interfaces, became significant. Weitsman [42] attributed the appearance of this second stage of uptake to a moisture-induced damage at the fibre/matrix interface. The author shows the presence of microcracks situated predominantly in sites where adjacent fibres are positioned close to each other, but also at the interfaces between fibres and resin-rich regions. This phenomenon may be attributed to high residual stresses caused by water induced differential swelling.

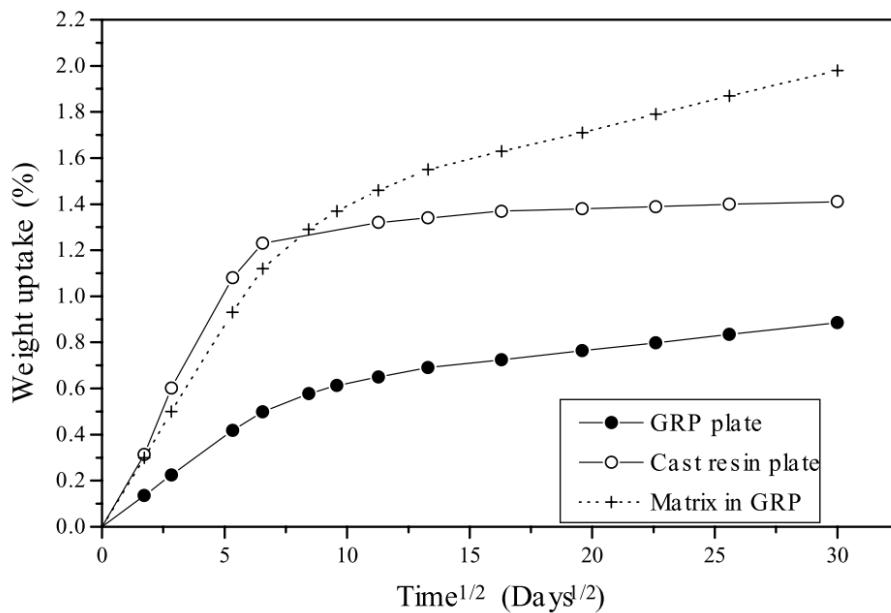


Figure I-VII Water uptake behaviour of plates of glass/polyester reinforced composites and neat cast resin, with the attributed uptake for the matrix in GRP based on the resin proportion [29].

A Carter-Kibler's model, which is referred to as the Langmuir model, was employed by Boukhoulida et al. [43] to describe the water uptake behaviour of glass/polyester composites (see Figure I-VIII). The curve (1)+(2) follows the Carter-Kibler's model to predict the sorption and diffusion parameters of glass fibre composites. The curve (1) represents the amount of "mobile" water molecules that diffuses through the composite following a Fickian model and the curve (2) shows the distribution of "bonded" water molecules. The curve (1)+(2) is simply the sum of the previous curves which means that a complex state of bonded and free water molecules is present within the composite material during water ageing.

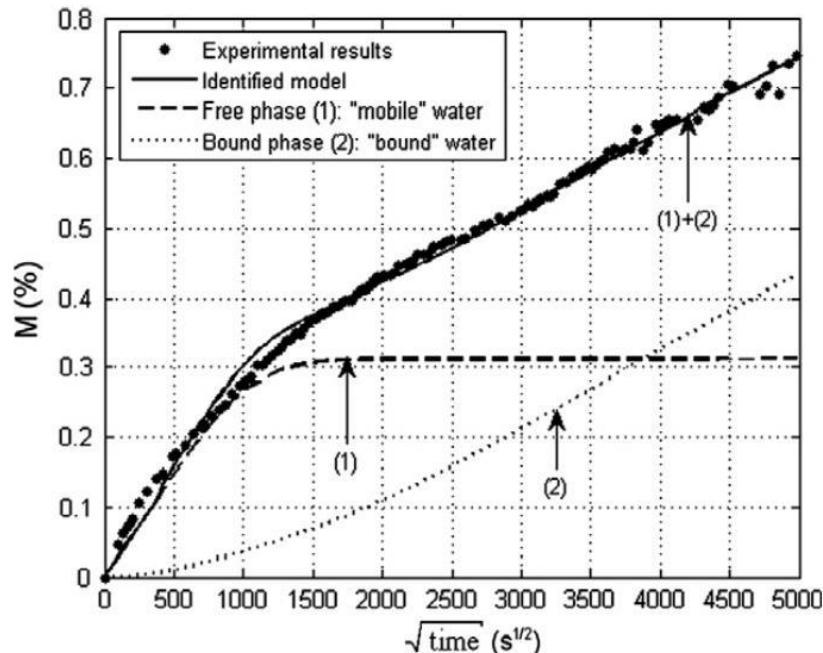


Figure I-VIII Identification of the water uptake behaviour as a function of ageing time for glass fibre composites using a Carter-Kibler model [43].

Another factor that influences the water uptake is the presence of voids in the matrix or at the interface. The effect of resin porosity on the water absorption behaviour was reported by Thomason [26]. It was shown that the water absorption varies linearly with the composites void content. Water uptake at saturation increases from 1% to 6% for a void content increasing from 1% to 4% in the composite. The theory of the free volume is the driving force here [33]. Another interesting fact reported by Thomason is that the void content can be considered as a more significant parameter than the fibre/matrix interface to explain the increase in water uptake.

Concerning the interfaces, glass fibres are frequently treated using organosilane agent that promotes adhesion between fibres and matrix. The interface in this case is characterised by a ternary composition: the matrix, the coupling agent and the fibre. Schutte [44] shows that interfacial water diffusion can lead to a decrease in mechanical properties by an hydrolytic attack at the interface. The author indicates that the pitting corrosion of the fibre surface is the main mechanism of ageing. Furthermore, the degradation can be exacerbated by the overstress induced by a differential swelling between fibre and polymer matrix [45] which enhances the water uptake and weakens the interface. Indeed, it was noted that the interlaminar shear strength, measured from ILSS test (4-point short beam shear test – ASTM D-2344), decreases from 28.6 MPa to 25.3 MPa (12% of loss) for aged laminates after 485 days of immersion [29]. A similar trend was observed by Thomason [46] (96 MPa before and 83 MPa after ageing – around 14% of loss) for the interlaminar shear strength (short beam shear test – ASTM D-2344) of a glass-epoxy composites exposed to boiling water during 48 hours.

Camino et al [2] studied the solubility and diffusivity of water in glass-polyester composites by taking into account the chemical and physical processes induced by water penetration into these composites. The water sorption causes the hydrolysis of chains for the styrene-crosslinked polyesters, besides the swelling and plasticisation of the matrix. Experimental and theoretical results show that the solubility coefficient of water in glass fibre reinforced composites depends on the activity of water

in the matrix. Furthermore, the diffusion coefficient of water in composites is dependent on the water concentration in the matrix and the swelling induced by water penetration [47]. The DMTA technique was employed to determine changes in composites mechanical properties due to water sorption: elastic modulus decreases with the increasing temperature and water ageing time exposure (see Figure I-IX). The authors explained the degradation of the elastic properties by the plasticising effect of the water absorbed in composites

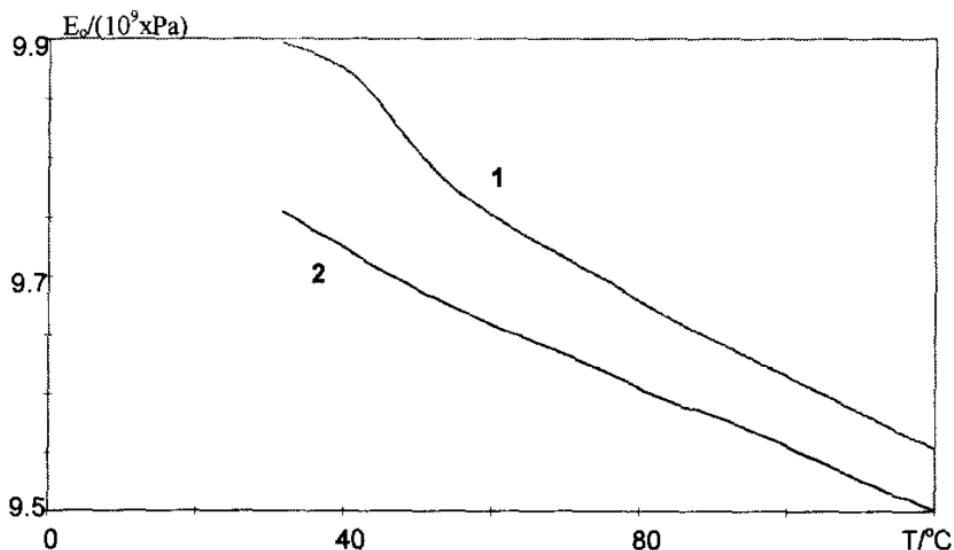


Figure I-IX Variation of elastic modulus with temperature for composites before ageing (1) and after immersion (2) in water for 11 days at 80°C [2].

Fraga et al. [48] highlighted the plasticising effect of water in polyester and vinyl ester composites. This mechanism (physical modification) is displayed by a decrease in the glass transition temperature during ageing. Samples were aged during more than 1,000 hours in water but no chemical modification (hydrolysis of chain molecules) was observed either at 40°C or 80°C. Otherwise, a weight loss is observed due to the removing of extractables (probably monomer and oligomers) during immersion.

Furthermore, the polymer matrix shows an evolving behaviour during ageing related to instability of its molecular configuration. This phenomenon is generally observed in thermoset resins that post-crosslink during their lifetime. Water and temperature can accelerate the post-crosslinking kinetics. In the specific case of nautical products, the composites cure at room temperature at the shipyard and should be post-cured in order to optimise their cross-linking rate. However, the marine composites are generally not post-cured because of the cost of this procedure. In this case, the polymer composites are in an under-crosslinked state before immersion and continue to crosslink over long periods. Perrot [9] shows that polyester resins present a crosslinking degree of around 80% and a glass transition temperature of around 60°C before ageing. The T_g increases to 75°C approximately after ageing in water at 40°C during 9 months, which indicates that the density of crosslinked bonds in the polymer had also increased.

Long-term durability studies were performed over the last decades concerning the evolution of composites' mechanical properties during ageing in water. A study performed by EDF company in collaboration with various research institutes [49][50] reported the evolution of the mechanical properties of glass/epoxy composites for periods over 10 years exposed to water ageing. A loss in properties was observed after 2.5 years in water at 60°C which was attributed to the hydrolysis of

epoxy resin. Changing the hardening system of the epoxy resin solved the problem and no degradation was observed for the composite material immersed into water at 20°C for 10 years.

Otherwise, few studies highlight the effect of mechanical loading on the water uptake behaviour of glass fibre composites. Gellert and Turley [29] studied the seawater immersion ageing of glass fibre composites for marine applications. Composites were immersed in water at 30°C during 2.5 years and loaded under set-strain (four-point loading at a set of 20% of the flexural fracture strain). It was reported that loading had no significant influence on the saturation uptake of glass-polyester composites while diffusion coefficient increased by about 25%. Concerning the evolution of mechanical properties during ageing, it was reported that loading had little effect on changes to the flexural properties of the polyester laminates. The flexural strength decreased by 17% for the unloaded water saturated glass-polyester composite while a decrease of 11% was observed for loaded and water saturated laminates. A decrease of 6% in flexural modulus was observed for both loaded and unloaded materials after ageing.

I-1.3.3 Phenomena of ageing

It was shown that the glass fibre composites water uptake is controlled by the resin and the interface. Water absorption of polyester resin shows a Fickian behaviour but can also display non-Fickian behaviour linked to the presence of bonded water molecules in the composite during ageing. The absorbed water can disrupt the interfacial bonds, occupy the voids and cause changes in the free matrix volume (possibly leading to resin cracking). Changes in resin can either be reversible (plasticisation and swelling) or irreversible (dissolution, hydrolysis and microcracking). The chemical composition of resin appears to affect the equilibrium content of water. Iso- and ortho-phthalic polyesters are different in this sense. Of course this affects the mechanical performance; the larger the water content, the greater the swelling stresses for composites exposed to water ageing during long periods or sufficiently high temperatures. Moreover, another irreversible effect observed was the creation of a secondary cross-linking in the matrix, due to a specific kind of hydrogen bond that forms between resin and water molecules. This phenomenon depends on the chemical structure of the resin, the temperature and the total period of exposure to water [51]. Finally, the diffusion of water into polymers and composites may lead to the leaching of some resin molecules of low molecular weight, which can also lead to an irreversible stiffening of these materials [52] [53].

I-2. Biocomposites

The increasing environmental collective consciousness and demands from government authorities to promote bioresources led to the growing interest on the use of natural fibres to replace the conventional ones such as glass fibres. Among natural fibres flax, hemp, jute, sisal and ramie have received much attention in the last decades not only from academic community but also from industry.

This study sets out some concepts of biomaterials by presenting their interest and characteristics. The intent here is to provide a review of the last advances in the area of biocomposites but in contact with industrial application.

I-2.1. Concepts and generalities

Biocomposites consists in a matrix (bio-sourced or not) reinforced by natural fibres. According to the origin of its components, a classification of biocomposites is proposed by Mohanty et al. [54] (see Figure I-X) : biocomposites are composite materials made from natural fibre and petroleum-derived nonbiodegradable polymers (such as PE, PP, epoxies, etc.) or biopolymers (such as PLA, PHAs, etc.).

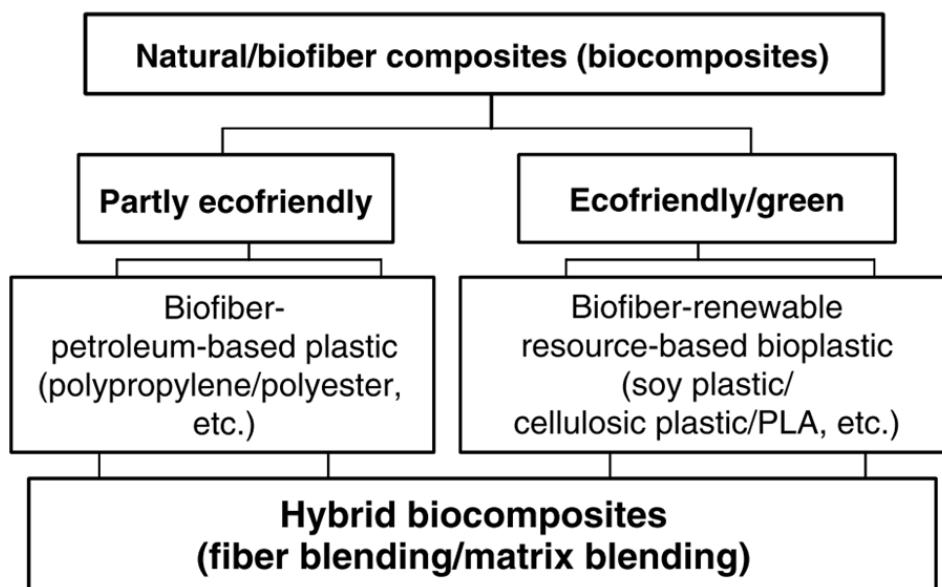


Figure I-X Classification of biobased composites [54].

More and more people are interested in using 'bio' or 'green' materials but do not want to spend more for less efficient materials. It is difficult to replace petroleum-based materials from a cost and performance perspective. An alternative is to combine materials from both non-renewable and renewable sources to produce materials that respect the cost-performance relationship for real-world applications. In this case, a partly eco-friendly material is a viable solution that finds its place in a transition period of renewable sourcing. Although not biodegradable, partly friendly composites may consist in a transitory solution to study the viability of the natural fibres application to industrial products.

Mohanty et al. [54] stated “Biocomposites produced from the combination of biofibres and bioplastics produce the necessary performance either entirely or in combination with petroleum-based polymers and offer a path to achieve ecofriendly materials in the 21st century. However, the need to produce 100% biobased materials as substitutes for petroleum-based materials is not immediate. Biocomposites that contain a significant content of biobased materials can presently achieve this at an affordable cost–performance ratio to compete with petroleum-based materials and still maintain a positive balance among ecology, economy, and technology”.

A first step can consists in substituting conventional fibres by natural fibres to produce partially biosourced composites that respect two important criteria:

- **Technology:** the performance of the new biosourced materials needs to be equal or superior to the conventional materials;
- **Ecology:** the improvements of the new material can be identified by energy and materials used during manufacturing, and the waste released to the environment.

Shah et al. [55] presented the economical, technical and ecological properties of plant fibres compared to E-glass fibres (seeTable I-III). The results place plant fibres as potential substitute to glass fibre reinforcements in composites [56]. It is an opportunity to develop a new market as, according to statistics over the period 2000-2010, 87% of the 8.7 million tonnes global fibre reinforced polymer market is based on E-glass fibre reinforced composites (GFRC).

Table I-III Comparaison between plant and E-glass fibres [55].

	Properties	Plant fibres	E-glass fibres
Economy	Annual global distribution (tonnes)	31,000,000	4,000,000
	Distribution for FRC's in EU (tonnes)	Moderate (40,000)	High (600,000)
	Cost of raw fibre (€/kg)	Low (0.5 - 1.5)	Low (1.3)
Technical	Density (g cm ⁻³)	Low (1.35 - 1.55)	High (2.50)
	Tensile stiffness (GPa)	Moderate (30 - 80)	Moderate (73)
	Tensile strength (GPa)	Low (0.4 - 1.5)	Moderate (2.0 - 3.5)
	Tensile failure strain (%)	Low (1.4 - 3.2)	Low (2.5)
	Specific tensile stiffness (Gpa/g cm ⁻³)	Moderate (20 - 60)	Low (27)
	Specific tensile strength (Gpa/g cm ⁻³)	Moderate (0.3 - 1.1)	Moderate (0.7 - 1.3)
	Abrasive to machines	No	Yes
Ecological	Energy consumption (MJ/kg of fibre)	Low (4 - 15)	Moderate (30 - 50)
	Renewable resources	Yes	No
	Recyclable	Yes	Partly
	Biodegradable	Yes	No
	Toxic (upon inhalation)	No	Yes

The following part addresses the technological aspects involved in the substitution of conventional fibres by natural fibres and reviews several studies about the environmental aspect of this change. The cost is another important factor in an economical context but will not be addressed in detail in this study.

I-2.1.1 Technological aspects

Before proposing a biosourced alternative to the use of glass fibres in composites, it is necessary to verify the viability of this change from a technical point of view. Several studies compare the elastic and strength properties of natural fibre reinforced composites (NFRC) with the properties of conventional glass fibre reinforced composites. Some results are presented in the Figure I-XI. In the 1970s, the use of natural fibres has grown with the production of jute and sisal fibre composites to build low cost housing, grain silos and fishing boats [57]. The properties of these composites were reported during the 1970s, 1980s and 1990s with the introduction of other natural fibres such as flax and hemp.

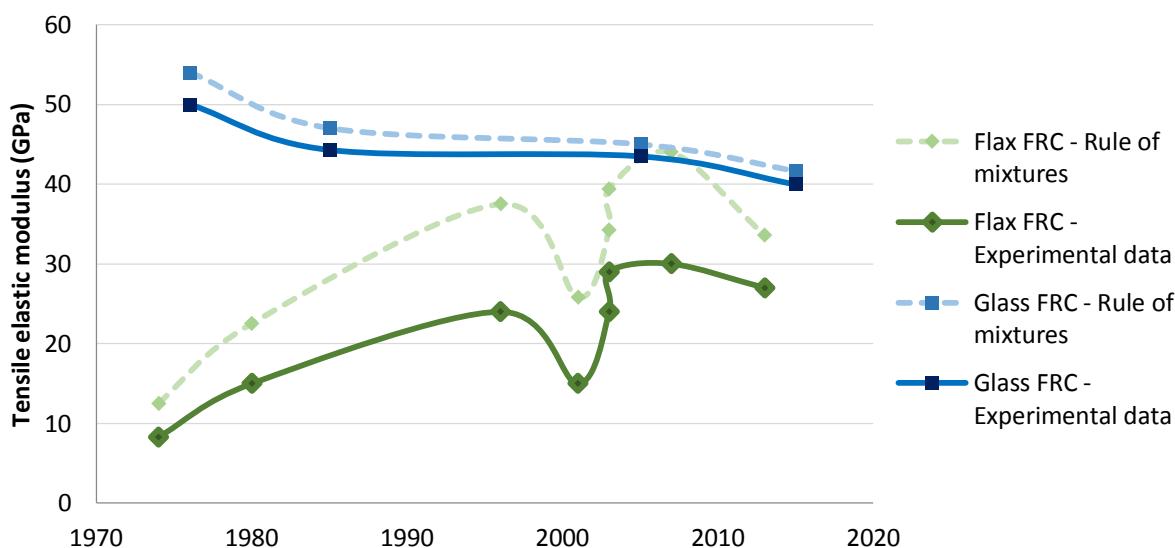


Figure I-XI Evolution of the GFRC and NFRC stiffness during the last decades (experimental data compared to the expected result calculated from the rule of mixtures)

References of Figure I-XI:
 Glass fibre reinforced composites [58] [59] [60] [61]
 Flax fibre reinforced composites [62] [63][64][65][66][67][68][69]

From the Figure I-XI it can be also observed that the difference between the experimental results and the rule of mixture is much higher for the NFRC compared to GFRC. This means that the mechanical properties of these composites can be still improved by working on the optimisation of the genotype of fibres, on the compatibilisation treatments, or on the processing conditions. The number of studies based on the influence of processing conditions on the mechanical properties of natural fibre reinforced composites is still low, but is gaining attention in the last decades. In general, the same processing techniques as used for glass fibre composites are transposed to the manufacturing of NFRC without taking into account the complexity of natural fibres and especially their permeability to polymer matrix impregnation.

Madsen [70] had investigated the effect of the process temperature on the mechanical properties of thermoplastic hemp fibre reinforced composites manufactured by compression moulding technique. The process temperature used for composite manufacturing is shown to affect the tensile properties of the composites (see Figure I-XII). When processing temperature is increased from 180 to 220 °C, stiffness is increased from 19 to 23 GPa, while ultimate stress is decreased from 240 to 170 MPa, and ultimate strain is decreased from 0.021 to 0.012. The measured stress-strain curves are

nearly identical in relation to the process temperature, only ultimate properties are changed. Thus, it is indicated that the effect of thermal degradation is mainly confined to the failure mechanisms in the hemp yarn fibres, and they fail prematurely in composites processed at high temperatures. The porosity of the composites is also affected by the process temperature. Actually, when process temperature is increased from 180 to 220 °C, porosity is decreased from 0.043 to 0.018. This is explained by the decrease in matrix viscosity. Composite porosity is found to be linearly related to the logarithm of matrix viscosity.

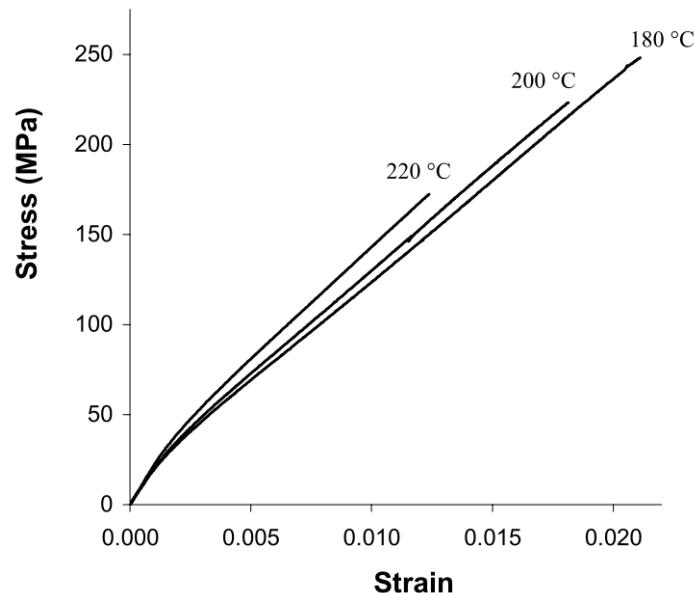


Figure I-XII Representative stress-strain curves of hemp/PET composites fabricated with different temperatures [70].

A wide literature study on the mechanical properties achieved by flax fibre reinforced composites was realised by Duflou et al. [71]. In Figure I-XIII different categories of flax fibre reinforced composites are distinguished according the nature of the polymer matrix, the structure of the flax fibre reinforcement and the applied manufacturing technique. The authors state that the low mechanical strength of flax fibre composites (compared to glass fibre composites) represents an obstacle to their implementation for structural components. When stiffness is the main design criterion, flax fibre composites can offer a real solution providing that sufficiently high volume fractions of flax fibres are used and that the component lifetime is not significantly shorter than for an equivalent glass fibre composite.

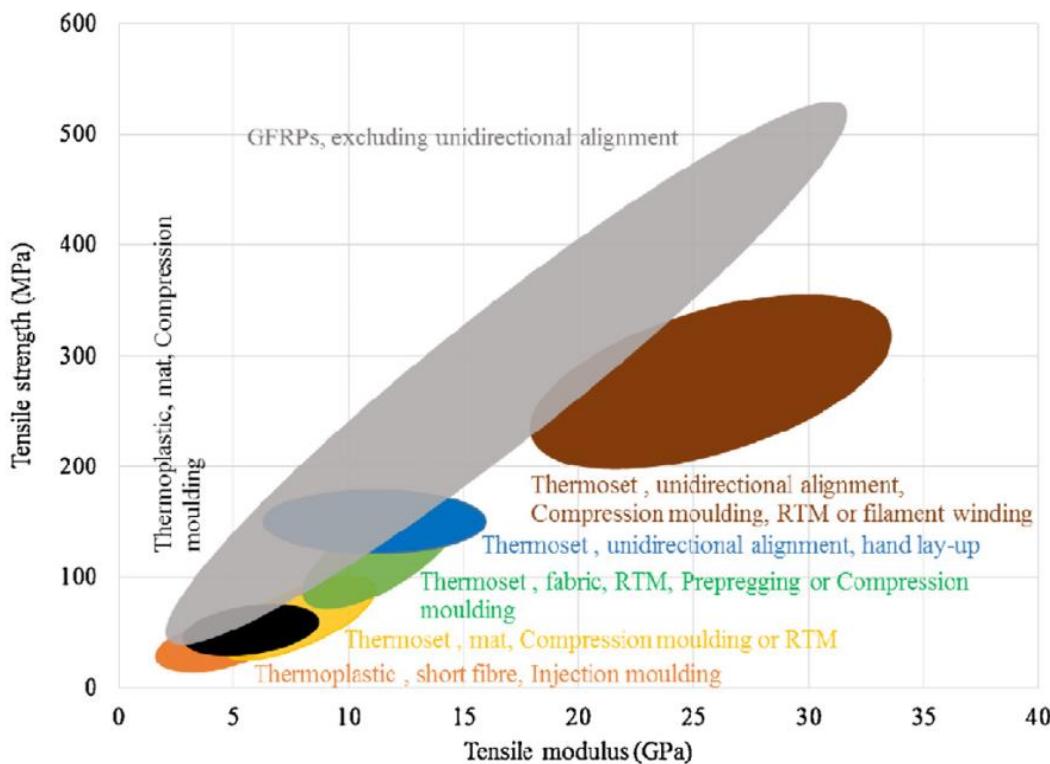


Figure I-XIII Mechanical properties of flax fibre composites compared to glass fibre composites [71].

The influence of processing on the mechanical and morphological properties of natural fibre reinforced composites is the subject of an experimental study in the subchapter III-2 (page 105).

Another important challenge associated with the use of natural fibres in composite for outdoor applications concerns the control of water sorption in these materials when exposed to humid environments. Actually, water molecules are absorbed by the hydroxyl and other polar groups of the natural fibres cell walls leading to changes in composites dimensional and mechanical properties. Although hydrophobic polymer matrix provides protection from moisture uptake, composites absorb water when exposed to humidity for long service periods and specially if the composite is subjected to damage which exposes the fibres directly to water absorption [72].

The durability aspects of biocomposites are addressed in detail in the subchapter I-4 (page 43), and experimental results are shown in Chapter IV (page 117).

I-2.1.2 Environmental assessment

By definition, biocomposites or green composites are assumed to be designed with the lowest possible environmental ‘footprint’. The terms ‘green’, ‘eco’, ‘sustainable’ or ‘clean’ assume that effective environmental improvements have been made instead of merely creating labels to generate fundings from governmental bodies. The materials choice and design in producing composites will impact the environment but also the society [73]. Different instruments have been developed in the last years aiming to evaluate the environmental impacts of a product, including an interesting instrument named life cycle assessment (or LCA). According to the Society of Environmental Toxicology and Chemistry, life cycle assessment is defined as an objective process to evaluate the environmental borders associated with a product, a process or an activity by identifying energy and materials used

and wastes released to the environment, and by evaluating and implementing opportunities to perform environmental improvements. However, life cycle assessments are so complex and in times subjective that they are frequently ignored or taken as a supplement established at the end of a project.

Recent studies show different tendencies for the environmental impact of natural fibres compared to conventional ones. The choice of inputs and outputs for the inventory can change from one study to another leading to different results and subjective comparisons.

Corbiere-Nicollier et al. [74] compared the LCA of a transport pallet produced using glass fibre reinforced PP (containing 42% by weight of glass fibre) to a China reed fibre reinforced PP (containing 53% of China reed fibre). The cumulative nonrenewable energy used for each composite was of 1400 MJ for glass fibre reinforced composites compared to 717 for China reed fibre reinforced composites. Overall, the NFRC pallets are environmentally superior to GFRC pallets in almost all the studied scenarios. However, the environmental impact of NFRC pallet is worst if the life-time of each product is taken into account (3 years for the NFRC pallet compared to 5 years for the GFRC pallet).

Joshi et al. [75] revised the life cycle nonrenewable energy requirements for the production of glass fibres and natural fibres by comparing results from different authors (see Table I-IV). As observed, glass fibre production requires 5 times more nonrenewable energy than flax fibre production. The polluting emissions from glass fibre production are significantly higher than that from natural fibre production, except for the life cycle eutrophication impacts that is found to be higher for certain natural fibres.

Table I-IV Nonrenewable energy used in the production of different fibres (MJ/kg) [75].

Nonrenewable energy requirements (MJ/kg)					
Glass fiber mat ^a		Flax fiber mat ^a		China reed fiber ^b	
Raw materials	1.7	Seed production	0.05	Cultivation	2.50
Mixture	1.0	Fertilizers	1.0	Transport plant	0.40
Transport	1.6	Transport	0.9	Fiber extraction	0.08
Melting	21.5	Cultivation	2.0	Fiber grinding	0.40
Spinning	5.9	Fiber separation	2.7	Transport fiber	0.26
Mat production	23.0	Mat production	2.9		
Total	54.7	Total	9.55	Total	3.64

Source ^a: Ref. [76] Source ^b: Ref. [74]

The authors proposed that NFRC are likely to be environmentally superior than GFRC for the following reasons: (I) lower environmental impacts; (II) higher fibre content for equivalent performance which reduces the amount of more polluting base polymers; (III) reduction of fuel consumption and emissions during the use phase related to a lower weight of NFRC; and (IV) end of life incineration of natural fibres results in energy and carbon credits.

Le Duigou et al [77] highlights that most of the environmental indicators (climate change, acidification, non-renewable energy consumption...) are favourable to flax fibres but the eutrophication indicator, due to the use and production of fertilizers, remains higher for flax than glass fibres. Possible optimisation is studied by means of reduction of mechanical extraction steps and chemical products use.

On the other side, some authors observed that the environmental superiority of biocomposites compared to conventional synthetic fibre composites is still questionable. Biocomposites processing demands relatively excessive requirements, which leads to high consumption of energy: Some categories linked to the agricultural activities, such as land use and freshwater toxicity generates typically high environmental impacts [71]. Therefore, careful life-cycle assessment of biocomposites is essential in order to retain the main advantage in the process of developing high performance biocomposites.

I-2.2. Polymer matrix

Thermoset polymers used in natural fibre composites keep fibres together to provide a shape, transfer the load to the fibres by adhesion and/or friction and protect the fibres from external sources of damage (such as mechanical impacts, chemical corrosion and humidity sorption). Matrix also provides rigidity and shape to the structural component and influences the impact and ductility of biocomposites.

The principal thermoset resins used in natural fibre composites are unsaturated polyester, vinyl ester and epoxy resins (their properties are compared in Table I-V). Although thermoplastics currently dominate as matrix for biocomposites, nowadays the researchers are more interested by thermosets because of their mechanical properties, chemical resistance, thermal stability, and overall durability [78]. Another advantage to the use of thermoset resins is their low processing temperature that avoids the degradation of natural fibres (for example, some structural components of the flax fibres starts to decompose at about 200°C [79]).

Table I-V Properties of thermoset resins used in natural fibre composites [80]

Property	Epoxy	Polyester	Vinyl ester
Density (g/cm3)	1.1 - 1.4	1.2 - 1.5	1.2 - 1.4
Elastic modulus (GPa)	3 - 6	2 - 4.5	3.1 - 3.8
Tensile strength (MPa)	35 - 100	40 - 90	69 - 83
Elongation (%)	1 - 6	2	4 - 7
Cure shrinkage (%)	1 - 2	4 - 8	2 - 3

Most recently, the research on bio-based polymers has increased substantially thanks to the availability of natural polymers from renewable sources. Partly bio-sourced epoxy and polyester resins are commercially available showing satisfactory mechanical properties when compared to the petro-sourced resins [81]. A limitation of these polymers is the high initial cost at this stage, from three to five times the cost of the synthetic polymer resins [82].

I-2.3. Vegetal fibres

Natural fibres are a broad category of materials that are gaining popularity due to an increasing interest by the industry and the society for sustainable solutions to the use of synthetic fibres. These fibres are classified into three categories (vegetal, animal and mineral fibres), but the most used fibres to reinforce composite materials are the vegetal fibres, mainly those extracted from the outer cell layers of the stems of plants (called bast fibres) [83].

Approximately 315,000 tonnes of natural fibres were used as reinforcement in composites in the European Union (EU) in 2010 (accounting 13% of the total reinforcement materials in fibre reinforced

composites, including synthetic and natural fibres). This number can increase to 830,000 tonnes in 2020, corresponding to 28% of the total reinforcement materials, driven by the adoption of modern environmental policies [84].

A classification of natural fibres (non-lignous fibres) is proposed by Shah [85] and illustrated by a Venn diagram in Figure I-XIV. Natural fibres can be classified according to the part of the plant there are extracted from, or their application upon extraction. In the first case, natural fibres are categorised as bast fibres, seed fibres, leaf fibres, and others (such as wood fibres and root fibres). In the second case, primary plant fibres are cultivated specifically for their fibre content, and secondary fibres are waste or by-products from some other application.

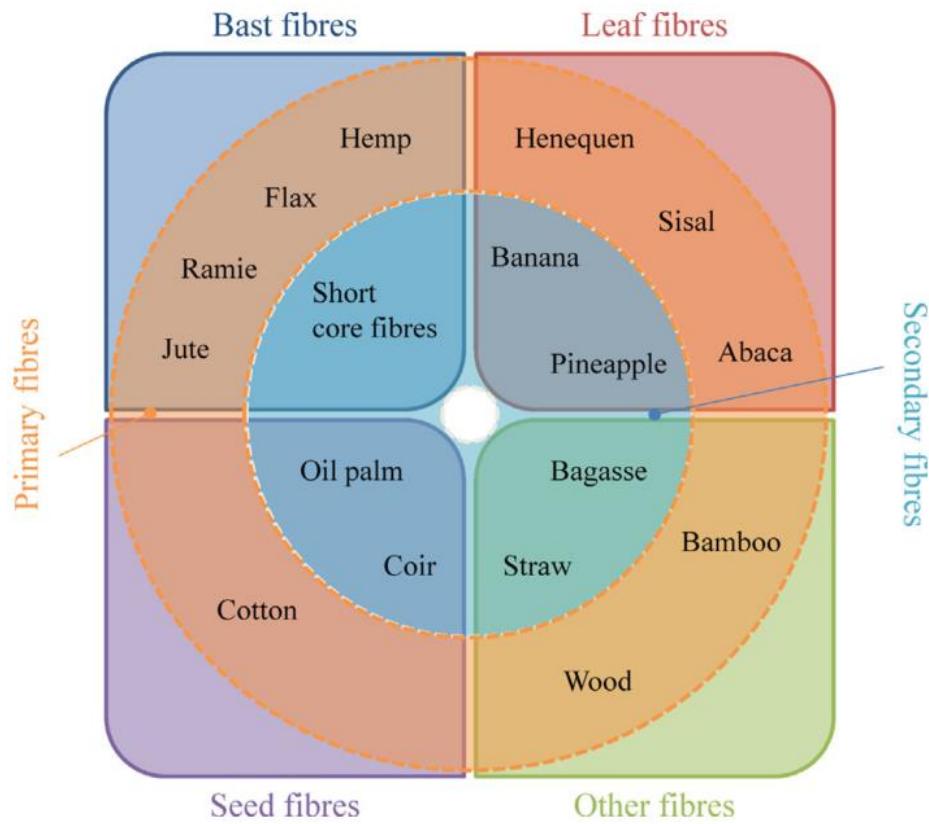


Figure I-XIV Schematic classification of non-lignous vegetal fibres based on the part of the plant they are extracted from (leaf, seed, bast and others), or their application upon extraction (primary or secondary). [85]

Natural fibres present several advantages compared to synthetic fibres such as low density, large availability, biodegradability, low abrasivity, and specific mechanical properties comparable to those of glass fibres. In Europe, flax and hemp fibres are the most used in reinforcing polymer composites due to their interesting specific mechanical properties and large availability, being produced in France, Belgium and the Netherlands [15].

The next part focuses more specifically on characterizing the flax fibres by comparing their physical and mechanical properties to those of glass fibres and other bast fibres (such as hemp, jute and ramie).

I-2.3.1 Flax fibres

Flax is one of the most widely used natural fibre in the world; they have been produced in America, Europe and Asia. The flax plant presents a short growing cycle, with only 100 days between sowing in March and harvesting in July in Western Europe [86] depending on the variety (there are 180 species of flax plants [87]). Canada, France, Belgium and Netherlands are the leading producers with nearly 31,000,000 tonnes of annual global production [88]. The use of flax fibres in the textile industry is well known but their use as reinforcement in polymer composites has been an important area of study in the last decades. Most of the works have been devoted to clarify the influence of flax fibre composition and processing on their mechanical properties [89]. A description of the flax fibres composition and structure provides elements to better understand its physical and mechanical properties.

a. Presentation

Flax fibres are extracted from the stem of flax bast plants [90]. These fibres are found assembled into bundles of fibres (each single fibre is 12 – 26 µm in diameter [91]) maintained by pectin. The elementary fibres generally present a polygonal transverse shape and a non-constant longitudinal dimension (see Figure I-XV). On average, a flax fibre presents a diameter of 19 µm and a length of 33 mm, however a large dispersion is observed for its geometrical dimensions: transversal and longitudinal dimensions range from 5-76 µm and 4-77 mm respectively [92].

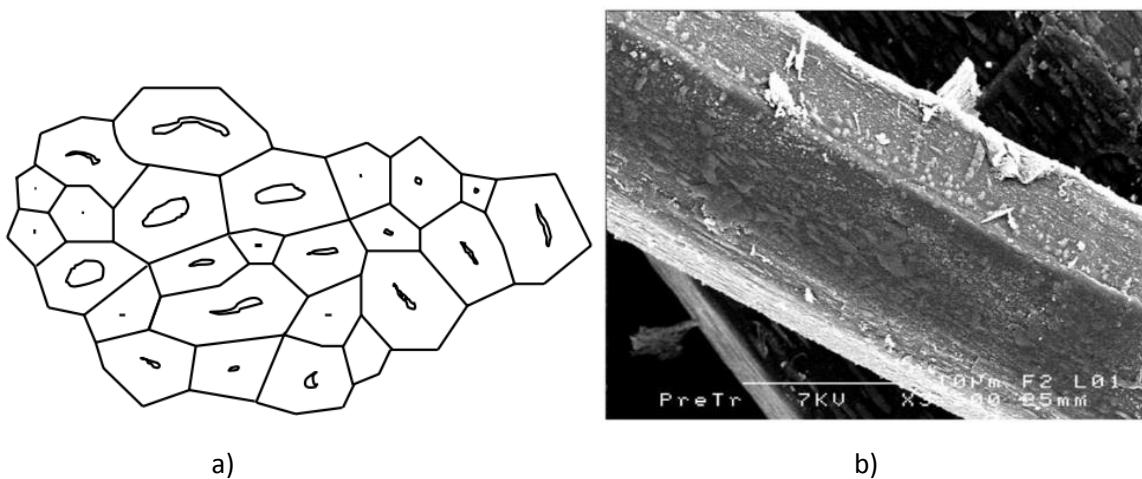


Figure I-XV Section of a bundle of fibres (a) and longitudinal view of a single flax fibre (b) [92].

b. Structure and composition

A schematic view of the multi-scale structure from macro to nano scale shows the organisation of flax fibres in the stems (see Figure I-XVI):

- **Macroscopic scale:** the flax stem extracted from the plant is composed, from the outer to the inner part, of bark, phloem, xylem, and a central void;
- **Mesoscopic scale:** various bundles containing between 10 to 40 unitary fibres are linked together mainly by pectin [86] ;
- **Microscopic scale:** is the most complex organisation due to the presence of different materials in variable proportions [92]. Each elementary fibre is made of concentric cell walls, which differ from each other in terms of thickness and the arrangement of their

components. At the center of the elementary fibre, concentric cylinders are disposed around a small open channel in the middle of the fibre, called lumen.

- **Nano-scale** : the microfibrils are constituted of cellulose chains (crystalline zones) placed in an amorphous matrix mainly made of pectin and hemicellulose [86].

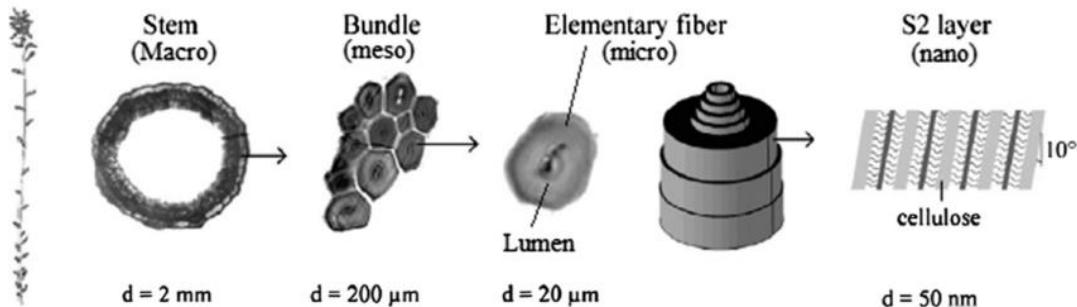


Figure I-XVI Flax structure from the macroscopic scales (flax stem) to the nano-scale (cellulosic fibrils) [86][93].

The elementary flax fibres exhibit a multi wall structure of which two principal cell walls can be distinguished: the primary and the secondary cell wall (see Figure I-XVII). The other components that compose the flax fibre structure are the lumen and the middle lamella. The Figure I-XVII presents a schematic representation of the flax fibre cell walls. From the outer to the inner part:

- The **middle lamella** is an interfacial component, that enables fibres to remain stuck together. It is composed of amorphous polysaccharides, particularly pectins, presenting a composition that changes from one natural fibre to another. The primary cell wall is often difficult to be separated from the middle lamella because of their proximity and very close biochemical composition. This primary wall is a porous and elastic layer mainly composed of pectin and random oriented cellulose microfibrils [94].

- The **secondary wall** is the thicker cell wall of the fibre with a thickness of about $10 \mu\text{m}$ (the S2 occupies about 75 to 85% of the total fibre wall thickness), composed of three layers, S1, S2 and S3, each one presenting different biochemical composition, thickness and structure. It is the secondary cell wall that ensures the global mechanical rigidity of the flax fibre. The primary and secondary walls are composed of cellulose, hemicellulose and pectin. In the secondary wall, the cellulose microfibrils are arranged substantially parallel to one another in a matrix of lignin, and surrounded by hemicellulose at the interface [95]. The microfibrils are spirally oriented around the axis of the fibre forming an angle called microfibrillar angle.

- Finally, at the center of the flax fibre there is a blank space called **lumen**, variable in dimensions along the fibre length and sometimes considered as a void.

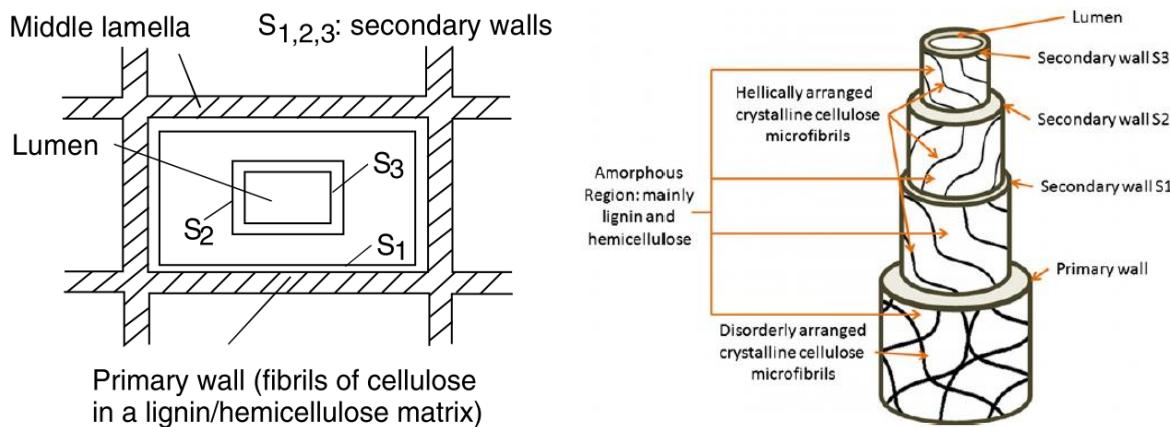


Figure I-XVII Schematic representation of the multi cell wall structure of the flax fibre cell (edited from [96] and [1]).

c. Mechanical properties

Flax fibres present specific mechanical properties comparable to those of glass fibres and generally superior to other natural fibres (see Table I-VI). One of the reasons that their properties are comparable to those of glass fibres is their low density. However, some caution must be taken when comparing these fibres because of the large variability of flax fibre mechanical properties and its non-linear behaviour.

Table I-VI Specific mechanical properties of flax fibres [78][97][98][99][86]

Fibre	Density (g/cm ³)	Diameter		Tensile strength (MPa)	Specific tensile strength (σ/ρ)	Young modulus (GPa)	Specific Young modulus (E/ρ)
		(μm)					
E – Glass	2.5	20		2300 – 2500	920 – 1000	72 – 74	28 – 29
Flax	1.5	40 - 600		345 - 1300	230 – 867	39 – 79	47
Hemp	1.5	25 - 500		454 - 1200	303 – 800	65	43
Jute	1.3 – 1.5	25 - 200		393 - 800	208 - 570	15 – 35	12 – 23
Kenaf	-	-		930	-	53	-
Ramie	1.5	-		400 - 938	266 - 625	31 – 70	21 - 46
Sisal	1.4	50 - 200		468 - 700	334 - 500	9 - 22	7 - 15

Indeed, flax fibres display a non-linear behaviour when subjected to a tensile load. This phenomenon is not observed for glass fibres but other natural fibres display the same behaviour that can be explained by two effects [100]: the microfibrils reorientation during the tensile tests and their slippage with respect to each-other. The result is an increase in fibres rigidity during testing that makes more difficult the determination of the Young modulus. The curve stress vs strain for flax fibres can be divided into three parts (see Figure I-XVIII):

- (1) A **first linear** part (strain from 0% to 0.3%) is referred to a global elastic deformation of the fibre;

(2) a **second non-linear** part (0.3–1.5%) is interpreted as an elasto-visco-plastic deformation of the fibre, especially of the thickest cell wall (S2), since the alignment of the cellulosic micro-fibrils with the tensile axis led to the re-arrangement of the amorphous parts of the wall (mainly made of pectin and hemicelluloses);

(3) the **final part** remains linear until the rupture (1.5% to rupture) [86].

This linear part before fracture corresponds to the elastic response of the aligned micro-fibrils to the applied tensile strain. A similar tensile response of a flax fibre was observed by Bourmaud and Baley for hemp fibres [101]. Again, some caution needs to be taken to the strain interval adopted in the calculation of the Young modulus.

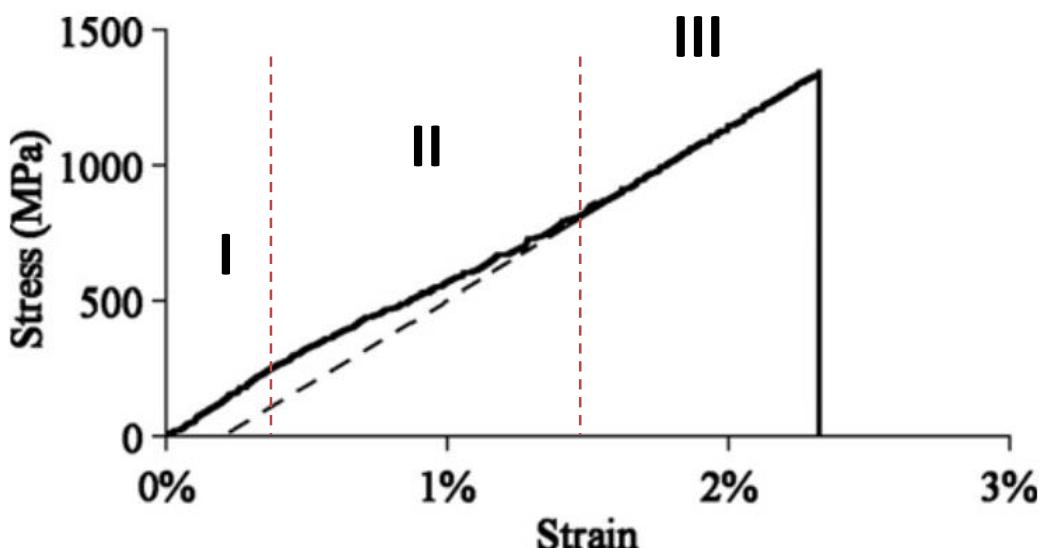


Figure I-XVIII A Typical tensile stress/strain curve of a flax fibre (adapted from [86])

The mechanical properties of natural fibres depend on the fibre density, the total cellulose content and the microfibrillar angle. Flax fibres show one of the best mechanical properties between other natural fibres because of their low microfibrillar angle and high cellulose content (see Table I-VII). The large variation in the mechanical properties of flax fibres clearly shows that the natural variability, but also technical processing, are important factors to take into account when using fibres for technical application. Indeed some of the natural variability of flax fibres comes from the growing conditions, their location in the plant stem and from the fibre length [86]. Another reason for natural variability is fibrenodes, which are regions in the fibre cell wall where the cellulose microfibril orientation differs substantially from the surrounding orientation of cellulose [102]. These fibrenodes are inherent in the fibre plant body, but they can also be induced during fibre processing, and can act as initiation points for fibre fracture [103].

Table I-VII Mechanical properties, microfibrillar angle and cellulose content of flax fibres compared to other natural fibres. [97]

Natural fibre	Microfibrillar angle (°)	Cellulose content (%)	Young modulus (GPa)	Tensile strength (MPa)	Deformation at break (%)
Flax	5 - 10	70	70	700	3
Hemp	2 - 6	70	65	800	3
Ramie	7 - 10	72	65	800	3
Jute	7 - 10	65	30	500	1.8
Sisal	10 - 25	66	12	600	3

Shah [85] presented some Ashby-type materials selection charts aiming to compare natural fibres mechanical properties to those of glass fibres (see Figure I-XIX). In terms of absolute and specific properties, flax fibres exhibit high strength and stiffness compared to other natural fibres. It is interesting to note that while E-glass is not displayed on the chart for absolute properties (Figure I-XIXa), flax fibres appear to be more comparable to E-glass in terms of specific properties (Figure I-XIXb) due to the higher glass fibre density of around 2.5 compared to around 1.5 for flax fibres. Another interesting point is that flax fibres present actually a specific tensile stiffness comparable to those of glass fibres, but the specific tensile strength is still lower for all natural fibres compared to glass ones.

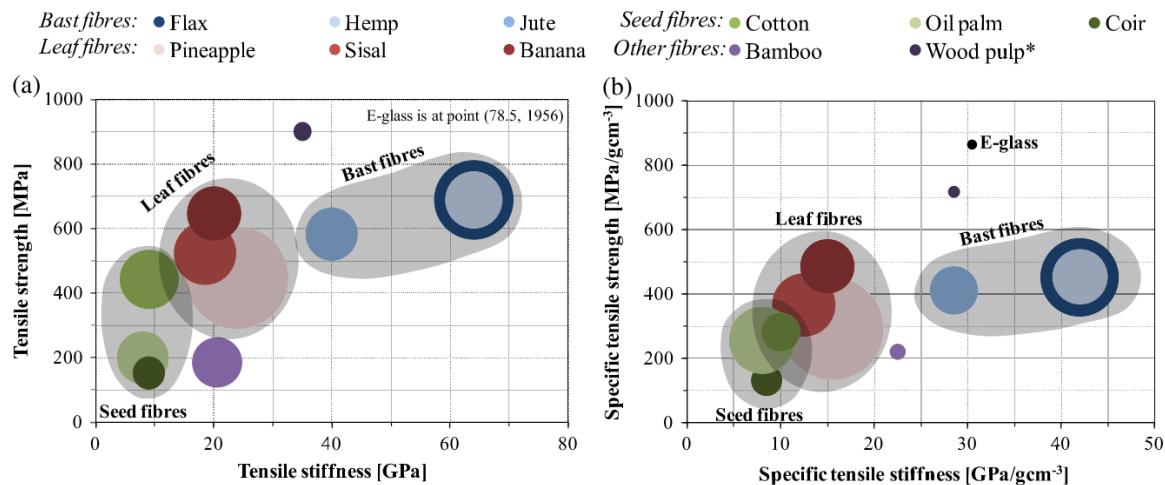


Figure I-XIX Charts comparing absolute tensile properties (a) and specific tensile properties (b) for various categories of natural fibres compared to glass fibres [85].

I-3. The phenomenon of ageing

I-3.1. Generalities

The response of materials to external conditions is measured by a modification of its performance over (long or short) periods. These external solicitations include environmental factors (temperature, liquids exposure, UV radiation, etc.), mechanical stresses and the combination of several causes. The latter is called coupling effect and can associate for example, physico-chemical to mechanical sources of ageing [33].

Several type of ageing can be distinguished depending on observable mechanisms or sources of degradation. The so-called physical ageing only modifies the composition or the spatial configuration of the material while the chemical ageing leads to a modification of the chemical structure.

The consequences of ageing can be classified in two categories:

- The **reversible ageing** corresponds to a time dependent behaviour that is observed only while the source of ageing is acting. The suppression of the ageing source leads to progressive return to the initial material properties.
- The **irreversible ageing** concerns the permanent modification in the material properties.

In this study, the phenomenon of ageing will be classified into three categories according to the involved mechanisms: physical, chemical and mechanical ageing. The effect of the coupled ageing on biocomposites behaviour will be addressed in the section I-4.5 (page 61).

I-3.2. Physical ageing

I-3.2.1 Water sorption and diffusion

Polymers are in general permeable to water diffusion. The water molecules spread into these materials occupying the space between the macromolecules and leading to a weight gain [97]. The kinetics of water sorption depends on the nature of polymer, the characteristics of water (pH, de-ionised or salt water) and other thermodynamic parameters. The mass gain continues along the exposure to water until samples reaches a saturation plateau. The latter is associated to the total amount of the hydrophilic sites (zones in polymer sensitive to accommodate water molecules) available in the polymer chains [48]. The equilibrium at saturation is observed only if no damage was introduced during ageing.

The diffusion behaviour of polymers is often based on Fick's model. Weitsman [42] represented examples of Fickian and non-Fickian behaviour for polymers exposed to damages during ageing (see Figure I-XX):

- The curve **LF** is related to the Fickian absorption behaviour showing an equilibrium state at the saturation plateau.
- Cases **A** and **B** are related to polymer materials presenting a diffusion behaviour without a saturation plateau. The curve **A** is related to pseudo-Fickian behaviour and the curve **B** shows more specifically the diffusion behaviour in two steps;
- Cases **C** and **D** show a typical behaviour for certain polymers. The curve **C** presents a fast increase in water uptake accompanied by a premature damage, more specifically a mechanical

damage. The curve **D** presents an inverse trend assigned by a chemical damage. In most cases macromolecular chains suffer hydrolysis attack by water followed by a release of the lixiviated polymer ;

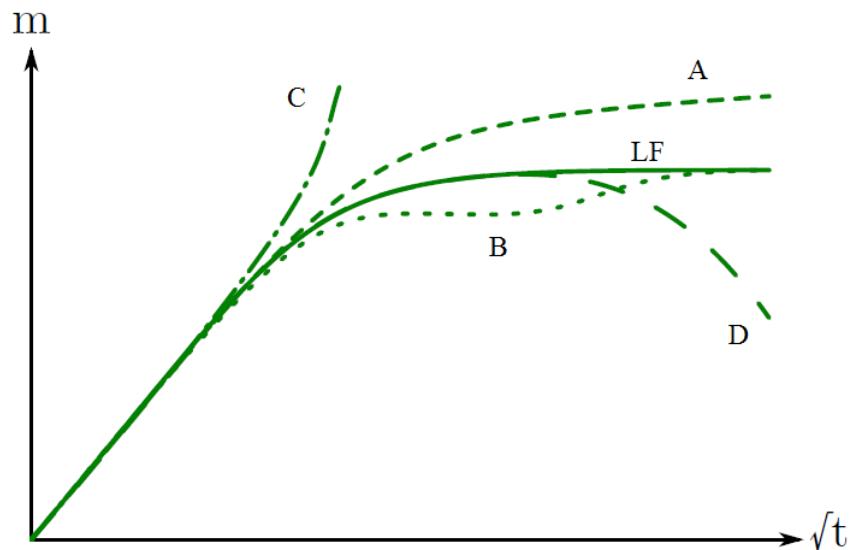


Figure I-XX Schematic representation of four categories for non-Fickian absorption behaviour [42].

In a polymer composite, the transport of water can be facilitated in three distinct paths, which are:

- Inside the matrix;
- In the imperfections within the matrix (microspace, pores or cracks);
- Through the capillarity along the fibre/matrix interface [1].

Moisture diffusion into a polymer depends on its molecular and microstructural aspects which include polarity, crosslinking state and the presence of residual hardeners or other water attractive species [104]. The water absorbed in polymers is generally found in two states: free (or mobile) water and bonded water. The water molecules, that are relatively free to travel through the macro and micro voids and holes contained in the free volume of polymers, are known as free water molecules. The water molecules attached to the polar groups of the polymers are identified as bound water.

I-3.2.2 Plasticising effect

The plasticising effect is observed when water molecules penetrate in polymer composite materials. Its effect on the composite behaviour operates differently in the polymer matrix and natural fibres.

The absorption of water by the polymer resin leads to a decrease in its glass transition temperature [33]. The reduction in the glass transition temperature of the “wet state” polymer (T_g) is characterised by the fact that the glass transition of water (T_{gw}) is lower than that of the “dry state” polymers (T_{gp}):

$$T_{gw} \leq T_g \leq T_{gp}$$

Equation I-IX

Several physical approaches aim to explain this phenomenon and predict the relationship between structure and properties along the time. The free volume theory is the most commonly used and is based principally on two hypotheses:

- At the temperature $T > T_g$ the free volume fraction of a mixture is the sum of the free volume of the two components;
- The free volume at $T=T_g$ is a universal constant (generally equal to 0.025).

These two hypotheses lead to a calculation of the T_g which can be simplified by using the rule of Simha-Boyer [105] to obtain :

$$\frac{1}{T_g} = \frac{1}{T_{gp}} + A\nu \quad \text{Equation I-X}$$

with

$$A = \frac{1}{T_{gw}} - \frac{1}{T_{gp}} \quad \text{Equation I-XI}$$

where A is plasticising coefficient and
 ν is the volume fraction of water in the mixture polymer + water.

This relation provides a basis for the understanding of the structure-properties relationship:

- The plasticising effect increases with the concentration of water in the polymer;
- The plasticising effect is more important (at constant concentration) for polymer with high T_g (T_{gp}).

The glass transition temperature of water is generally around -153 °C [33].

One of the most common consequences of the plasticising effect (which justifies the term used plasticisation) is the decrease of the stress at the limit of elasticity commonly referred as yield stress.

I-3.2.3 Swelling

Upon absorption, the water induces expansional strains into polymer and polymer composite that are similar to a thermal expansion phenomenon. Water molecules diffuse between the macromolecular chains of the polymer and fill the free volume resulting in an increase in the distance between the macromolecules. The widening distance between the polymer chains causes swelling of the polymers or the composites (see Figure I-XXI).

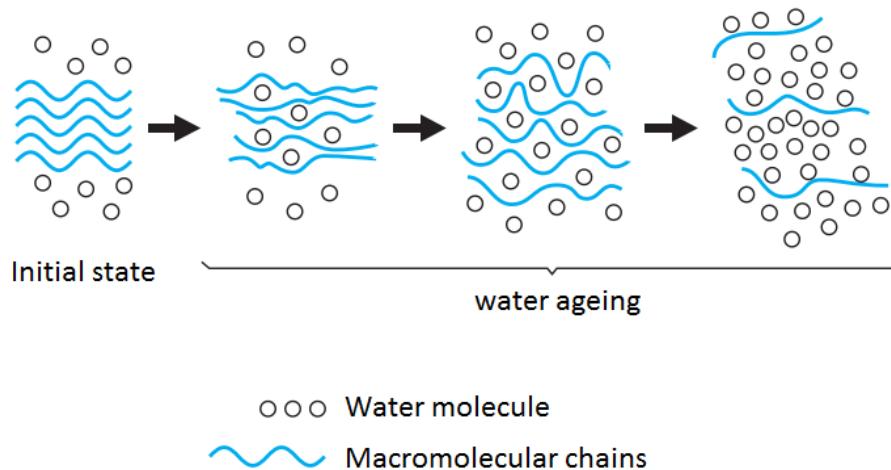


Figure I-XXI Schematic representation of the water penetration in the polymer chains (adapted from [33]).

The swelling behaviour of polymers can be distinguished by two cases depending on the polymer state:

-If glassy polymers maintain their initial state during water absorption, the total volume variation is the sum of the polymer volume, the water volume and the variation in volume introduced by the interaction between polymer and water (negative or positive). The difficulty to predict the swelling behaviour is that glassy polymers are in a thermodynamic disequilibrium and the absorption of water deviates further from equilibrium. In any case, it is the water-polymer interaction (at molecular scale) that governs the swelling behaviour.

- If glassy polymer changes state and become rubbery, the swelling behaviour is governed by the stretching of polymer chains. Two concurrent forces act: an expansion force and a restoring force that tend to bring the polymers chains to a “static ball configuration”. Equilibrium is reached when the two forces are balanced. In the case of a crosslinked polymer, the swelling behaviour depends on the chain length between nodes, decreasing with the polymer crosslinking degree.

The mechanism of swelling can also be approached by the filling of the free volume with the absorbed water. The water molecules spread along the material structure and fill the interstices in the polymer network (as a function of their size). For this reason, the beginning of the water diffusion involves a low swelling as the free volume filling behaviour corresponds to a water uptake without volume variation (see Figure I-XXII). Other phenomena like plasticisation can further increase the distance between the polymer chains leading to complementary swelling.

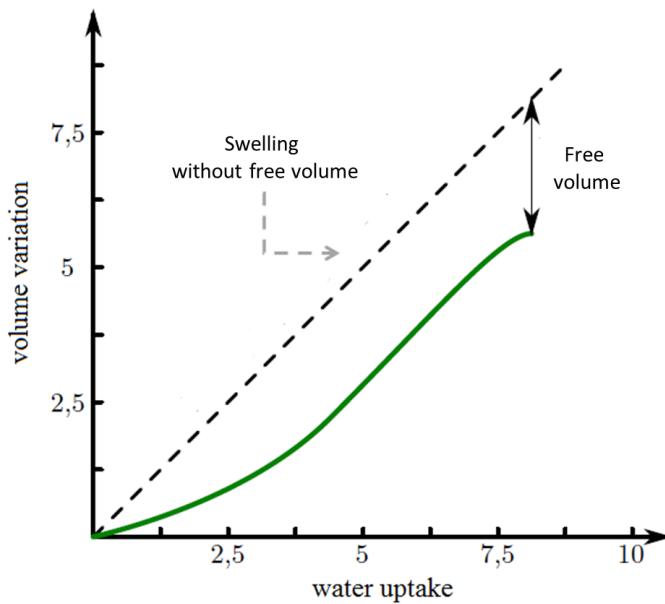


Figure I-XXII An example of the swelling kinetics : first the water fills the free volume and then the swelling rate meets that of the water absorbed volume(adapted from [106]).

As the real swelling is verified to be lower than the theoretical swelling, the development of numerical models implies the use of empirical rules for modelling. An analogy with the thermal expansion is frequently used [107] [108] for the modelling of the swelling behaviour (finite elements are employed in 2D and 3D models). Some variables and coefficients are changed for that: the variation of the thermal potential ΔT and the coefficient of thermal expansion α are substituted by the variation of the water concentration (at a local scale) Δc and the coefficient of hydroscopic dilatation η respectively. The local deformations for polymer and composites are determined as the following equations:

Thermal deformation:

$$\varepsilon_T = \alpha \cdot \Delta T \quad \text{Equation I-XII}$$

Hydroscopic deformation:

$$\varepsilon_H = \eta \cdot \Delta c \quad \text{Equation I-XIII}$$

Here the hypothesis is based on the proportionality between the deformation and the variation of concentration into the polymer or composite.

I-3.3. Chemical ageing

I-3.3.1 Thermolysis

The anaerobic thermal ageing of materials, also known as thermal decomposition or thermolysis, is a chemical decomposition frequently observed in polymers. It consists in a static break of the polymers covalent bonds when exposed to temperature. The principle of the thermolysis is related to

the intrinsic stability of materials when exposed to temperature, which depends mainly on three parameters:

- The **interatomic interactions in polymers**: it indicates the thermal stability state of the macromolecular chains. The evaluation of the thermal stability is deducted from the energy of dissociation;
- The **structural irregularities**: such as the end-of-chain, the peroxydes, the nearby entanglement, which are the sites more sensitive to the thermal degradation;
- **The process of degradation in a chain reaction**: the thermolysed polymer chains can become reactive and degrade the polymer by creating a chain reaction.

Its mechanism of action involves the random breaking of the covalent bonds starting from the weaker energy bond in the polymer and spreading in a statistical manner along the other bonds. The number of broken bonds η_t in units of mole per gram at the time t quantify this process [109]:

$$n_t = \frac{1}{\overline{M}_{n_t}} - \frac{1}{\overline{M}_{n_0}} \quad \text{Equation I-XIV}$$

where $\frac{1}{\overline{M}_{n_t}}$ and $\frac{1}{\overline{M}_{n_0}}$ are the number of chains per gram at the time t and before ageing respectively.

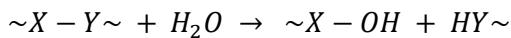
\overline{M}_{n_t} and \overline{M}_{n_0} are the average molecular masses ($\text{g} \cdot \text{mol}^{-1}$)

The pyrolysis study of a classical unsaturated polyester resin show that depolymerisations take place between 200°C and 400°C [110] and styrene monomers are formed during the reaction. This thermically activated degradation mechanism can be noted depending on the polymers nature. A depolymerisation phenomenon is observed when the weaker energy bond stands within the polymer chain. However, depolymerisation generally occurs when a polymer is exposed to temperatures much higher than the polymer glass transition temperature. For this reason, the depolymerisation process remains negligible compared to thermolysis with respect to the long-term behaviour of polymers and polymer composites.

I-3.3.2 Hydrolysis

The water diffusion in polymer materials can induce physical phenomena but also chemical interactions with the polymer chains. The hydrolysis is the main damage mechanism observed in polymers when exposed to humidity or immersed in water. Its principle is based on a chemical reaction between the polymer chains and the water molecules, generally a chain cleavage mechanism.

This mechanism induces the chain cleavage in the presence of water leading to the formation of two broken chains: an hydrogen ion linked to one extremity and a hydroxide ion to the other extremity, as schematised below:



The esters, amide and epoxyde groups are the most likely to be hydrolysed in the presence of water [111]. The hydrolysis is generally a slow process but the exposure to high temperatures nearly always lead to an increase in the reaction kinetics, mainly when polymers are subjected to temperatures close to their processing temperature.

The effect of hydrolysis on polymers degradation can be measured by a decrease in the molecular mass (the same mechanism is observed for the thermolysis) [97], a decrease of the glass transition temperature [112], but also the irreversible loss in mechanical properties (by classical tensile or flexural tests) and the degradation of the ester functions (analysed by FTIR technique) [113].

I-3.3.3 Post-crosslinking

The polymer crosslinking rate of polymers is the density of bonds that links one polymer chain to another. When polymer chains are linked together by cross-links, they lose some of their ability to move as individual polymer chains, which leads to changes in polymer properties, such as the elastic modulus and the ultimate properties (strain and stress) but also the glass transition temperature and damping. The mechanism for unsaturated polyester resins is the copolymerisation of the monomer (styrene) with the double-bonds (unsaturated) of the polyester. A tridimensional structure is created during the curing step, activated by the catalytic system. This process is represented on Figure I-XXIII:

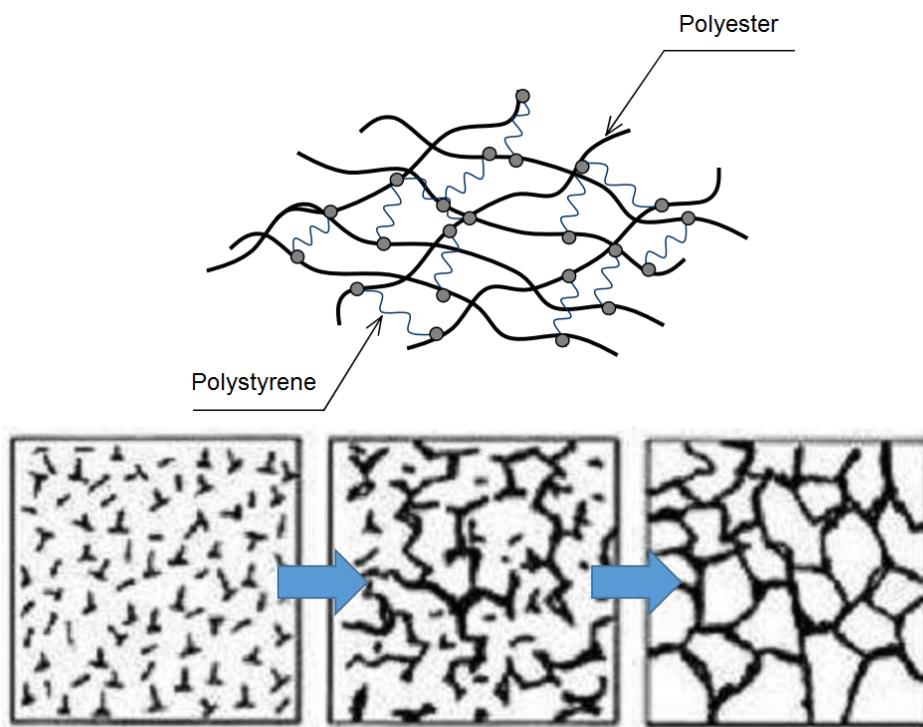


Figure I-XXIII The principle of copolymerisation and post-crosslinking of polyester resins (adapted from [9])

The crosslinking rate influences the ageing of polymer materials. Thermoset polymers present an incomplete crosslinking rate after curing, which can be optimised by a post-crosslinking treatment. However a 100% crosslinking rate is never achieved [114]. Accelerated ageing tests at high temperatures tend to increase the post-crosslinking kinetics. The evolution of the crosslinking rate during ageing results in an increase in glass transition temperature and storage modulus.

I-3.3.4 Stress cracking

Mechanical loading can lead to a premature failure of polymers or polymeric composites when exposed to environmental ageing sources such as water and other solvents. It is a common cause of

failure of polymers, and despite considerable research into this area some phenomena are not yet completely understood. The main reason for this is the complexity of the phenomenon, with many aspects such as chemical compatibility, the rate of liquid diffusion, viscoelastic behaviour, craze formation and craze growth that take place simultaneously [115].

In the absence of a high level of solvent diffusion, the craze initiation has been found to occur when the inelastic strain (the component of strain due to main chain motion) reaches a critical value. However, other phenomena take place when important solvent diffusion occurs. The magnitude of these phenomena depends on the degree of diffusion and the amount to which the solvent can plasticise the polymer.

The effect of solvent diffusion in under-stress polymers was found to introduce compressive stresses that can hinder the formation of crazes and the growing of flaws as effect of the plasticisation. However the main action that promotes crazing under stress is the localized diffusion along voided zones and the void formation in plasticised zones that leads to an earlier crazing formation and a substantial reduction in strength [116].

I-3.4. Mechanical ageing

Composite materials are frequently subjected to mechanical stresses during their life-time, and these stresses are generally the main parameter take into account for composites structural part design. In real service conditions, these materials are exposed to impact, creep and fatigue loadings that can lead to damage and failure. The principle and the mechanism of creep are addressed in this part, which is the mechanical source of damage that will be applied to composites during mechanical hydro-thermal coupled tests.

I-3.4.1 Creep behaviour

Creep, sometimes called static fatigue, represents the strain behaviour of materials exposed to constant stress at a constant temperature. It corresponds to a viscoelastic response of the material where the strain varies during the time (see Figure I-XXIV). Analysing more specifically the case of the creep behaviour of composite materials, the material behaviour depends of some important parameters, such as the fibre content, the dimensional aspects, the fibres orientation and distribution, and the fibre-matrix interface [117].

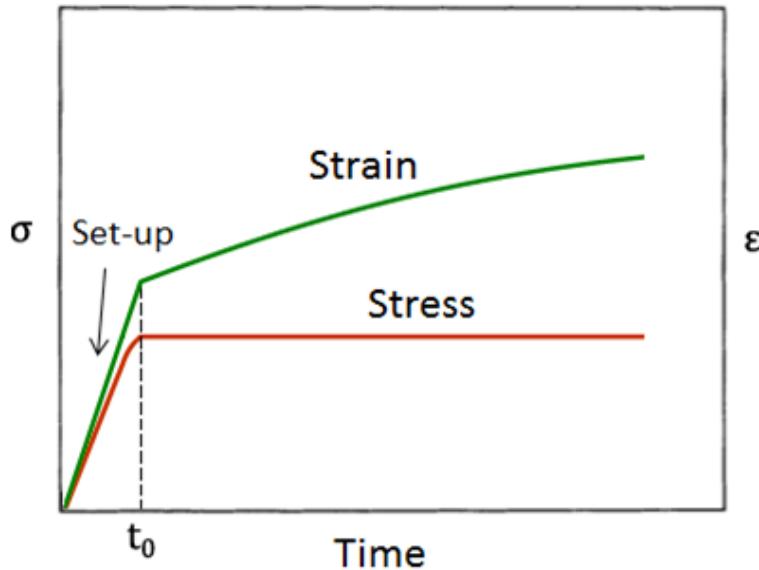


Figure I-XXIV Creep configuration showing the strain behaviour for materials loaded by continuous stress at a constant temperature (adapted from [117]).

Materials exposed to creep loadings present a permanent deformation (related to an irreversible flow) under the influence of mechanical stress. It can occur at levels of stress lower than the yield stress of the material for long periods of exposure. Creep is a time/temperature dependent behaviour that can be described by Arrhenius rules [118].

The stages of creep are presented in strain vs time or strain rate vs time graphs. Three states are frequently observed (see Figure I-XXV):

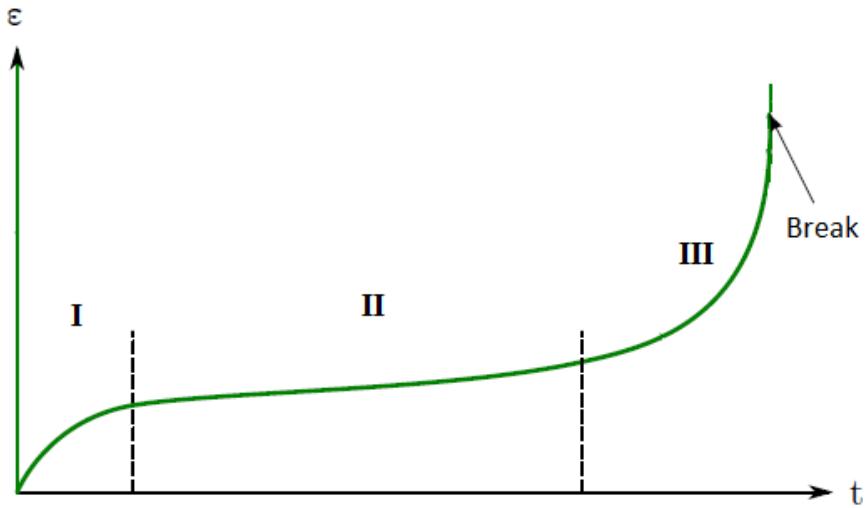


Figure I-XXV The creep behaviour at different stages (adapted from [117]).

I - Primary creep: The strain rate is relatively high but decreases with the increasing creep resistance of the material (or work hardening);

II - Secondary creep: This is the most understood stage where the strain slowly increases but the strain rate remains constant;

III - Tertiary creep: The strain and the strain rate exponentially increase and a necking phenomenon can eventually be observed. Fracture generally occurs at the tertiary state.

In general the creep rate increases with the increasing temperature and applied stress, becoming more severe when subjected to heat for long periods. Materials exposed to low temperatures present one-stage creep behaviour, also called logarithmic creep, in which only the primary stage (or transient stage) is observed.

The creep behaviour in thermoset composite materials becomes significative when the testing temperature is close to the polymer glass transition temperature [119]. This phenomenon can be accelerated when composite materials are exposed to humid environments. The material absorbs water, which act as a plasticiser and leads to a decrease in polymer's T_g , leading to an increase in the creep strain during ageing. Another phenomenon is observed in thermoplastic composites that can begin to creep at room temperature by a stress induced stretching[120].

Additionally, the molecular weight of the polymer of interest is known to affect its creep behaviour. The effect of increasing molecular weight tends to promote secondary bonding between polymer chains and thus make the polymer more creep resistant. Similarly, aromatic polymers are even more creep resistant due to the increased stiffness from the sterically hindered rings. Both molecular weight and aromatic rings add to polymers' thermal stability, increasing the creep resistance of a polymer [121].

I-4. Biocomposites in water

This part describes the phenomena and mechanisms of degradation observed for biocomposites when exposed to water ageing. Some general aspects were introduced in the last part and are discussed in details here for each type of degradation that biocomposites are subjected to during ageing. The impact of water, thermal exposure and mechanical loading and their coupled impact on biocomposites behaviour are presented in the next sections.

I-4.1. Generalities

Composite materials are exposed to environmental conditions (water, temperature, UV radiation, humid and saline atmosphere, biological environment) and/or to mechanical solicitations (creep, fatigue, accumulation of damage) during their lifetime [25]. The causes of ageing act simultaneously, or in synergy, on each component of composite materials: matrix, fibres and interfaces are affected individually or in a combined configuration [113]. Considering these ageing mechanisms is particularly important when studying the biocomposites evolving behaviour during ageing. Indeed, natural fibre reinforced composites tend to absorb much more water than glass fibre reinforced composites, which can lead to a critical loss in mechanical properties and dimensional instability.

Regarding the natural fibre composition, it is reported that the hemicellulose is the main factor responsible for this decline in properties because of the moisture absorption and the thermal degradation (see Figure I-XXVI).

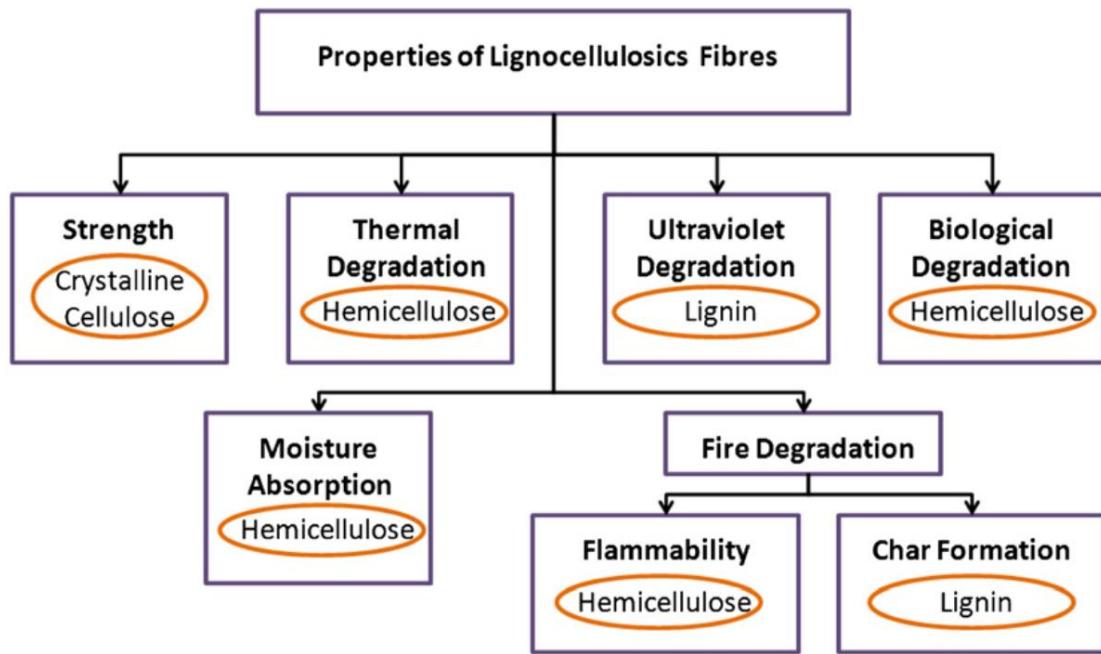


Figure I-XXVI Cell wall polymers responsible for the properties of lignocellulosic fibres [1].

Water and temperature induce different mechanisms of ageing in biocomposites:

- The **natural fibres** undergo physical ageing related to the fibres water uptake, plasticisation and swelling (a few studies relate the chemical degradation of natural fibres);
- The **polymer matrix** undergoes both chemical and physical ageing such as plasticisation and hydrolysis;
- The water may also lead to a debonding at the **interface**.

In the following part, the impact of each source of damage (water, temperature and mechanical loadings) on the evolving behaviour of NFRC (natural fibre reinforced composites) is related separately aiming to describe the phenomena that take place during ageing (such as plasticisation, hydrolysis, thermolysis, creep, etc). Other phenomena related to the ageing of biocomposites, such as the development of fungus and bacteria [122], are related in the literature but will not be addressed in this work

I-4.2. Hydric ageing

Several studies analyse the important role that natural fibres play in the physico-chemical ageing of biocomposites [123] [124] [3], [4], [69]. Due to their hydrophilic character, the use of natural fibres in applications where water is involved requires a good understanding of their behaviour in a wet environment. In general, the biomaterials present a water sorption behaviour dictated by three main mechanisms:

- The **diffusion of water molecules in the polymer matrix** is the first observed mechanism, mainly inside the micro gaps between polymer chains [125] ;

- The second mechanism is the **water transport via capillarity along the fibre-matrix interface**. This mechanism becomes active during ageing when there is a space between fibre and matrix or it can be induced by an incomplete impregnation of natural fibres coming from non-optimised processing conditions;
- The third mechanism concerns the **water diffusion in natural fibres**, which show diffusion kinetics much higher than that of the polymer matrix;
- The fourth mechanism is the **transport of water via the micro cracks** created by a differential swelling between fibres and matrix. The fibres swelling induces internal stresses and micro cracks on the brittle polymer where water molecules are trapped [126].

Some care is required in the taking these phenomena into account because no information is available in the literature for the flax fibres swelling behaviour under stress [127]. The differential swelling behaviour between fibres and matrix (that could lead to matrix cracking) is claimed by many authors without been however experimentally demonstrated.

This part presents a literature review on the hydric ageing of biocomposites when exposed to hygroscopic (humidity) or hydroscopic (water immersion) conditions and compares their evolution during time to models that have been developed to describe the moisture absorption behaviour of composite materials (mainly Fick and Langmuir models). The water uptake behaviour of biocomposites will be studied separately for the natural fibre, the polymer matrix and natural fibres composites in order to highlight the specific mechanisms related for each material. Furthermore, the effect of fibre treatment on the composites moisture sorption is also related.

I-4.2.1 Diffusion behaviour in natural fibres

The natural fibres, as detailed before in this work, are composites in themselves mainly composed by cellulose, hemicellulose, lignin, pectin, wax and moisture (in the case of flax fibres) [128]. The fibre component responsible for moisture absorption is the hemicellulose which is the plant cell wall associated with the cellulose [129]. Higher content of hemicellulose, associated to the fibres morphology related to hollow cavities, results in higher moisture sorption and biodegradation.

The hydrophilic behaviour of natural fibres and their relation with the presence of free hydroxyl group in its structure was related by many practical [130] [131] and modelling studies [132] [133]. These authors employed physical models applied to polymers to describe the diffusion behaviour of water in natural fibres, such as Fick's law [134], the Langmuir theory [36] and dual-stage Fick's law [135].

Celino et al [132] used Fick's and Langmuir's models to describe the diffusion behaviour of sisal, jute, hemp and flax fibres immersed in water at room temperature and exposed to vapor humidity at 80% rh and 23°C. Despite their different origins, the four natural fibres showed a similar diffusion behaviour. The Langmuir model was found to describe very well the diffusion inside fibres immersed in water while the Fick's law better described the diffusion behaviour of fibres exposed to relative humidity ageing (see Figure I-XXVII). Gouanv   et al [133] found that the water diffusion in flax fibres exposed to hygrothermal ageing at 23°C may be explained on the basis of a combination of Langmuir and Henry sorption models at low levels of relative humidity. The diffusivity increased with the relative humidity whereas a decrease in the diffusivity at high levels of relative humidity was attributed to the immobilisation of sorbed water by aggregation.

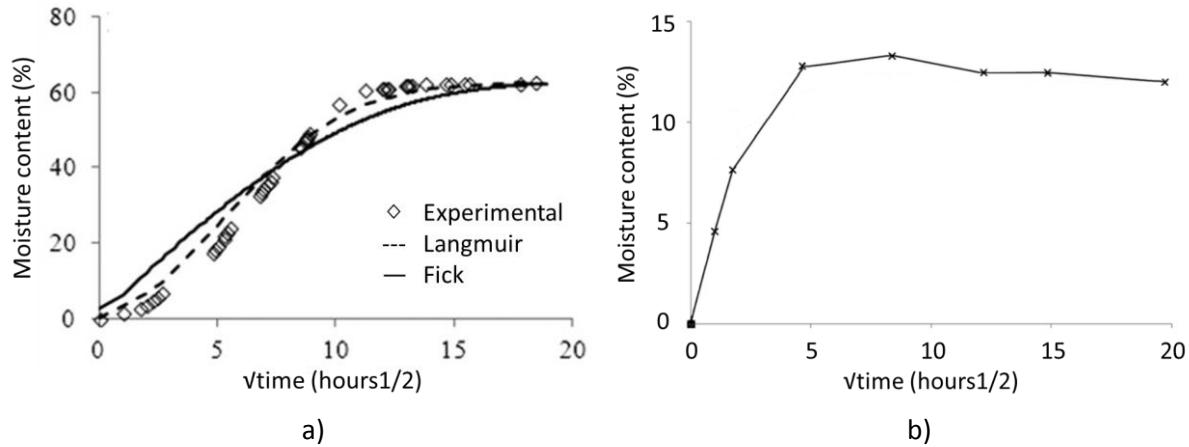


Figure I-XXVII The flax fibres water diffusion behaviour (a) in immersion at room temperature (a) and (b) in hygrothermal conditions (80% rh and 23°C) (adapted from [132]).

Celino et al also showed that the widely more important mass gain displayed by natural fibres immersed in water compared to those exposed to relative humidity (62% compared to 12% for flax fibres) was explained by the specimen's geometry. The free volume in natural fibres was filled by water during the immersion tests, and by vapor when fibres were exposed to relative humidity. Because vapor could be released easily, the mass gain is less important. Furthermore, absorption and reabsorption cycles highlighted that there is no damage during ageing in both cases.

Furthermore, the diffusion behaviour of flax fibres was found to be related to the relative humidity (RH) [136]. Flax fibres exposed to hygrothermal ageing presented a water uptake that increased with the increasing RH, and a diffusion coefficient that increased linearly with the RH. However, these fibres showed the same time to saturation independently on the level of RH.

The results of several studies on the diffusion behaviour of natural fibres are presented in Table I-VIII.

Table I-VIII Diffusion properties of natural fibres.

Fibre	Model	Ageing conditions	Parameter	Reference
			D (m ² /s)	M _{sat} (%)
Flax	Fick	water at 23°C	1.2 10 ⁻¹²	[132]
	Langmuir		6.8 10 ⁻¹²	
	Fick	80% rh / 23°C	2.0 10 ⁻¹⁰	
Hemp	Fick	water at 23°C	4.0 10 ⁻¹²	[132]
	Langmuir		5.6 10 ⁻¹²	
	Fick	80% rh / 23°C	2.3 10 ⁻¹⁰	
Jute	Fick	water at 23°C	1.2 10 ⁻¹²	[132]
	Langmuir		5.9 10 ⁻¹²	
	Fick	80% rh / 23°C	4.0 10 ⁻¹⁰	
Sisal	Fick	water at 23°C	2.2 10 ⁻¹²	[132]
	Langmuir		9.1 10 ⁻¹²	
	Fick	80% rh / 23°C	1.2 10 ⁻¹⁰	
Flax	Fick	75% / 23°C	3.7 10 ⁻¹⁰	-
Flax	Fick	66% / 23°C	4.0 10 ⁻¹⁰	[137]

I-4.2.2 Polymer water uptake

Unsaturated polyester resins present good resistance to water absorption, however an incomplete polymerization, as well as the presence of a large number of ester links, can induce low resistance to hydrolysis and greater degree of swelling in solvents than the fully polymerized systems [138].

An interesting study investigated the glass transition temperature (T_g) variation of epoxy resins under hygrothermal environment exposure [139]. The investigations revealed that the change of T_g does not depend solely on the water content absorbed in epoxy resins, but also depends on the hygrothermal history of the material. Higher values of T_g were observed for longer immersion time and higher exposure temperature. It was found that the water/resin interaction characteristics (Type I and Type II bound water) have quite different influence on T_g variation.

Indeed, two types of bound water molecules were found in epoxy polymers [51]. Type I bonding correspond to a water molecule which forms a single hydrogen bond with the polymer network. This water molecule possesses lower activation energy and is easier to remove from the resin. It is the dominant form of the total absorbed water. Type II bonding is a result of a water molecule forming multiple hydrogen bonds with the resin network. This water molecule is harder to remove, its amount depends strongly on the exposure temperature and time. Higher immersion temperature and longer exposure times result in a greater amount of type II water in the polymer. The Type I bound water was found to disrupt the initial interchain Van der Waals force and hydrogen bonds resulting in increased chain segment mobility. So Type I bound water acts as a plasticiser and decreases T_g , while Type II bound water contributes, to an increase in T_g in water saturated polymer by forming a secondary crosslink network with hydrophilic groups such as hydroxyls and amines in the epoxy network.

Furthermore, the immersion in water may lead to weight and strength losses of the polyester resin since some components of the macromolecular segments present initially in the resin are leached out during water exposure. Ester links are hydrolysed during ageing resulting in the formation of carboxyl groups which have been shown to catalyse further decomposition [140]. This process of hydrolysis is accompanied by the plasticising effect of absorbed water causing a decrease in the polymer mechanical properties to a degree which is dependent on temperature. Even if they are in competition, the two processes can be identified, as the plasticisation is a reversible phenomenon which disappears after drying, while hydrolysis is irreversible.

The water uptake behaviour of unsaturated isophthalic polyester resin was reported by Appicela et al. [18] for samples immersed in water at 20°C and 90°C for more than 40 days. Polyester resins immersed in water at 20°C present a Fickian water diffusion and a saturation weight gain of around 0.7% (see Figure I-XXVIII). The exposure to water at 90°C strongly alters the shape of the sorption curves. Weight gain increases faster than curves at 20°C by absorbing water in the same manner up to 1%. A light progressive weight loss is then followed by a subsequent weight regain suggesting that physical and/or chemical degradation are altering the polyesters resin water uptake behaviour. Indeed microscopical analysis shows a large number of two dimensional disc shaped cracks in the bulk of polyester resin samples, confirming the change in the morphology of polyester resin during ageing at 90°C.

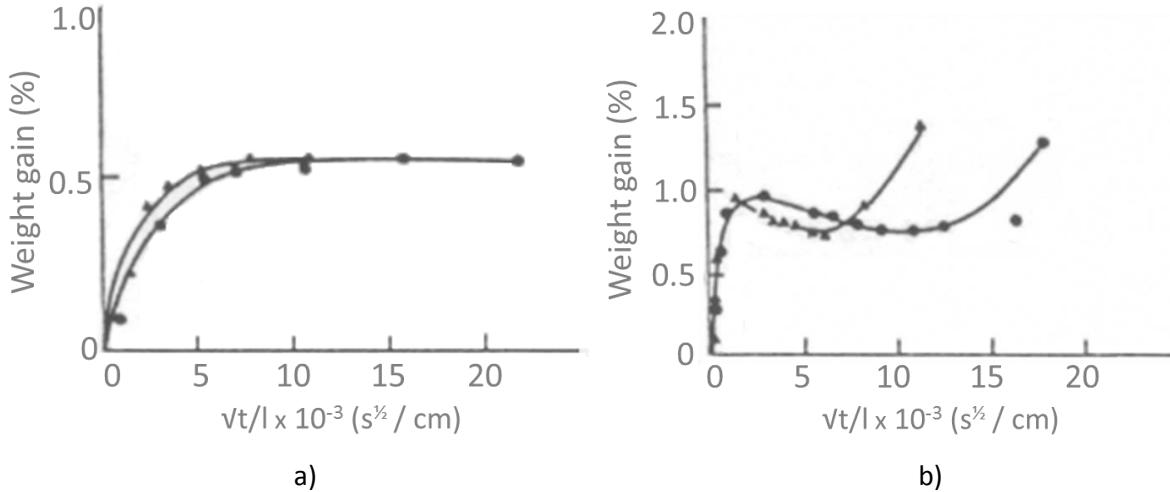


Figure I-XXVIII Weight gain for isophthalic polyester resin immersed in water at (a) 20°C and (b) 90°C [18].

Apicella et al. also verified the reversibility of the polyester resin water uptake after dessication. At 20°C the polyester resin lost 21% of the absorbed water (0.15% of water loss compared to 0.71% of water gain at saturation). At 90°C, the resin lost 36% of the absorbed water (0.73% of water loss compared to 2.03% of water gain). The authors do not explain the irreversibility of the water sorption and report that no further analysis of the water uptake curves was performed for the sorption and drying behaviour of polyester resin due to the multiplicity of the phenomena associated with the water sorption.

I-4.2.3 Composites water uptake

Polymer composites exposed to hygroscopic or hydroscopic conditions at room temperature often show a Fickian water diffusion behaviour. Fick's model for a composite material is based on three-dimensional diffusion in a homogeneous material presenting a constant thickness (see Figure I-XXIX). A bidimensional or also a unidimensional diffusion model can be employed when one dimension of the specimen geometry is much smaller compared to the two others.

At higher temperature of immersion, moisture uptake is accelerated and the time-to-saturation can be greatly shortened. It is a non-Fickian behaviour that can be attributed to the different state of water molecules existing in the composites as discussed before in this work (part I-1.3.1 – page 13).

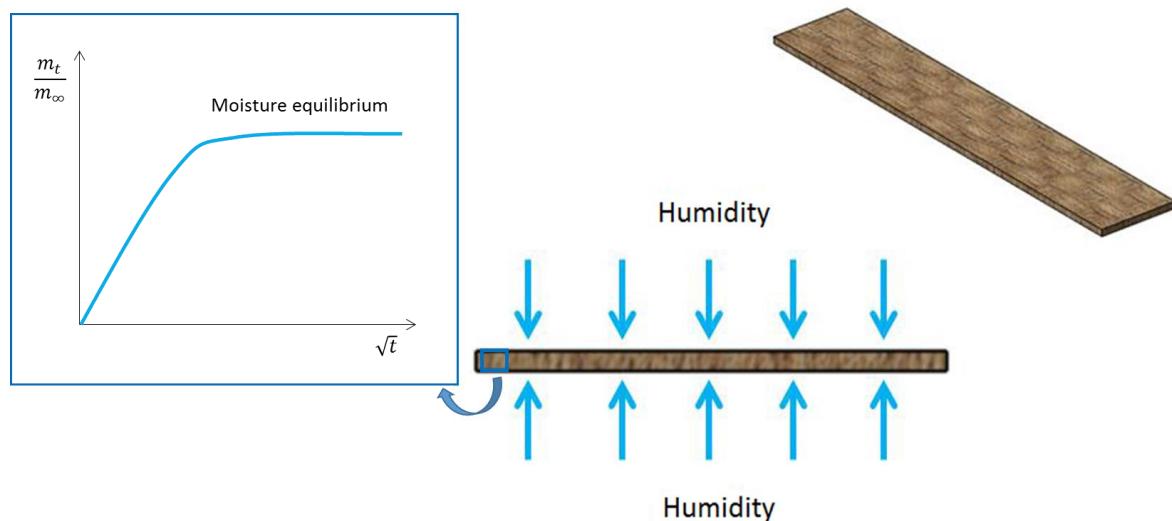


Figure I-XXIX Schematic representation of the UD diffusion of a composite sample exposed to humidity.

Assarar et al. [4] presented the water uptake behaviour of flax-fibre epoxy composites immersed into a water bath at room temperature, and compared the results to the water uptake of composites reinforced with glass fibres. The water uptake pattern of flax fibre composites appears to be Fickian, with a linear part and an equilibrium plateau (at saturation) (see Figure I-XXX). The curve was calculated by using the diffusion coefficient for values of relative water uptake lower than 60% (the absorbed water mass varies linearly according to the square root of immersion time until 0.6 approximately), and for the second half-sorption, an approximation proposed by Shen and Springer [141] was employed. The composites saturated weight gain was found to be around 13% for flax fibre composites compared to around 1% for glass fibre composites. The higher water uptake observed for flax fibre composites often lead to more degraded mechanical properties than glass fibre composites.

The correlation between water uptake and mechanical properties will be analysed in section I-4.4 (page 55).

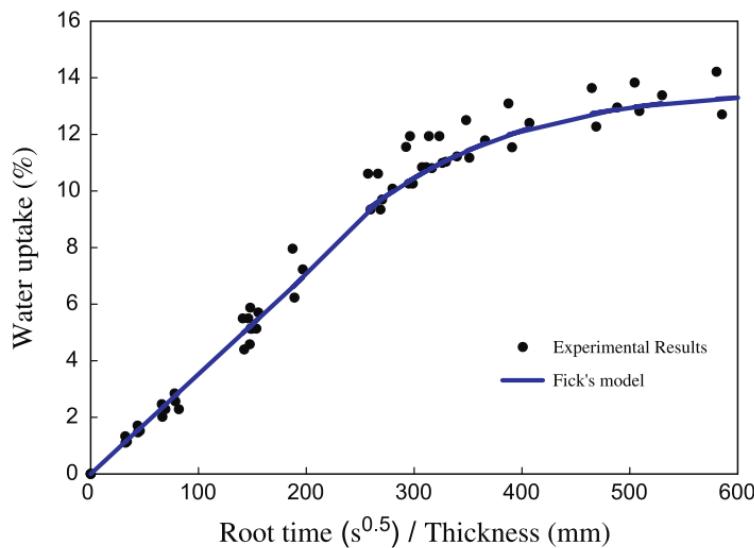


Figure I-XXX Water uptake evolution behaviour of flax fibre composites [4]

The water sorption behaviour displayed by composite materials depends upon several factors such as temperature, matrix, fibre volume fraction, orientation of reinforcement, permeability nature of fibres, area of exposed surfaces, reaction between water and matrix and surface protection [1] [5] [142].

The fibre volume fraction was related to the amount of water (or moisture) absorbed by natural fibre reinforced composites. In the literature it was reported that the water absorption amount increased in poly-lactic acid (PLA) and poly-butylene succinate (PBS) composites as bamboo fibre content increased which lowered the strength of PLA and PBS. In other work, the authors highlight the fact that the increase in bamboo fibre content caused an acceleration on the diffusivity because of the strong hydrophilicity of bamboo fibres [143]. Dhakal et al [3] presented the absorption behaviour of hemp fibre reinforced unsaturated polyester composites immersed in de-ionised water at room temperature (23°C). Composites with different hemp fibre content (15%, 21% and 26% of fibre volume fraction) were processed and their water uptake behaviour compared to a non-reinforced polyester (UPE only) and to a glass-fibre reinforced composite (UPE/CSM) (see Figure I-XXXI). The biocomposites maximum weight gain increased with the hemp fibre content, and presents higher values than glass fibre composites and non-reinforced unsaturated polyester. The curves for all specimens (except glass fibre composites that present low water absorption) present a linear trend at the beginning and then tend towards the saturation levels, following a Fickian diffusion behaviour. Moreover, the authors related that the diffusion coefficient increased greatly with the increase in fibres fraction due to the higher cellulose content in biocomposites.

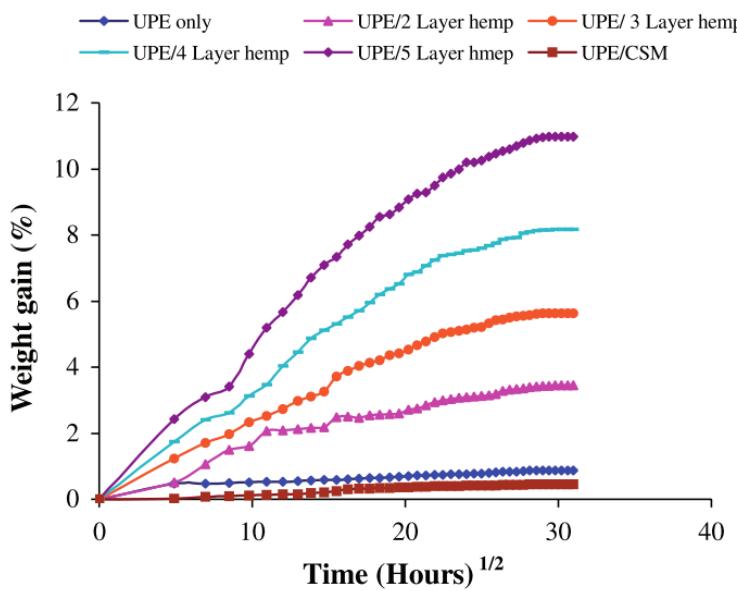


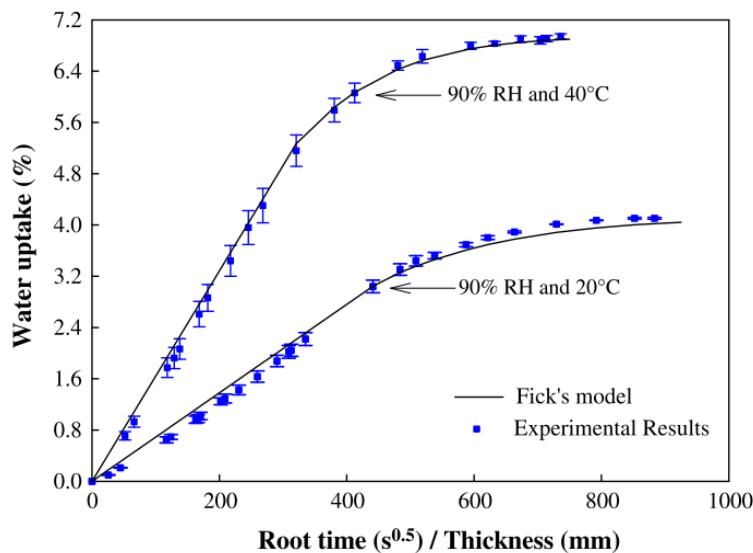
Figure I-XXXI Water absorption curves at RT for non-reinforced unsaturated polyester (UPE only), hemp fibre reinforced composites at various fibre content levels and glass fibre composites (UPE/CSM) [3].

The influence of the fibre volume content on the diffusivity and the water uptake at saturation of natural fibre composites compared to glass fibre composites is summarised in Table I-IX.

Table I-IX Influence of the fibre volume fraction on the diffusion behaviour of various composites.

Matrix	Fibre	Fibre volume content	Parameter	Ageing conditions	Reference
			D (m^2/s)	M_∞ (%)	
UP	Glass	25%	$5.2 \cdot 10^{-6}$	3.6	water at 23°C
		65%	$5.1 \cdot 10^{-7}$	3.5	
	Hemp	0%	$5.7 \cdot 10^{-3}$	0.9	
		10%	$1.5 \cdot 10^{-3}$	3.4	
		15%	$3.6 \cdot 10^{-3}$	5.6	water at 25°C
		21%	$3.8 \cdot 10^{-3}$	8.2	
		26%	$4.4 \cdot 10^{-3}$	11.0	
PP	Flax	30%	$7.5 \cdot 10^{-14}$	5.9	water at 23°C
		60%	$8.6 \cdot 10^{-13}$	14.0	

The influence of the temperature on the acceleration of composites water uptake was also reported by some authors. Dhakal et al have also investigated the influence of the temperature on the diffusion behaviour of hemp fibre composite immersed in water at room temperature and at 100°C. The saturation moisture uptake was found to increase with temperature. The composites reinforced with five layers of hemp (reference 5L hemp – 26% of fibre content) show a saturation water uptake around 2.5% higher at 100°C than at room temperature. The diffusion coefficient of composites greatly increases with the increasing temperature. A similar effect was reported by Scida et al [69] for flax-fibre reinforced epoxy composites exposed to hygrothermal ageing at 90% rh at 20°C and 40°C (see Figure I-XXXII).

*Figure I-XXXII Water diffusion behaviour of FFRC exposed to hygrothermal ageing at 90% HR / 20°C and 40°C.*

The influence of the ageing conditions on the diffusivity and the water uptake at saturation of natural fibre composites compared to glass fibre composites are summarised in Table I-X.

Table I-X Influence of the ageing conditions on the diffusion behaviour of various composites.

Matrix	Fibre	Fibre volume content	Ageing conditions water or RH	Temperat.	Parameter D (m^2/s)	M_{sat} (%)	Reference
UP	Glass	65%	100% RH	32°C	$6.0 \cdot 10^{-13}$	3.6	
				50°C	$1.8 \cdot 10^{-12}$	4	
				65°C	$3.4 \cdot 10^{-12}$	3.5	
			60% RH	30°C	$4.3 \cdot 10^{-12}$	1.25	[144]
				30°C	$6.9 \cdot 10^{-12}$	0.65	
			water	23°C	$5.1 \cdot 10^{-13}$	3.5	
				50°C	$2.1 \cdot 10^{-12}$	3.75	
				25°C	$4.4 \cdot 10^{-3}$	11.0	
				100°C	$6.7 \cdot 10^{-2}$	13.5	[3]
Epoxy	Flax	44%	90% RH	20°C	$5.5 \cdot 10^{-13}$	4.1	
				40°C	$1.1 \cdot 10^{-12}$	6.9	[69]

I-4.2.4 Influence of fibre treatment on the water uptake behaviour

Biocomposites' sensitivity to moisture, which leads to dimensional changes and loss in mechanical properties, encourages the study of the protection of natural fibres through a physico-chemical treatment. There are two main areas in the field of the treatment of natural fibres : (I) treatments aiming to promote better adhesion between natural polar fibres with non-polar polymers (the incompatibility may not be an issue when using polar matrix such as unsaturated polyester and epoxy resins) [145]; and (II) the study of treatments aiming to improve the water resistance of fibres. In this part we will focus on the treatments aiming to improve water resistance in composites reinforced by natural fibres.

Xie et al. [145] revised the application of a variety of organosilanes as coupling agents in natural fibre reinforced composites. The hydrophobation treatment of natural fibres can promote surface and/or bulking resistance to water depending on the dispersion of silane molecules on the natural fibre. A surface coating only decreases the water diffusion rate while a bulking treatment decreases the water absorption by deactivating or masking the hydroxyl sites of the natural fibre [146]. The treatment of sisal fibres with 1% of a MPS (methacryloxypropylmethoxysilane) in benzene has been reported to reduce the weight gain at saturation of fibres from 12.8% to 1.7% [147].

Sreekala and Thomas [148] investigated the effect of the fibre surface modification on the water sorption characteristics of oil palm fibres. Various fibre surface modifications such as mercerization, latex coating, gamma irradiation, vynilsilane treatment (VPS) and acetylation treatment were tried to reduce the hydrophilicity of the fibres. The fibre water uptake at saturation was reduced from 13.4% to around 8% in all cases (the untreated and treated fibres were immersed in water at 30°C). Although the reduction in water uptake was found to be similar for all treated fibres, each treatment changed the fibre structure in a different manner. Mercerization results in the leaching out of the amorphous fibre wax layer; Latex coating partially masked the pores on the fibres surface; Gamma ray irradiation partially eliminated the porous structure and caused microlevel disintegration of the fibre; Silane

treatment gave a coating to the fibre surface; Acetylation also removed the wax layer from the fibre surface.

However, some caution needs to be taken when analysing the impact of treatment on fibres and composites, because the impact of the treatment on the diffusion behaviour of the fibre may not be the same on the composite.

The water resistance behaviour is modified when treated fibres are impregnated with a polymer matrix. A co-polymerisation mechanism is proposed to explain the coupling reaction between silane-treated fibres and an unsaturated polyester resin. The methacryl groups of the silane molecule are able to react with the double bonds of the unsaturated polyester in the presence of a peroxide initiator (see Figure I-XXXIII). The treatment of oil palm fibres treated with MPS was found to afford a significant degree of protection to water uptake of unsaturated polyester composites [149].

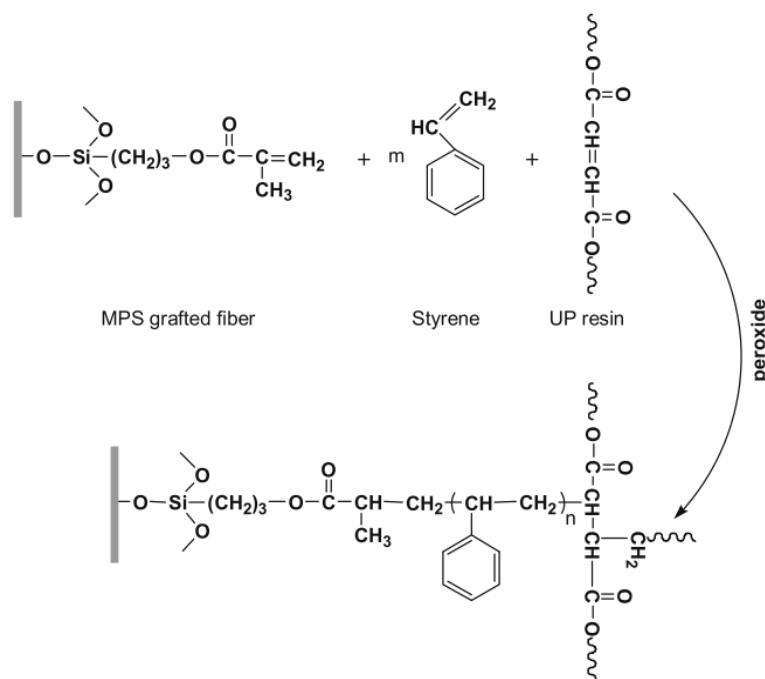


Figure I-XXXIII Reaction of a MPS-grafted fibre with an unsaturated polyester resin in the presence of a peroxide initiator

Silane (Si) and styrene (S) treatments were applied on flax fibres by Alix et al. [150] in order to increase the resistance to moisture of flax fibre unsaturated polyester composites. After 300 hours immersed in distilled water at 20°C, the water absorption of composites reinforced with 40% (wt./wt.) of untreated flax fibres was increased to around 6% while the water absorption of treated fibre composites was found in the range of 5 – 6%. Also the diffusion kinetics were reduced for styrene treated composites which was explained by a mechanism of trapping of water molecules into micro and macro voids of the bundles fibres (space between fibres) and inside the single fibres (lumen) which slows the water sorption. In this case, fibres may act as a tank able to retain water molecules and promoting a “water tank” effect. In the case of silane treated composites, the reduction in water diffusivity was found to be related to the improvement of the interface fibre/matrix quality [151], which means that the fibre surface was modified by a grafting reaction. Ideally, a compromise between

these two mechanisms might be reached: fibres could be modified in surface but also in the core in order to provide a better resistance to moisture.

I-4.3. Thermal degradation

Composite materials destined for marine applications may be exposed to thermal degradation during service. The thermal degradation corresponds to a long duration change in materials behaviour induced by the temperature. The latter represents the mechanism that controls the kinetics of degradation, representing a complex parameter to study because often coupled to other mechanisms of ageing. The analysis of the thermal degradation is even more complex to be studied for biocomposites that presents a matrix thermal behaviour completely different from natural fibres. Another level of complexity is added if natural fibres are taken as a composite material that presents different thermal behaviour for the lignin, the hemicellulose, and other components.

In this part the effects of the temperature on the biocomposite materials behaviour are studied apart for the thermoset matrix and the natural fibre. Two mechanisms were addressed :

- 1) The scission of chemical bonds of the matrix (resin thermolysis);
- 2) The thermal degradation of fibres (fibres thermolysis);

As seen before in the last section, the effect of temperature can also lead to other phenomena than degradation such as the polymer post-curing [152].

I-4.3.1 Resin thermolysis behaviour

The thermal degradation of unsaturated polyester implies a random chain cracking where relatively few chain breaks cause a large drop in molecular weight. The thermal degradation was found to start from 300°C (rare in marine sector) by statistical chain rupture in which styrene is the primary product.

Some differences can be found on the thermal behaviour of polyester resins depending on their molecular structure. These differences arise from secondary reactions of endgroups formed by ester scission [153].

I-4.3.2 Thermal degradation of natural fibres

The non-homogeneous character of the natural fibres determines its behaviour when exposed to temperature. Few studies consider this parameter when reporting the thermal degradation of natural fibres when exposed to hygrothermal ageing.

Placet [154] studied the thermal degradation of natural fibres by characterizing the viscoelastic behaviour of the wood. The viscoelastic properties of wood are activated by the temperature to a certain level beyond which the temperature leads to the wood degradation. The hemicellulose is the most sensitive component of the wood to the thermal degradation (wood is composed by three polymers: lignin, hemicellulose and cellulose). The thermolysis of the hemicellulose starts from 80-90°C and increases with the temperature. A condensation of the lignin is also reported starting from temperatures between 110°C and 120°C. The thermal degradation of the hemicellulose leads to a decrease in the materials rigidity, for temperatures between 80°C and 120°C, thwarted by the condensation of the lignin.

Azwa et al. [1] reviewed the thermal degradation of natural fibres. The authors highlight that approximately 60% of the thermal decomposition of most natural fibres occurred within a temperature range between 215 and 310°C (see Figure I-XXXIV). It is a multi stage degradation behaviour that begins at around 100°C by the evaporation of moisture in the fibres:

- **50 – 100°C** : Evaporation of moisture in the fibres;
- **200 – 300°C** : Decomposition of hemicelluloses;
- **300 – 400°C** : Thermal degradation of cellulose;
- **400 – 500°C** : Lignin and cellulose degradation.

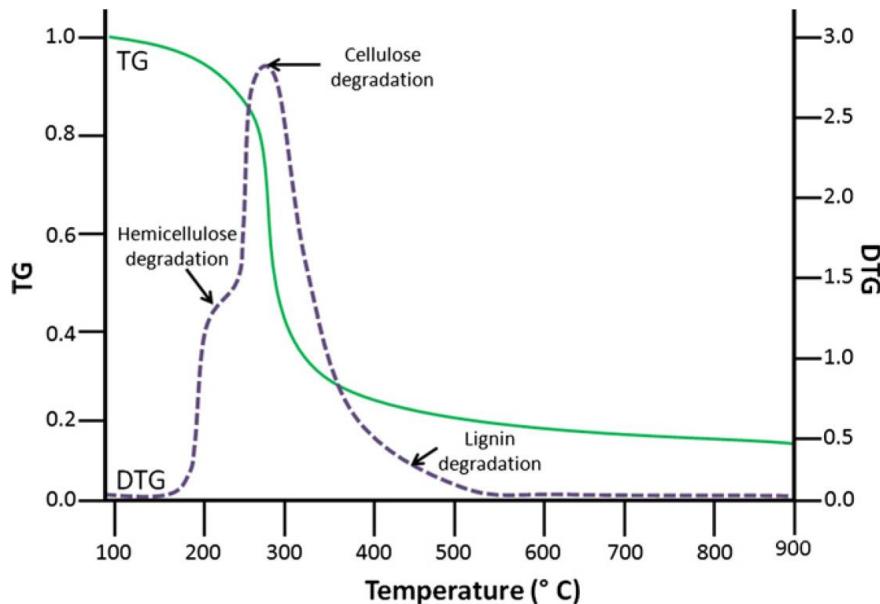


Figure I-XXXIV Thermogravimetric analysis (TGA) of the decomposition process of natural fibres [1].

Other components of natural fibres are affected by the thermal degradation but they will not be addressed in this work.

I-4.4. Mechanical behaviour

The sorption of water in polymeric composites and their effects on composites performance are complex issues that require interdisciplinary efforts more than individual undertaking [37].

The decrease in mechanical properties of biocomposites with moisture content may be caused by the formation of hydrogen bonds between the water molecules and cellulose fibres. The hydrophilic character of natural fibres is due to a high presence of hydroxyl groups (-OH) in the fibre structure forming a large network of hydrogen bonds between the macromolecules of cellulose and the polymer. When water spread into the fibres structure by forming hydrogen bonds with cellulose, this can lead to dimensional variation of composites and subsequent degradation of the interfacial bonding between fibre and matrix [155].

This part will address two approaches for the study of the evolving mechanical behaviour of biocomposites during ageing. A first approach concerns the evolving behaviour of natural fibres when exposed to moisture absorption, followed by the study of the whole composite.

I-4.4.1 Influence of water on the fibre mechanical properties

The evolution of natural fibre's mechanical properties submitted to various environments is related by many authors [131] [156]. However the study of unitary fibres behaviour when impregnated into a polymer matrix requires specific characterisation and/or the use of estimation models (such as rule-of-mixtures or Halpin-Tsai). Natural fibres are permeable to polymer impregnation (mainly to polar resins) during processing, which is one of the mechanisms involved in the processing of biocomposites. That is why authors are searching to develop new methods to investigate the in-situ properties evolution of natural fibres when exposed to environmental ageing.

Le Duigou et al. [157] observed a drop of about 55% in flax fibre stiffness after water ageing at 23°C during 8 weeks. The tests were realised on dried samples which means that only irreversible degradation was measured and the plastification effect is not apparent.

The mechanical properties of natural fibres in biocomposites can also be estimated by using Halpin-Tsai model [127]. Here, the Young modulus of the PLA matrix, the anisotropy ratio of flax fibres, and the fibre/matrix adherence are assumed to be constant during the immersion time. In this way, the Halpin Tsai model estimates that the evolution of the composites modulus is due to the evolution of the flax fibre modulus. The initial longitudinal modulus of flax fibres before ageing was estimated at 54 ± 14 GPa [158] and the transverse modulus at 7 ± 2 GPa [159] for an anisotropy ratio of 0.13. The evolution of mechanical properties for flax fibres into biocomposite indicated a large decrease in the longitudinal and the transverse fibre moduli with the immersion time and stabilisation after an ageing time of around 200 days (see Figure I-XXXV). After drying, flax fibres partially recover their initial properties until around 90 days, showing a plasticising effect of the fibre cell walls [160]. The definitive loss in fibre properties may be related to the release of soluble components into the water bath during ageing.

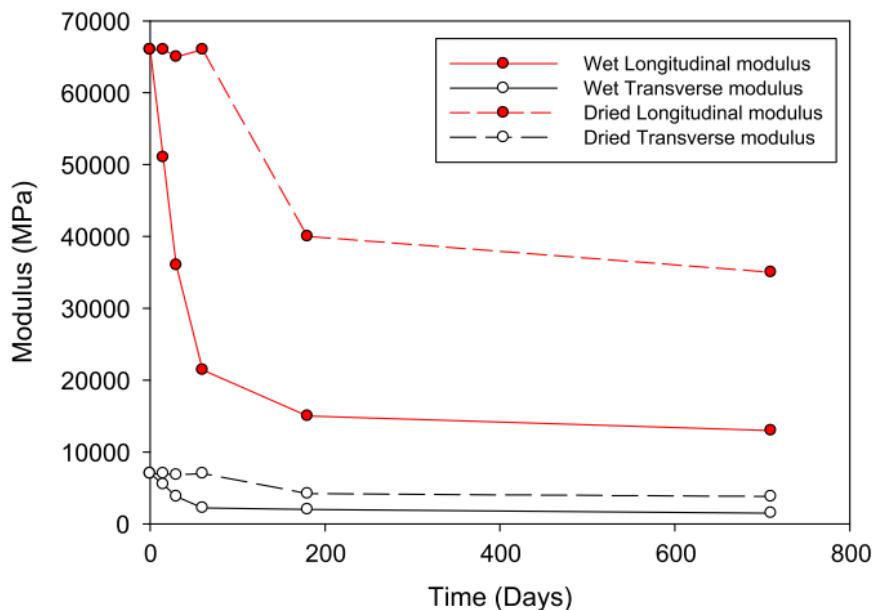


Figure I-XXXV Evolution of the longitudinal and transverse modulus of flax fibres (for wet and dried conditions) estimated by using the Halpin Tsai equations [127].

I-4.4.2 Influence of water on biocomposites mechanical properties

a. Evolving behaviour of modulus and ultimate properties

Water induces an important swelling on flax fibre composites but it also acts as plasticiser leading to a decrease in the biocomposites elastic modulus. Water can also lead to fibre-matrix interface degradation, the hydrolysis and microcracking of the resin. When these phenomena takes place simultaneously, an important decrease of composites mechanical properties is observed [161]. The drop of composites mechanical properties can also be explained by a partial degradation of natural fibres, mainly of the external cell walls (the middle lamella and the primary cell wall).

The effect of moisture absorption on the mechanical properties of hemp fibre unsaturated polyester composites was studied by Dhakal et al. [3]. First, the non-reinforced unsaturated polyester was analysed by tensile test after being immersed in water at room temperature. It was observed that both the tensile stress and strain of the resin had increased after 37 days of immersion in water (see Figure I-XXXVI). This increase in tensile stress can indicate that further crosslinking or other mechanisms than polymer plasticisation are taking place enhancing the material strength. Although the standard deviation obtained make analysis difficult, it is interesting to note that the same behaviour is observed for composites reinforced with 26% (vol.) of hemp fibres: the ultimate tensile properties of wet samples are higher than that for dry samples. For the authors, this could be related to the fact that fibre swells and fills the gaps between the fibre and the polyester matrix, leading to an increase in the ultimate properties of composites.

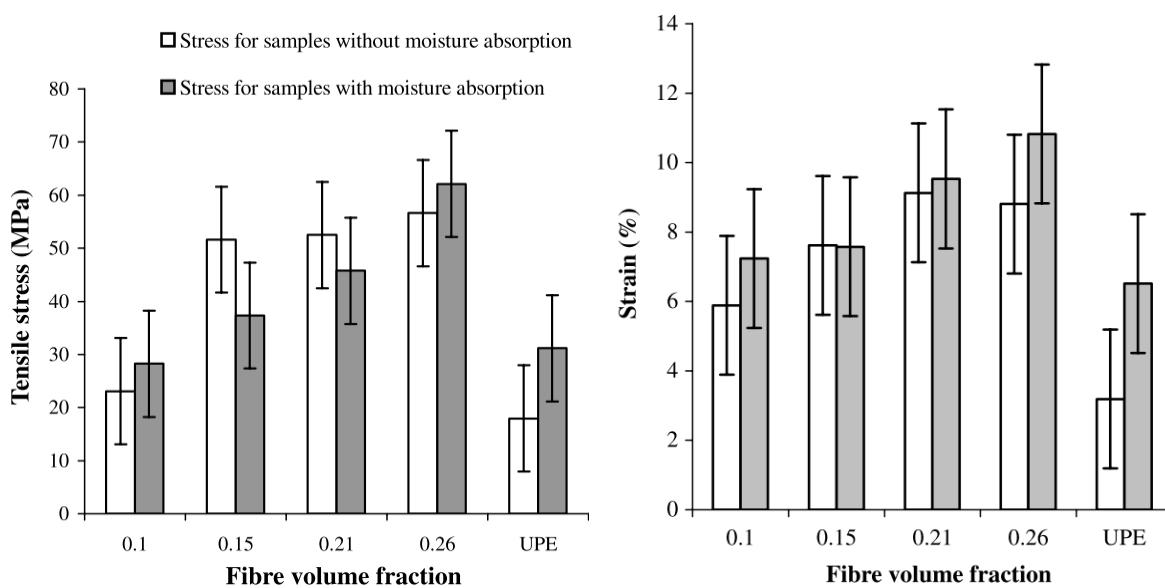


Figure I-XXXVI Tensile stress and strain as a function of fibre volume fraction for hemp fibre unsaturated polyester composites [3].

Dhakal et al. also studied the influence of moisture on the tensile and flexural modulus of hemp fibre reinforced composites with different fibre volume content up to 26% (see Table I-XI). The tensile modulus of the composite reinforced with 26% of fibre volume content for example, decreased from 1.27 GPa before ageing to 0.68 GPa after ageing (around 46% of loss). However, the flexural modulus

does not follow the same trend because the flexural samples fail in a combination of compression, shear and tension modes.

Therefore, it appears that it is preferable to set up tensile tests instead of flexural tests in order to analyse the evolution of the mechanical behaviour of biocomposites during ageing.

Table I-XI Tensile and flexural modulus for dry and wet samples of hemp fibre reinforced unsaturated polyester composites [3]

Specimens	Fibre volume (%)	Tensile modulus (GPa)		Flexural modulus (GPa)	
		Dry	Wet	Dry	Wet
UPE only	0	0.56	0.60	5.51	5.81
2 Layer hemp	10	0.72	0.64	4.20	5.76
3 Layer hemp	15	1.0	0.62	5.34	6.08
4 Layer hemp	21	1.22	0.62	7.30	6.06
5 Layer hemp	26	1.27	0.68	6.49	8.05

The evolution of mechanical properties as a function of water uptake follows a linear trend in some cases for composites immersed in water. This behaviour was observed by Le Duigou et al [127] for flax fibre reinforced PLLA composites aged during 2 years in seawater. Flax composites were immersed in water and dried in order to highlight the reversibility of water ageing.

It is important to note here that various works relate a “pseudo-reversibility” instead of a real reversibility because the drying conditions are not the same as the conditions before ageing. This difference can compromise the measure of the reversibility because the biocomposites will never return to the initial state before ageing.

From the reversibility tests realised by Le Duigou et al., it was observed that the strength at break was found to be more sensitive to irreversible degradation than stiffness. By contrast, the ultimate strength (UTS) depended on the interactions between the fracture properties of each component and the damage accumulation induced by ageing. Indeed, it was observed by the authors that the failure behaviour of biocomposites had changed: the PLA breakage became ductile after ageing and some fibre breakage was present with long debonding lengths (compared to non-immersed samples). Moreover, the presence of peeled fibres after ageing highlights the efficiency of the interfacial stress transfers. Another interesting observation was that the presence of water induced a division of fibre bundles which may be related to the washing out of soluble components. Indeed, Bourmaud et al [162] have shown that a soft water treatment could facilitate the extraction of elementary flax fibres by degrading the middle lamella pectins.

Another study [4] presents the evolution of the Young modulus, failure stress and maximum strain for flax fibre reinforced epoxy composites compared to glass fibre reinforced epoxy composites. The failure stress of glass fibre composites decreases for about 10% while flax fibre composites present 25% of loss in failure stress for specimens immersed in water at room temperature during 40 days. The Figure I-XXXVII show the evolution of the normalized mechanical properties (mechanical properties at time t divided by the initial properties) as a function of normalised immersion time (test time divided by time at saturation). The results show that glass fibre composites properties are slightly affected by water absorption: the Young Modulus decreases by 9% and the maximum strain by 10% at saturation. The flax fibre composite loses 39% of Young modulus at saturation, but the maximum strain increases

by about 63%. The plasticising effect of water on the matrix and flax fibre can be the reason of the observed modulus loss and maximum strain increasing.

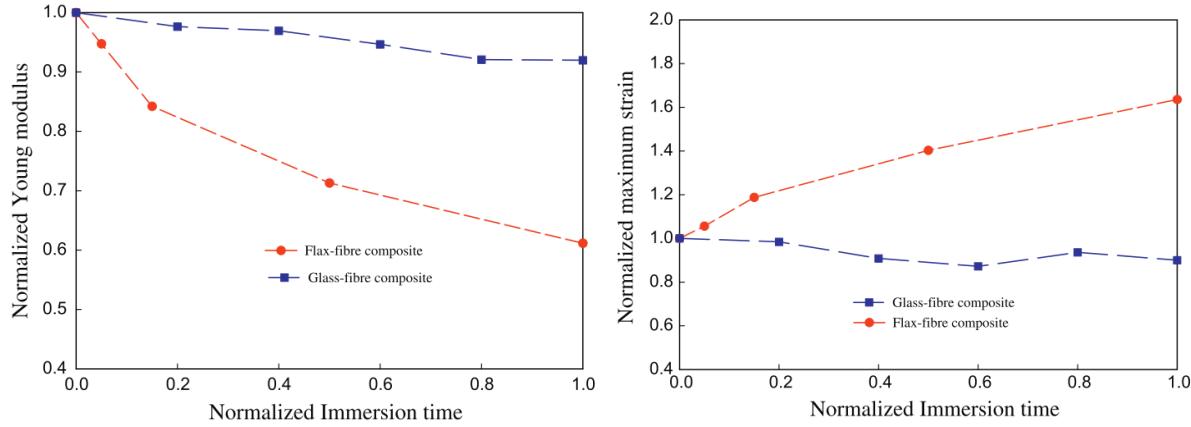


Figure I-XXXVII Evolution of the normalized Young modulus and the normalized maximum strain as a function of ageing time for glass and flax fibre composites [4].

Assarar et al also investigated the ageing behaviour of glass and flax FRC by Acoustic emission (AE) technique (see Figure I-XXXVIII). The signals of type A are related to the matrix cracking, type B to the fibre/matrix debonding, and type C to the fibre failure. The damage behaviour of glass fibre composites before ageing (see Figure I-XXXVIII-a) was dominated by the matrix cracking (signals type A). When the composites reached saturation in water (see Figure I-XXXVIII-b), it can be observed that the number of hits of type A decreased while the activity of types B and C increased, showing that fibre/matrix debonding and fibres failure damage modes took place in glass FRC with the presence of water. A different behaviour was observed for flax composites. The main damage mechanism of biocomposite samples before ageing (see Figure I-XXXVIII-c) and after saturation (see Figure I-XXXVIII-d) was the matrix cracking. The number of events decreased for water saturated samples, what shows that biocomposites deteriorated during ageing. In addition, the decrease of the number of type A signals and the absence of B signals for aged samples, show that an interface weakening mechanism was induced by the water uptake.

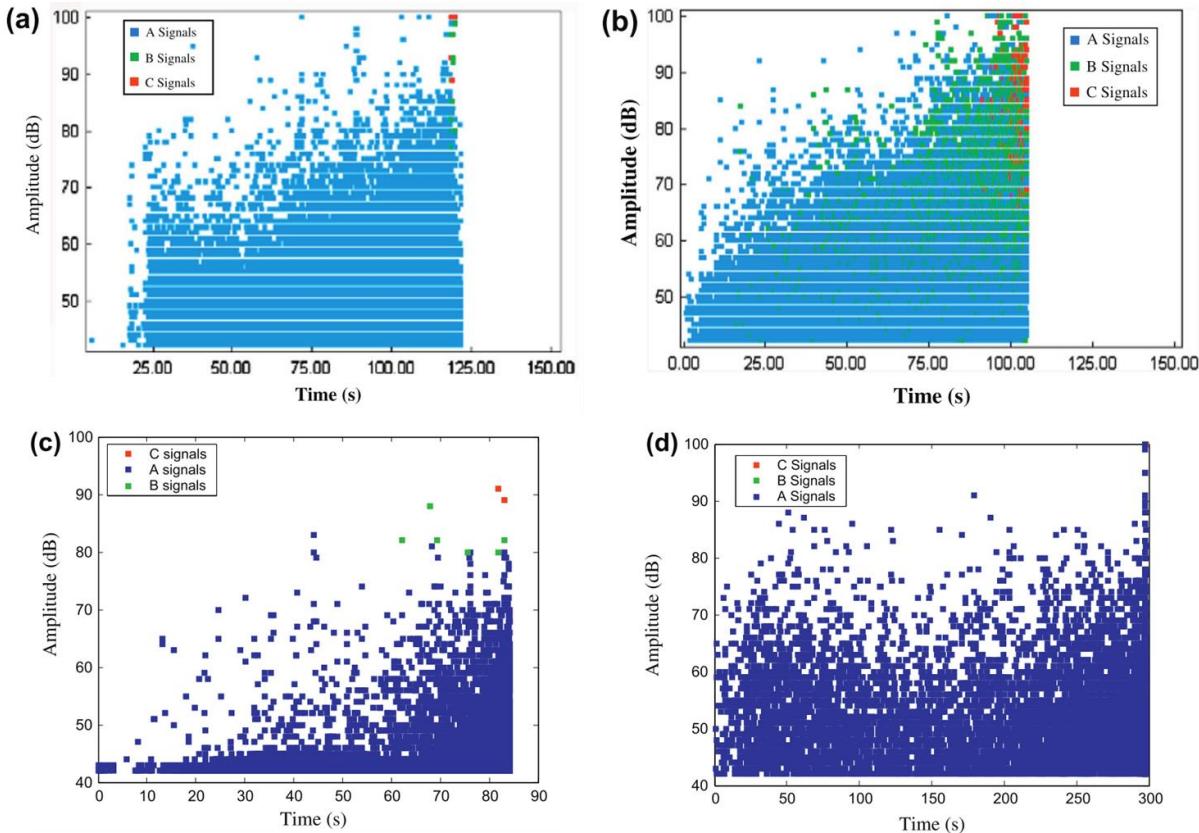


Figure I-XXXVIII Amplitudes of AE signals versus tensile test time for glass fibre composites (a) unaged and (b) at saturation, and flax fibre composites (c) unaged and (d) after saturation [4].

b. Interfacial damage

Chen et al. [163] highlighted that exposure of the bamboo/vinyl ester composites to moisture caused significant damage to the interfacial shear strength (IFSS). The pull-out tests performed show that relative humidity and water immersion cause a decrease of the composite's IFSS. Post-processing exposure to moisture was found to be less damaging than the moisture exposition during composites manufacturing. Bamboo composites show an interfacial shear strength of around 6 MPa at room temperature conditions (20°C and 60% RH) while negligible interfacial strength is observed for composites produced at relatively high humidity conditions (see Figure I-XXXIX). Exposure of composites to water at room temperature causes a 38% reduction in IFSS during the first 9 days of water immersion, but further immersion up to 100 days did not cause further reduction in the interfacial shear strength.

The authors tested separately the polymer matrix and the natural fibres which present no reduction in the tensile strength until 50 days of immersion in water. The reduction of IFSS in the initial nine-day period can be attributed to the water damage at the interface. Espert et al attributed this phenomenon to the debonding and weakening of the interface adhesion [125].

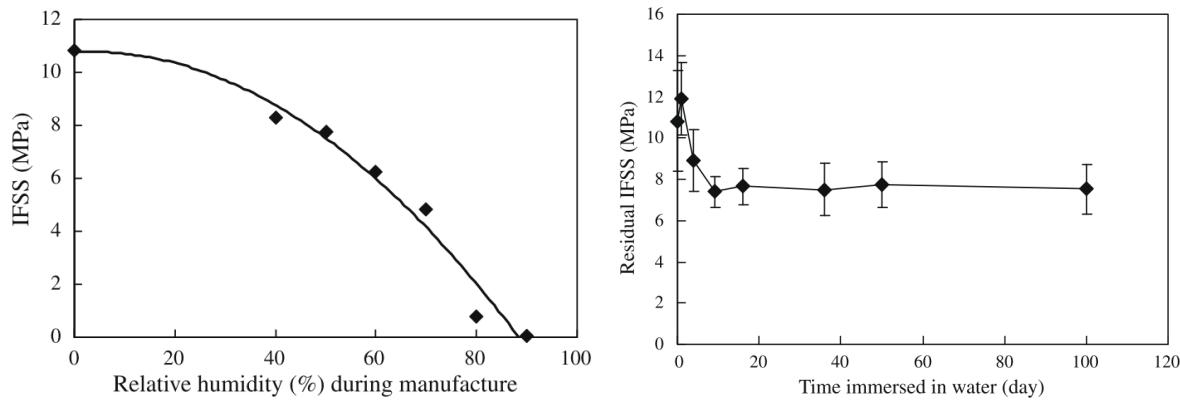


Figure I-XXXIX Interfacial shear strength evolution of bamboo/vynil ester composites in function of the (a) relative humidity and (b) time immersed in water [163].

I-4.5. Coupling effect

In real conditions, the different factors of damage act simultaneously, and their effects on biocomposites are coupled. Indeed, real conditions frequently couple simultaneously the action of temperature, humidity, mechanical loadings, and even other ageing mechanisms [164]. The few studies on the plant fibre composites behaviour in aggressive environment highlight the lack of knowledge in this area (mainly under coupled conditions).

During the last decades, some studies related the effect of coupled ageing on glass fibre composites. The work of McBagonluri et al [165] highlighted that the fatigue damage evolution and subsequent break of glass fibre composites have been found to be independent of moisture content or moisture regime in the short term, although long-term ageing and moisture ingress appear to affect the fatigue performance. The glass fibre composites show a decrease of about 10% UTS/decade for glass/vinyl ester composite exposed to ageing in salt water at 65°C. Furthermore, the temperature effect on fatigue response did not depend on the presence or absence of the ambient fluid. As the failure mechanism could be attributed to a fibre-dominant process [166], the authors concluded that the fatigue failure of glass fibre composites seems to occur as a result of gradual deterioration of the load-bearing fibres.

Regazzi [97] observed a degradation synergism for flax/PLA composites subjected to coupled mechanical-hydrothermal ageing. The long-term behaviour of these composites was evaluated by creep tests under environmental controlled conditions of water and temperature. The concept of degradation synergy was employed by the author to define the difference between the elastic modulus measurement in coupled and uncoupled ageing conditions. Which means that the evolution of biocomposites properties when exposed to *creep + water immersion* was not equal to the sum of the *creep* plus *water immersion* taken separately. The results highlighted the degradation of the biocomposite during ageing which is related to a decrease in the mechanical stiffness as well as the lifetime. The temperature is found to show a lower effect on the degradation synergy than fibre content. Furthermore, they present contrariwise effects since both temperature and fibre content are found to extend the composites lifetime but to the detriment of their mechanical stiffness (see Table I-XII). The increase in the biocomposites lifetime has been explained by the plasticising effect of the biocomposites components when exposed to water and temperature. The PLA presents a ductile

behaviour at this stage, which allows the imposed deformation to be dissipated into its structure before breaking. Finally, the presence of fibres seems to attenuate the propagation of fracture in the PLA matrix.

Table I-XII Modulus loss of PLA/flax composites subjected to mechanical-hydrothermal ageing [97].

Temperature	Material	Creep	water immersion	Creep + water immersion	Degradation synergy	Rupture
20 °C	PLA	-1.30%	-5%	-27.40%	-21.10%	20h
	PLA / flax 10%wt	-3.80%	-10.70%	-25.50%	-11%	115h
	PLA / flax 30%wt	-1.30%	-31.90%	-38.30%	-5.10%	none
35°C	PLA	-4.20%	-17.10%	-43.40%	-22.10%	75h
	PLA / flax 10%wt	-10.10%	-25.10%	-47.70%	-12.50%	none
	PLA / flax 30%wt	-18%	-51%	-68.80%	-0.10%	none

I-5. Positioning the methodology of the study

The present work aims to address a complete characterization of the use of flax fibres to substitute glass fibres in composite materials designed for nautical applications. Flax fibres present specific mechanical properties comparable to those of glass fibres and generally superior to other natural fibres. The substitution of glass fibres by flax fibres to produce composites requires a better understanding of the composites life cycle: from materials selection and processing to its behaviour when exposed to immersion in water, especially under real service conditions (exposure to water, temperature and mechanical loadings).

The first part of this work addresses a comparison between flax and glass fibres on two scales: fabrics and composites. The morphological aspects of glass and flax fibres before processing change when impregnated with a polymer matrix. The fibres geometry and distribution in the matrix plays a key role on the composites final properties (density, thickness, fibre content, mechanical properties, etc.). The initial properties and specific features of glass and flax fibre composites before ageing are described in this part.

Composite parts designed for nautical applications are produced by vacuum infusion technique and many other processes in the shipyard. The vacuum infusion technique is an efficient processing technique to produce large components presenting low porosity and relatively good mechanical properties. However this processing technique employs relatively low pressure (compared to RTM and compression moulding techniques), which result in a composite presenting low fibre content. The fibre content becomes an important factor to evaluate when a change in fibre reinforcements is considered. The influence of processing on the mechanical properties of FFRC and GFRC is also analysed, which completes the study of composites behaviour before ageing.

Then, ageing tests are realized in order to study the composite materials behaviour when exposed to damage conditions in service that leads to a decrease in mechanical properties during working. The environment as well as the initial properties of composite materials plays a key role in the type of damage and its evolution when exposed to ageing conditions. In the marine environment different sources of damage influence the composites behaviour: the water sorption, the temperature, the

creep, the impacts, the mechanical fatigue and the combination of several of these phenomena acts frequently simultaneously [167].

Many studies refer to the role of the water permeability on the evolution of mechanical properties of glass fibre composites, and more recently on the properties of natural fibre reinforced composites. These studies can be classified into three conceptual approaches: the first is based on the mechanisms of water penetration (kinetics of diffusion), the second concerns the monitoring of swelling and the presence of the residual stresses, and the third approach treats the decrease in mechanical properties due to the water uptake [168].

The methodology adopted in this work applies these three approaches to flax fibre composites and concerns the characterization of the composites behaviour when exposed to temperature, water immersion and mechanical solicitations.

First, the effect of the water immersion at a specific temperature is observed by hydrothermal ageing tests. The evolution of physico chemical, swelling and mechanical properties are characterized for flax fibre composites and compared to glass fibre composites and to the non-reinforced polyester resin. The flax fibres can be treated in order to improve their water resistance during ageing.

Once composites are completely saturated with water, the samples are dried in a low-moisture atmosphere in order to characterize the pseudo-reversibility of properties after the hydrothermal ageing. The methodology of this part is represented in Figure I-XL.

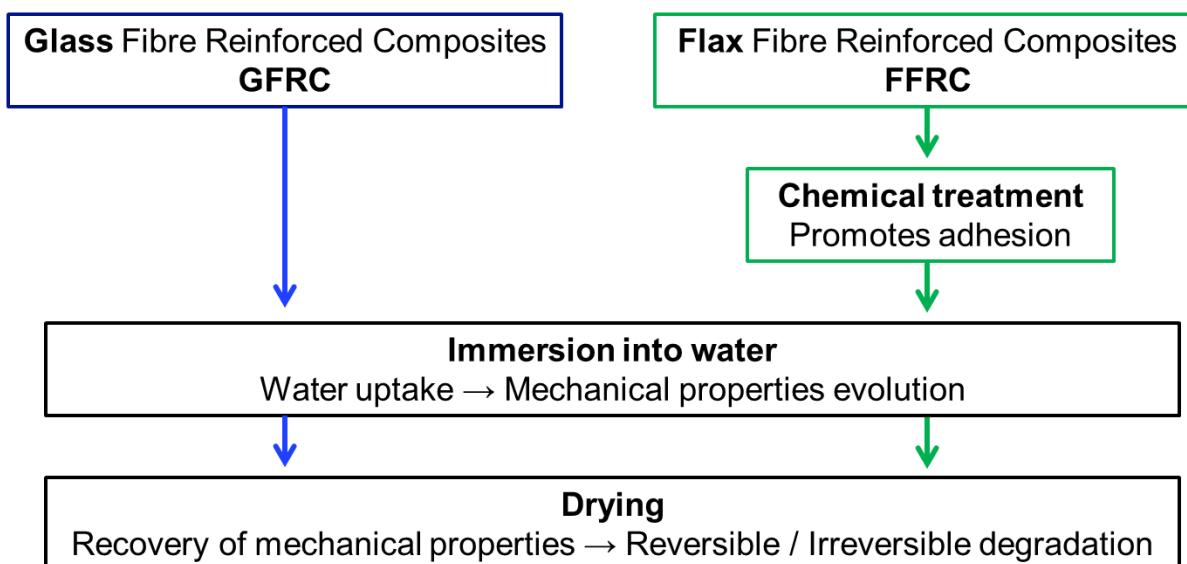


Figure I-XL Methodology of study for the hydrothermal ageing and recovery of properties.

Then, the hydrothermal ageing is coupled with a mechanical loading. Composite samples are immersed in water under stress in a creep configuration in order to characterize the mechanical-hydrothermal coupling of flax fibre composites. The creep behaviour and viscoelastic properties evolution during ageing are analysed for three testing configurations: a thermo-mechanical, a hydro-mechanical and a mechanical-hydrothermal set-up. The effect of coupling can now be evaluated by comparing the hydrothermal to thermo-mechanical, hydro-mechanical and mechanical-hydrothermal analysis (see Figure I-XLI).

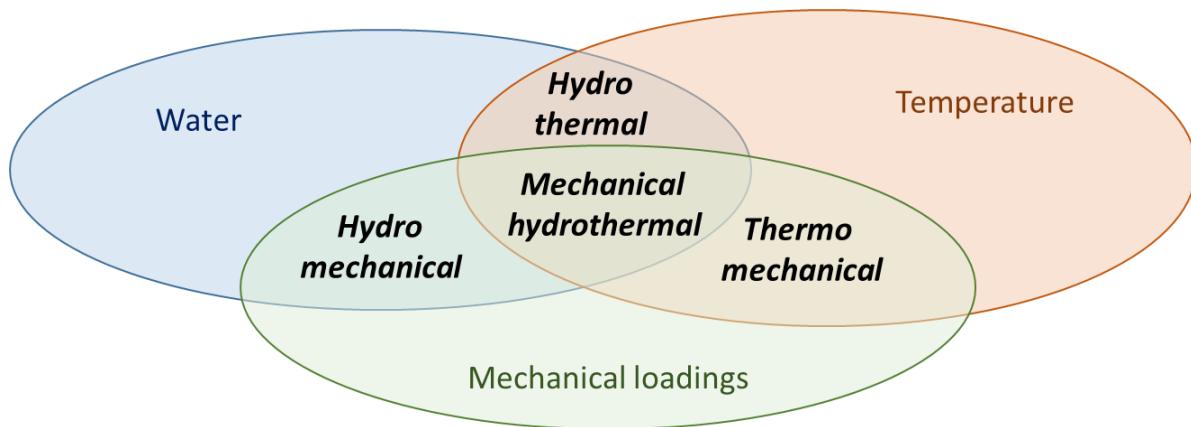


Figure I-XLI Methodology of study for the *in-situ* characterisation of the coupled ageing.

Finally, the modelling chapter aims to predict the water diffusion behaviour of flax fibre composites by taking into account their real morphology. A realistic description of the flax fibres distribution in the polyester matrix is realised in order to create two models: a direct and a parametric model. The direct model is based on the real composite's morphology and gives the basis to identify the parameters of the composites diffusion behaviour. The parametric model was developed in order to analyse the influence of the microstructural parameters on the diffusional macroscopic properties of flax fibre composites immersed in water. Furthermore, a critical analysis is realised based on the sensitivity of the composites diffusion behaviour on the fibre/matrix diffusion parameters (water uptake and diffusivity) and the difference between the *in situ* and *ex situ* properties.

Chapter II. Materials and methods

This chapter presents the materials and test procedures considered in this work.

This chapter first introduces the studied materials, i.e. the flax and glass fibres, the unsaturated polyester as well as the chemical treatments applied to flax fibres in order to improve their resistance to water uptake.

Then the second part concerns the manufacturing technique employed to produce unidirectional glass and flax fibre reinforced composites. The storage and processing conditions of flax fibres are detailed.

The third part details the techniques employed in this work to age composites under controlled conditions. Different set-ups were developed in order to reproduce the action of water, temperature and mechanical loadings on biocomposite samples during several hours of ageing. These sources of damage were coupled in hydrothermal (HT), thermo-mechanical (TM) and mechanical-hydrothermal (MHT) configurations.

Finally, the fourth part describes the testing methods employed for the characterisation of the materials properties. They are classified into two main categories: the tests for monitoring the composites evolving behaviour during ageing and the complementary analyses that are sub-divided into morphological, physicochemical analysis and mechanical testing.

Chapitre II – Matériaux et méthodes

Ce chapitre présente les matériaux et méthodes considérés dans cette étude.

Dans un premier temps, les matériaux étudiés sont introduits, à savoir des fibres de lin et de verre, une résine polyester insaturé et également des traitements chimiques appliqués aux fibres de lin dans l'objectif d'améliorer leur résistance à l'absorption d'eau.

Ensuite, la deuxième partie de ce chapitre concerne les techniques de fabrication utilisées pour produire les composites unidirectionnels renforcés par des fibres de verre et par des fibres de lin. Les conditions de stockage et de mise-en-œuvre des fibres de lin sont également décrites dans cette partie.

La troisième partie détaille les techniques utilisées dans cette étude pour faire vieillir les composites en conditions contrôlées. Différentes configurations ont été mises en œuvre afin de reproduire l'action de l'eau, de la température et des sollicitations mécaniques sur des éprouvettes biocomposites pendant une longue période d'exposition. Ces sources d'endommagement ont été couplées dans des configurations hydrothermiques (HT), thermo-mécaniques (TM) et hydrothermo-mécaniques (HTM).

Finalement, la quatrième partie de ce chapitre décrit les méthodes d'analyse utilisées pour caractériser les propriétés des matériaux composites précédemment décrits. Ces méthodes sont classées dans deux catégories principales : les essais de suivi des propriétés pendant vieillissement et les essais complémentaires qui sont subdivisés en caractérisations morphologiques, physicochimiques et mécaniques.

II-1. Selected materials

This part describes the materials used in this study: an unsaturated isophthalic polyester resin reinforced by glass and flax fibres. The chemical molecules and conditions employed to treat flax fibres are also presented here.

II-1.1. Unsaturated polyester resin

A dicyclopentadiene isophthalic unsaturated polyester resin Enydyne® (Cray Valley – Rouvroy, France) was used for this study (Figure II-I). The resin was polymerized with 1.8% w/w of methyl ethyl ketone peroxide Luperox K1S® (Arkema – Colombes, France). The technical datasheet gives a specific density of 1.12 g/cm³, a Young's modulus of 4.1 GPa, a tensile strength of 51.8 MPa and a deformation at break of 2.1% (properties of a polyester resin post-cured at 40°C during 16 hours plus 2 hours at 90°C).

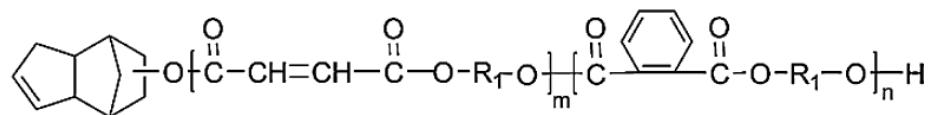


Figure II-I Chemical structure of a dicyclopentadiene unsaturated polyester prepolymer before crosslinking in presence of peroxide.

II-1.2. Glass and flax fibres

Unidirectional glass fibres were supplied by Chomarat (Le Cheylard, France) for an areal weight of 416 g/m² (weft: 408 g/m² / warp: 8 g/m²) under the trademark Chomarat 400 T/F (Figure II-II). The technical datasheet mentions a fabric thickness of 0.4 mm, a tensile strength of 1840 N/cm in the weft direction and 50 N/cm in the warp direction.

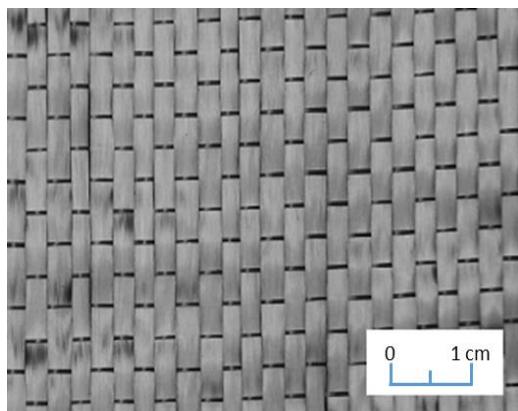


Figure II-II Unidirectional glass fibres – reference: Chomarat 400 T/F.

Unidirectional flax fibres were supplied by three different companies: Fibre Recherche Developpement (FRD - Troyes, France), Chomarat (Le Cheylard, France) and Biorenforts (Longvic, France) (Figure II-III).

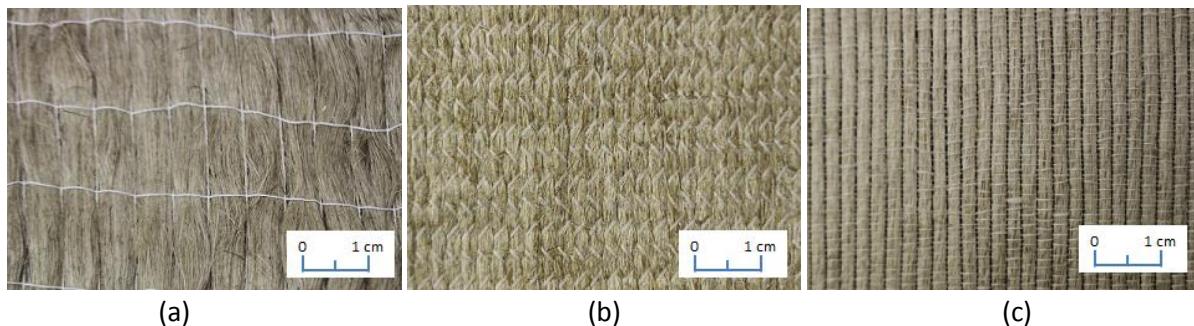


Figure II-III Unidirectional flax fibres supplied by (a) Biorenforts ; (b) Chomarat; and (c) FRD.

Few data are available concerning these three flax fabrics (Table II-I). Complementary characterization of the physical and mechanical behaviour of the flax fibres is addressed in the subchapter III-1.1 (page 91).

Table II-I Technical data sheet information about the flax fibres (Biorenforts, Chomarat and FRD) compared to glass fibres.

Fibres		Total weight (g/m ²)	weight (weft) (g/m ²)	weight (warp) (%)	Thickness (mm)
Type	Supplier				
Glass	Chomarat	416	408	98%	8
	Biorenforts	400	-	-	-
Flax	Chomarat	670	-	-	1.4
	FRD	360	-	-	0.5
					0.4

II-1.3. Chemical treatments of flax fibres

Three treatments were applied on flax fabrics in order to increase their resistance to water uptake and promote adhesion between fibres and matrix on composites. An organosilane treatment traditionally used for glass fibres sizing was used to treat flax fibres surface, and two copolymers were synthesized at laboratory scale and applied to fibres.

II-1.3.1 Methacryloxypropylmethoxysilane (MPS)

This chemical treatment consists in immersing the flax fabrics in an ethanol/water (60/40 wt%) solution containing 1.0 wt% of γ -methacryloxypropyltrimethoxysilane (MPS) (Figure II-IV). Silane was hydrolysed during 3h at pH 4 before flax fabrics impregnation. Flax fabrics were then dried in an oven at 105 °C during 2h and stored at 23°C and 50 % RH before processing.

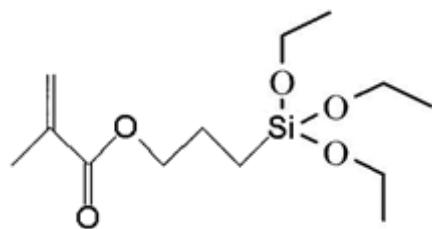


Figure II-IV Molecular structure of the methacryloxypropyltrimethoxysilane or MPS.

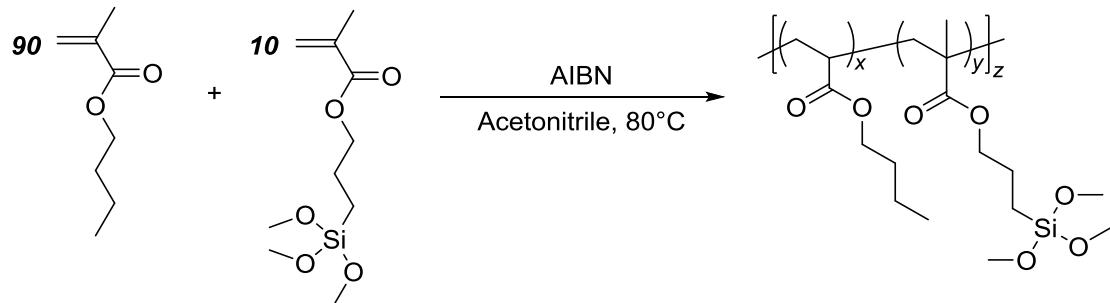
II-1.3.2 Butyl methacrylate (BMA) and styrene (S) / 3(trimethoxysilyl)propylmethacrylate (MPS) copolymers

a. Copolymers synthesis

The synthesis consisted in a radical copolymerization of butyl methacrylate (BMA) or styrene (S) with 3(trimethoxysilyl)propyl methacrylate (MPS) under argon atmosphere. A schematic representation of the copolymer synthesis is addressed in Figure II-V and described below.

The copolymer was synthetized into a 100 ml flask fitted with a condenser 10 g (7.0×10^{-2} mol) of BMA, 1.94 g (7.8×10^{-3} mol) of MPS, 0.13 g (7.8×10^{-4} mol) of AIBN and 22 g of acetonitrile were introduced. Argon was bubbled through the mixture for 15 min. The mixture was then stirred and heated at 80°C for 15 hours. After reaction, the polymer was purified by precipitation in methanol. A 90/10 (mole percent) BMA/MPS copolymer was obtained.

a) Synthesis of BMA/MPS 90/10 copolymer



b) Synthesis of Styrene/MPS 90/10 copolymer

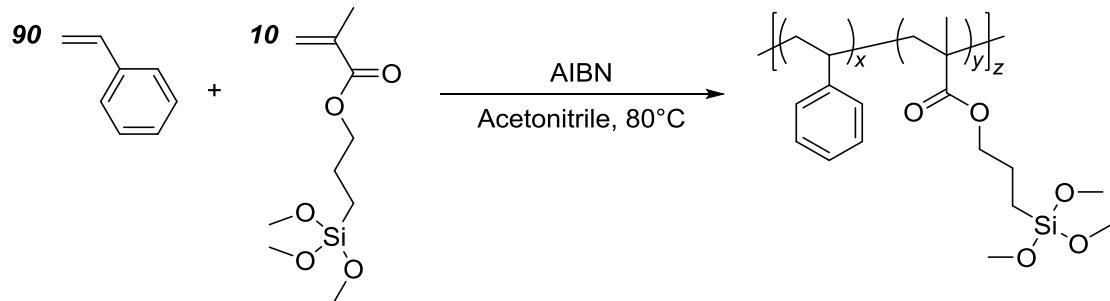


Figure II-V Schematic representation of the synthesis of BMA/MPS(a) and Styrene/MPS(b) copolymers

The same procedure was used to synthesize the styrene/MPS 90/10 copolymer and the BMA/MPS 90/10 copolymer.

b. General procedure for the flax fabrics surface treatment

In a first step, the flax fabrics were dipped 1 min into a solution of BMA/MPS 90/10 copolymer (or styrene/MPS 90/10 copolymer) in THF(copolymer concentration in THF about 5 wt%). In a second step, the fabrics were placed under a laboratory extractor hood to remove the solvent (THF). Fabrics were weighed before and after impregnation to evaluate the amount of copolymer that may have been deposited. Fabrics were then heated at 80°C in an oven for 24 hours and finally, they were washed with THF to remove the uncrosslinked part of copolymer, thus allowing to quantify the crosslinked part of copolymer that is attached to the flax fibres.

Two tests have been also performed to verify the absence of weight loss due to a solubilization by THF of some components present on the flax fibres. The first test was an impregnation test using only THF. The second test was the impregnation tests using solutions of BMA/MPS and styrene/MPS copolymers followed by THF washing.

II-2. Manufacturing process

Glass and flax fibre composites were manufactured by vacuum infusion and compression moulding techniques under controlled processing conditions. The manufacturing conditions, such as temperature and relative humidity are important aspects to take into account when working with natural fibres due to their environment dependent properties.

II-2.1. Vacuum infusion

The vacuum infusion is the main technique (with hand lay-up / spray) employed by marine manufacturers to produce composites. It is performed in this work according to the industrial practice except for the fact that composites are processed under regulated conditions (temperature and relative humidity). This technique employs vacuum pressure to impregnate fibres with resin and gives the final form to composites by the means of an infusion flat mould (Figure II-VI). Initially, a complete vacuum is achieved and possible leaks are detected and closed to obtain a completely sealed vacuum system. Then, the resin enters through an infusion tube placed next to the fibres flowing to the opposite side where the vacuum infusion point is located. This manufacturing technique employs an assortment of supplies and materials (infusion tarp, removable tissue, sealing gaskets, etc.). The vacuum pressure imposed to the material allows improving the fibre-to-resin ratio and expels air bubbles (porosities) from the composite.

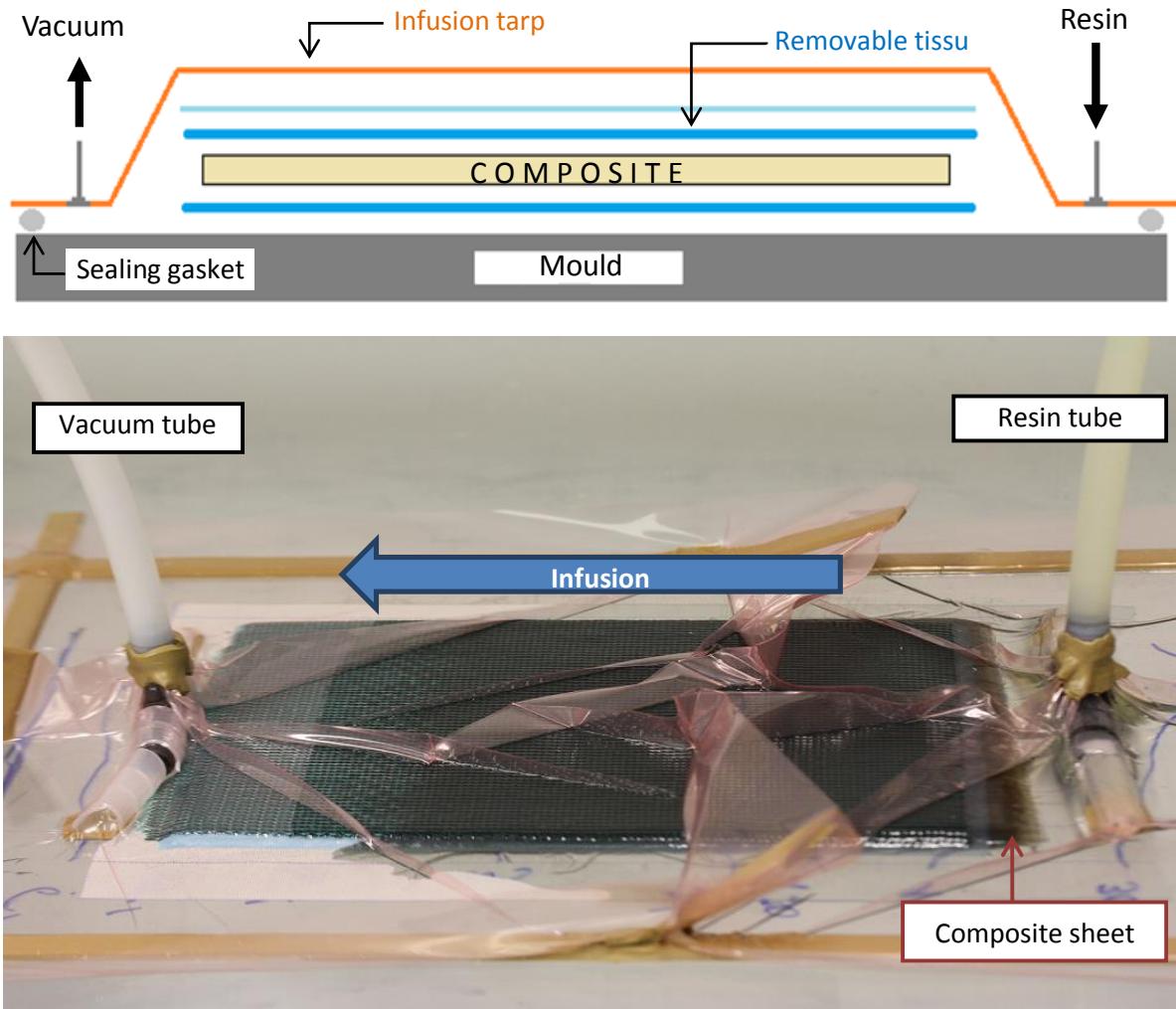


Figure II-VI Schematic representation and experimental set-up of the vacuum infusion technique.

In this work, four to six layers of unidirectionally oriented flax fabrics were vacuum infused with the unsaturated polyester resin under regulated temperature and relative humidity (23°C / 50%RH). The vacuum pump maintains a constant pressure of 100 mbar during 24 hours (curing at room temperature).

II-2.2. Compression moulding

The compression moulding method is a high-pressure technique that is suitable for moulding composites. It allows higher fibre contents than those achieved by vacuum infusion.

Before being pressed, flax fabrics were impregnated by the resin thanks to a technique called hand lay-up. It consists in depositing a layer of resin on the fabric and forcing it to penetrate between and into yarns thanks to a brush or a roller. Impregnated fibres are then placed in an open mould cavity between two metallic plates. Usually, the metallic plates are heated during processing, but in this study the process was realized at room temperature to maintain the same conditions as employed to produce vacuum infused composites. Then the mould is closed and the material is full-pressed under the required pressure. Fibres are then subjected to a pressure of 50 bar during 24 hours (curing at room temperature) to obtain the composite plate.

II-2.3. Manufacturing conditions

Before processing, all fibres were stored in a climatic room, at 23°C and 50% RH for minimum 15 days. This procedure is important in order to ensure that flax fibres have the same humidity content when employed to produce composites in different periods throughout the year. Indeed, it was verified that in the region of Alès, in south of France, the relative humidity of the air may range from 30% to 80% depending on the atmospheric conditions. For that reason, it was decided to work under controlled conditions from materials storage to processing and testing.

After being processed, the composite sheets (300 mm x 250 mm) were cut to size of 250 mm x 25 mm using a band saw and subsequently post-cured in an oven. The post-curing conditions (time and temperature) are the subject of a study on the thermal cycle of the polyester resin in Chapter III – “Preliminary characterisation of biocomposites”

All the composites sheets and specimens were stored in a climatic room at the same conditions as before processing (23°C and 50% RH) in order to ensure constant humidity content. Then, composites were immediately tested to assess their initial properties, or immersed into water to study the modification of their behaviour during ageing.

II-3. Ageing techniques and conditions

The composites produced by vacuum infusion and the non-reinforced polyester resin are exposed to hydrothermal ageing tests. These materials are tested at initial conditions, and then immersed into water at different temperatures where their behaviour is followed during ageing. Once saturation is reached, composites are dried in order to observe the reversible ageing mechanisms.

One feature of this work is to expose flax fibre composites concomitantly to water, temperature and mechanical loadings, in a so called hydro-thermo mechanical configuration, and to compare their coupled behaviour to hydrothermal and thermo-mechanical ageing. The objective is to define the effect of coupled conditions on the evolving behaviour of flax fibre composites.

Composite and polyester resin samples were exposed to ageing conditions at a controlled temperature of 30, 50 and 70°C. These temperatures were chosen in an interval between the room temperature and the glass transition temperature of the polyester resin (around 70-75°C). The water bath was changed in the interval of two weeks to prevent the leached products during long-term tests to modify the water composition [31].

Hydrothermal ageing: Composites and the polyester resin were immersed in a temperature controlled water bath up to 5 months. Temperature is controlled by a Julabo EH immersion thermostat equipped with a heating coil and a pump that homogenises water temperature (Figure II-VII). Specimens were removed from water, subjected to non-destructive characterisation and immediately returned to water.



Figure II-VII Hydrothermal ageing water bath equipped with a thermostat.

Samples drying: After saturation was reached, samples were desiccated inside a drying oven controlled 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.

Thermo mechanical ageing: Composite samples were subjected to creep loading in a hermetical chamber where the temperature was controlled by a water pipe coil system that heated the air around the sample. For the several temperatures of the study, specific relative humidities can be reached thanks to different salts, such as LiCl, Mg(NO₃)₂ and K₂SO₄ (see Table II-II).

Table II-II Relative humidity of selected saturated salt solutions as a function of the temperature [169].

Temperature (°C)	Relative humidity (%)		
	Lithium chloride	Magnesium nitrate	Potassium sulphate
30	11.28 ± 0.24	51.40 ± 0.24	97.00 ± 0.40
50	11.10 ± 0.24	50.93 ± 0.55	96.12 ± 0.40
70	10.75 ± 0.33	49.70 ± 1.10	-

Mechanical-hydrothermal ageing: The corresponding device, specifically designed for this study, was produced at the mechanical centre of the *Ecole des Mines d'Alès*. Aluminium and stainless steel were the materials employed to build this apparatus which was exposed for long periods to water and temperature.

The configuration consisted in placing a composite sample under creep stress inside a hermetically sealed chamber. The chamber was filled with water whose temperature was controlled by a circulation thermostat Julabo CF31 (Figure II-VIII). The creep stress was maintained by using a tensile Dartec mechanical device equipped with a 100 kN force sensor. A LVDT sensor was fixed to the mobile jaw and connected to the fixed jaw by a metallic rod, which allowed measuring the sample displacement (longitudinal direction) with a precision of 1 µm. More details about the monitoring of creep behaviour and Young modulus are addressed in the part II-4.1.3 (page 77).



Figure II-VIII Mechanical-hydrothermal set-up.

II-4. Test methods for the ageing characterisation

In this part, the presentation of the characterisation methodology is organised into two subparts. The first concerns the monitoring of the composites evolving behaviour, where tests are carried out at certain time intervals during the entire duration of the ageing tests. The second part presents the morphological, physicochemical and mechanical characterisations performed at the initial condition before ageing and at saturation. The mechanical tests were realised in order to evaluate the ultimate strengths and interlaminar shear resistance, which address some information about the fibres and the interface degradation.

II-4.1. Monitoring the composites physical properties and mechanical evolving behaviour during ageing

This first part concerns the monitoring of the composites evolving behaviour, i.e. the tests that were carried out during the entire duration of the ageing tests.

II-4.1.1 Water uptake, volume and density variations

a. Water uptake

Composite and polyester resin specimens were immersed in water for different periods and taken away from the bath for weight measurements. The samples were carefully wiped to remove water from surface, weighed and replaced into the water baths. A Mettler-Toledo AT200 balance was used to weigh samples to a precision of 0.001 g (Figure II-IX).

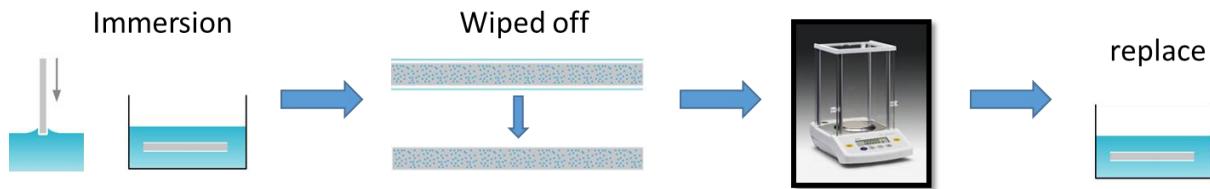


Figure II-IX Water uptake measurements

The reproducibility was measured on 6 (six) samples and the water uptake was determined according to the equations described in the part I-3.2.1 (page 34).

b. Volume and density variations

Volume variation was measured before returning the specimens to the water bath. Samples width, thickness and length were measured using a sliding caliper with a precision of 10^{-2} mm. A minimum of three measurements for each dimension were performed and the mean value was determined by an arithmetic average. The swelling is then calculated thanks to equation described in the part I-3.2.3 (page 36).

Once mass and volume variations have been determined, density is calculated as the ratio between mass and volume for each ageing time.

II-4.1.2 Viscoelastic mechanical characterisations

a. Vibration analysis

The viscoelastic parameters (elastic modulus and loss factor) of polyester matrix, FFRC and GFRC were determined using vibration analysis. From a general point of view, vibration techniques aim to study the dynamic behaviour of a structure thanks to its natural vibration modes [170]. This technique is non-destructive and easy to implement, so it is well suited for monitoring materials during ageing (Figure II-X).

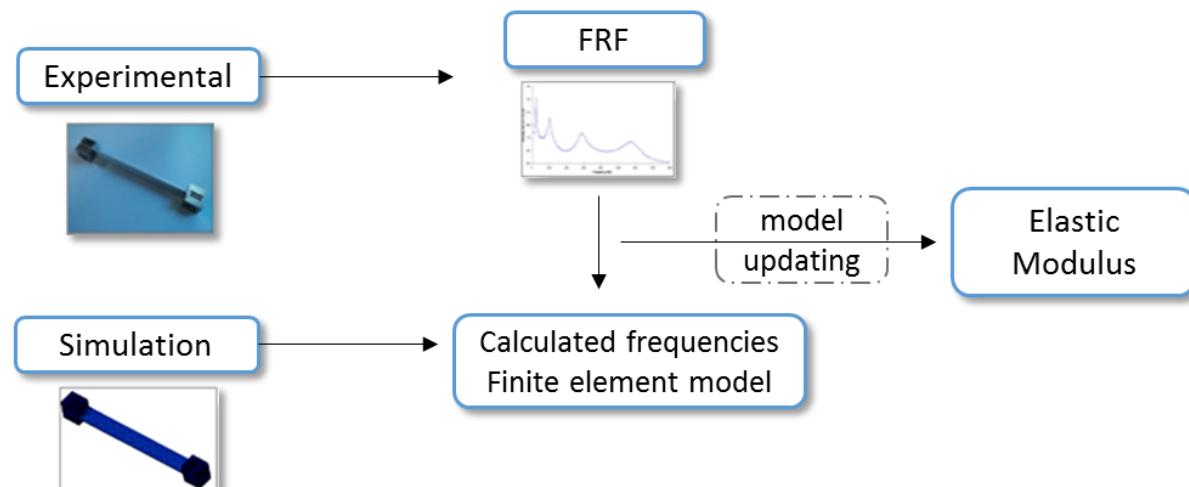


Figure II-X Schematic view of the elastic modulus determination by the vibration analysis technique.

For this study, the set-up simulates free boundary conditions by supporting the sample with soft suspensions [171]. The sample, a 250 mm x 25 mm beam, is excited in free vibration by an impulse hammer and its response is monitored by an accelerometer (see Figure II-XI). An additional steel mass ($m_0 = m_L = 86$ 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).

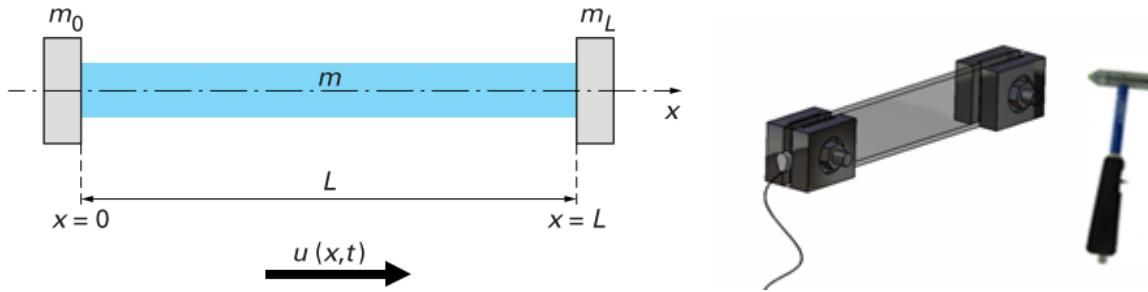


Figure II-XI Schematic representation of the vibration apparatus set-up (adapted from [172]).

The resonant frequencies of the sample are given by the series of peaks in the frequency response (Figure II-XII). The software MODAN®[®], developed by the FEMTO-ST (Université de Franche-Comté, Besançon, France), was used to extract natural frequencies and damping ratios from the frequency response function (by using a curve fitting technique).

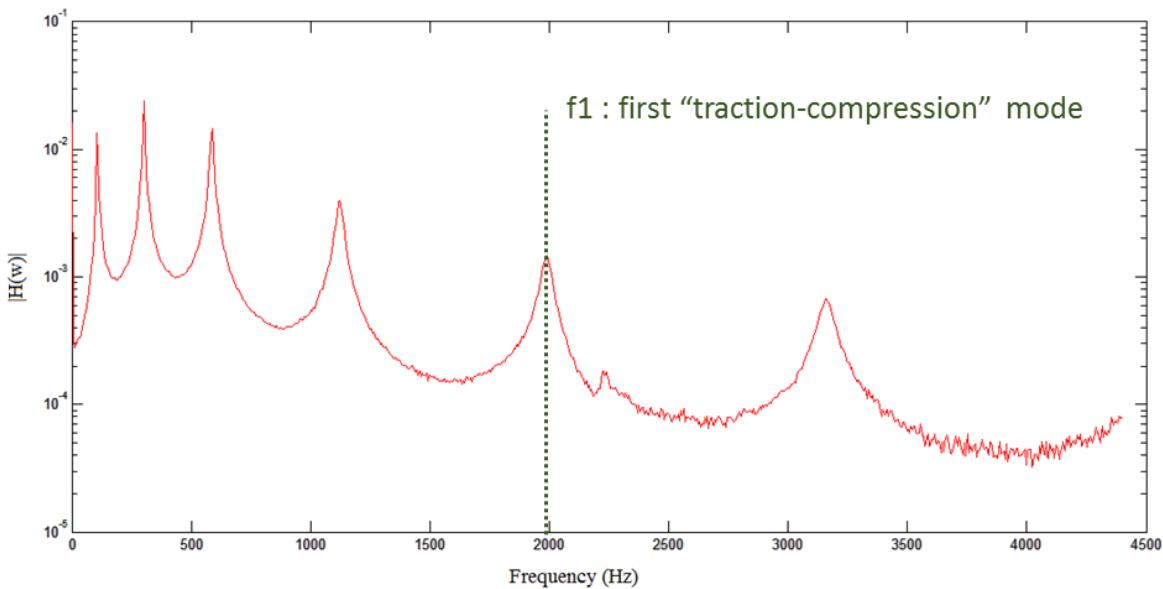


Figure II-XII Typical frequency spectrum of the impulse response of the composite samples.

Then, derived from the equation of the elastodynamic equilibrium of the first traction-compression mode, the expression of the axial (i.e. longitudinal) elastic modulus E is given by Equation II-I:

$$E = \frac{\rho L^2 f_1^2}{\left(\frac{\beta_1}{\pi}\right)^2} \quad \text{Equation II-I}$$

with β_1 being the lowest positive root of Equation II-II:

$$\beta_1 \cdot \tan \beta_1 = \frac{m}{M} \quad \text{Equation II-II}$$

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.

The damping ratio (a) of the first traction-compression mode is extracted from the impulse response in the vicinity of the corresponding resonance peak thanks to MODAN®.

The reproducibility of the vibration analysis technique was assessed. The dispersion (i.e. standard deviation divided by mean) was 1.4% for the elastic modulus and 2.6% for the damping ratio. Moreover, the elastic modulus measurement using the vibrations setup was validated with samples made of low viscous material (aluminium samples). For those materials, the difference between the elastic modulus measured using the vibrations technique and that from traction tests was lower than 2.0%.

b. Dynamic mechanical analysis

This technique is used to measure the viscoelastic properties of materials as a function of time and temperature. The dynamic properties were measured using a DMA 50 from *Metravib*. The samples were cut to size using a band saw. A tensile-compression configuration was used for testing samples presenting width and length of 10 and 50mm, respectively, at a frequency of 5 Hz. The linear domain was defined by preliminary strain sweep tests that led to a displacement of 10^{-2} mm. The storage modulus E' , loss modulus E'' and the $\tan\delta$ were recorded during testing.

II-4.1.3 Mechanical environmental coupling

A special set-up was developed in this work aiming to follow the creep strain and the elastic modulus of biocomposite samples exposed to in-situ coupled thermo-mechanical and mechanical-hydrothermal ageing (Figure II-XIII). A Dartec 100 kN machine is used to characterise the creep behaviour of composite samples by imposing a constant force to them. The samples displacement is measured by a LVDT sensor attached to the jaws. A recipient is attached to the inferior mobile jaw allowing to follow the mechanical properties of specimens immersed in water and exposed to humidity controlled atmosphere at 30°C, 50°C and 70°C.



Figure II-XIII Configuration of the mechanical-hydrothermal characterisation for flax fibre composites.

Composite samples are submitted to an initial charge that remains applied to the samples until the end of the test. During the test, samples are unloaded and immediately reloaded at a rate of 50 N.s^{-1} in order to monitor the evolution of the elastic modulus during the ageing test. Samples were loaded at 60, 90 and 120 MPa. The elastic modulus is determined during the unload phase (Figure II-XIV) from the slope of the stress vs strain curve. A measure is performed every 30 minutes until the fracture of the material or up to 900 hours. The reproducibility was measured on two or three samples.

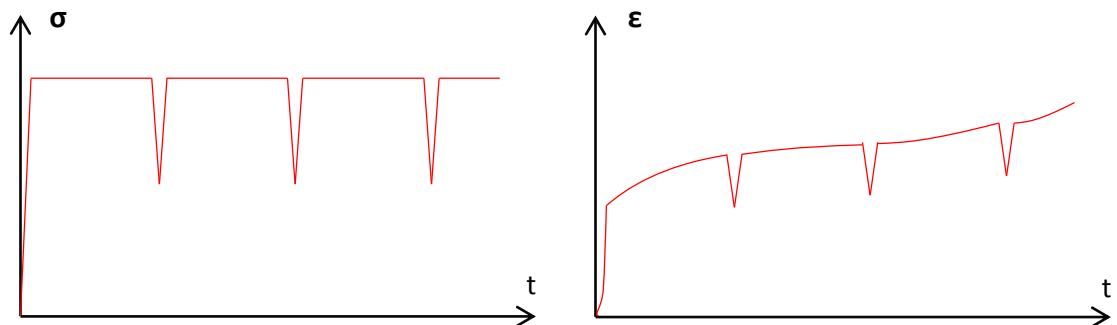


Figure II-XIV Schematic representation of the loading/unloading procedure employed to determine the elastic modulus during the creep tests

II-4.1.4 Synthesis of the monitoring tests

A schematic representation in Figure II-XV aims to provide a detailed view of the physical and mechanical monitoring tests realised in this work. All the characterisations are listed below:

Hydrothermal monitoring:

The composites physical properties (mass, volume and density) were monitored using a balance and a sliding caliper. The mechanical properties (elastic modulus and damping) were monitored by vibration analysis.

Mechanical-hydrothermal monitoring:

The composites mechanical properties (creep and elastic modulus) were monitored using a special creep set-up in a tensile mechanical press.

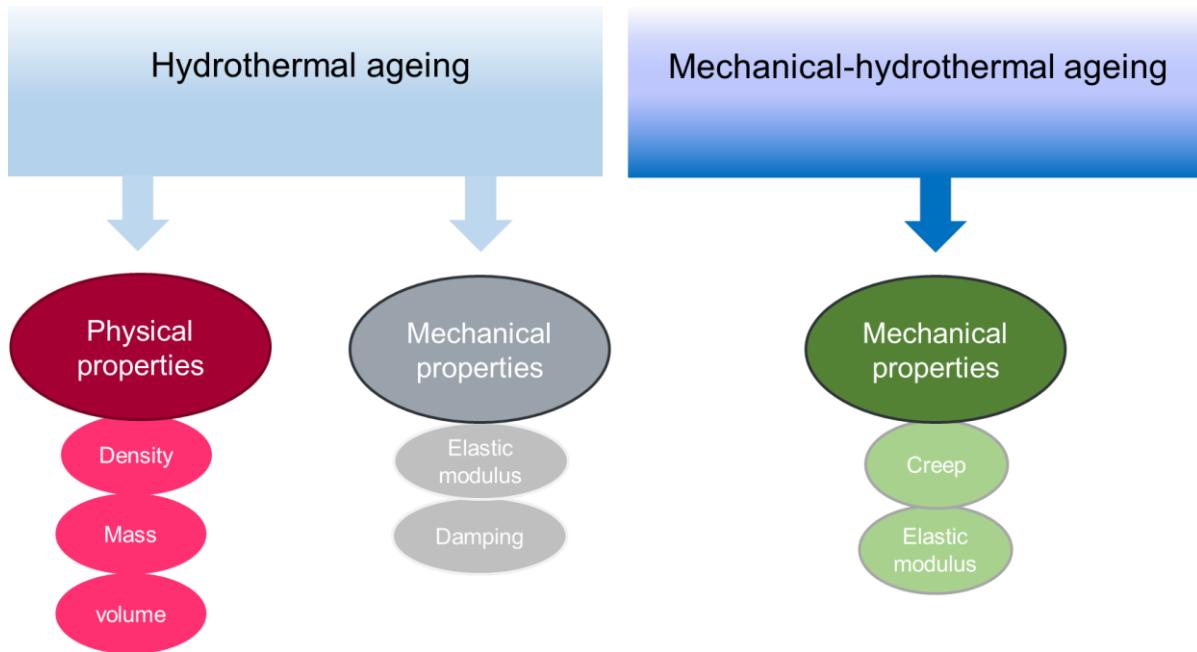


Figure II-XVA schematic view of the composites properties monitored during ageing tests.

This second part presents the morphological, physicochemical and mechanical characterisations performed at the initial condition before ageing and at saturation.

II-4.2. Morphological characterisation

II-4.2.1 Scanning electronic microscopy (SEM)

a. Fracture surface observation

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

b. Cross-section image analysis

The SEM technique was also used to observe the structure of the composite at different scales, and especially the morphology (shapes, dimensions, and arrangements) of flax fibres when impregnated by the polyester resin. A cross section of a composite sample is polished (without water) and prepared by depositing a thin layer of graphite. Microscopical images are then realized at the SEM, treated and analysed using the image analysis software *Aphelion®* that allows the statistical determination of morphological parameters, such as fibres and bundles surface area, perimeter, Feret width, Feret ratio and convexity (defined afterwards). The Figure II-XVI shows a schematic representation of an image analysed using *Aphelion®* software.

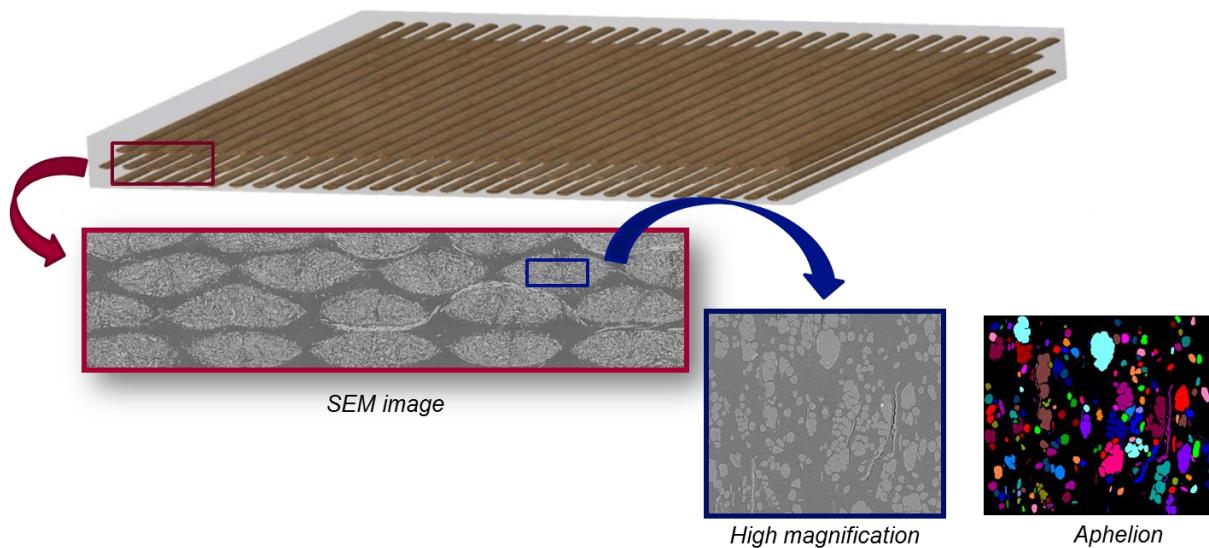


Figure II-XVI Schematic representation of the Image analysis from composites cross-sections.

The initial images processing was carried out using the open source Gimp 2.8. This software allows cleaning the images by using a manual pixel-by-pixel approach: carefully erase flaws, stem bark and blurred pixels on the outline of fibres. Also remove fibres crossing the image boundaries [173]. Then, the following steps were performed using *Aphelion®* software:

1 - The brightness contrast of grayscale was enhanced prior to converting to binary. A threshold value of approximately 170 on the grayscale (0–255) was found to allow sufficient differentiation and was therefore used for all pictures.

2 – The holes that correspond to the lumen of elementary fibres and the pectic cement inside the bundles were filled, in order to consider the whole bundle as a unitary particle.

3 - Then, fibre contours were smoothed by applying an opening-closing operation.

The morphological aspects of fibres and bundles are detected and treated by *Aphelion®* using the box minimum bounding rectangle (MBR) measurements. The following morphological features were determined by image analysis:

- The **surface area**, to be preferred to the equivalent diameter which is inaccurate for characterizing the geometric properties of natural fibres due to their complex shapes [174],

- the **perimeter** (here estimated from the Crofton method), uses a rotational average of the diametric variation to determine the perimeter of complex shapes. It is a robust measure of a perimeter (more complex than the 4-connectivity method)
- the **Feret width** defined as the breadth of the fibre bounding box onto a line of specified angle (see Figure II-XVII),
- the **Feret ratio** given by the ratio of the Feret length over the Feret width,
- the **convexity** is equal to the area of the fibre divided by the area of its convex hull. The latter is defined by the smallest shape that can completely contain the whole fibre such that for any straight line segment connecting two points on the convex hull's boundary, the entire line segment is contained inside the convex hull. This parameter varies from 0 to 1 where values closer to 1 refer to convex objects.

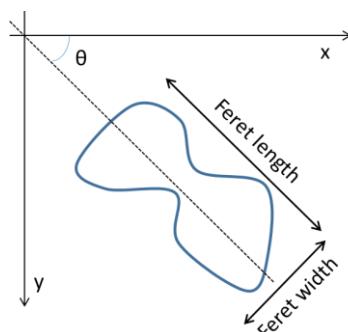


Figure II-XVII Feret length and width for a particle oriented at a specific angle.

II-4.3. Physicochemical analysis

II-4.3.1 Differential scanning calorimetry (DSC)

DSC was used to evaluate the glass transition temperature (T_g) and the cross-linking degree (X) of a partially and post-cured polyester resin. Thermograms were assessed using a Diamond DSC – Perkin Elmer (Figure II-XVIII). Polyester resin samples of approximately 20mg were analysed in aluminium pans. They were submitted to temperature ramps from 25°C up to 220°C at a heating rate of 10°C/min. The samples were cooled to 20°C and heated again to 220°C at 20°C/min. The cross-linking degree (X) was estimated from post-curing peak using the Equation II-III:

$$X = \frac{\Delta H_{total} - \Delta H_{peak}}{\Delta H_{total}} \times 100 \quad \text{Equation II-III}$$

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

The total reaction enthalpy was determined by curing the liquid resin in the calorimeter from 25°C to 220°C at a heating rate of 10°C/min.

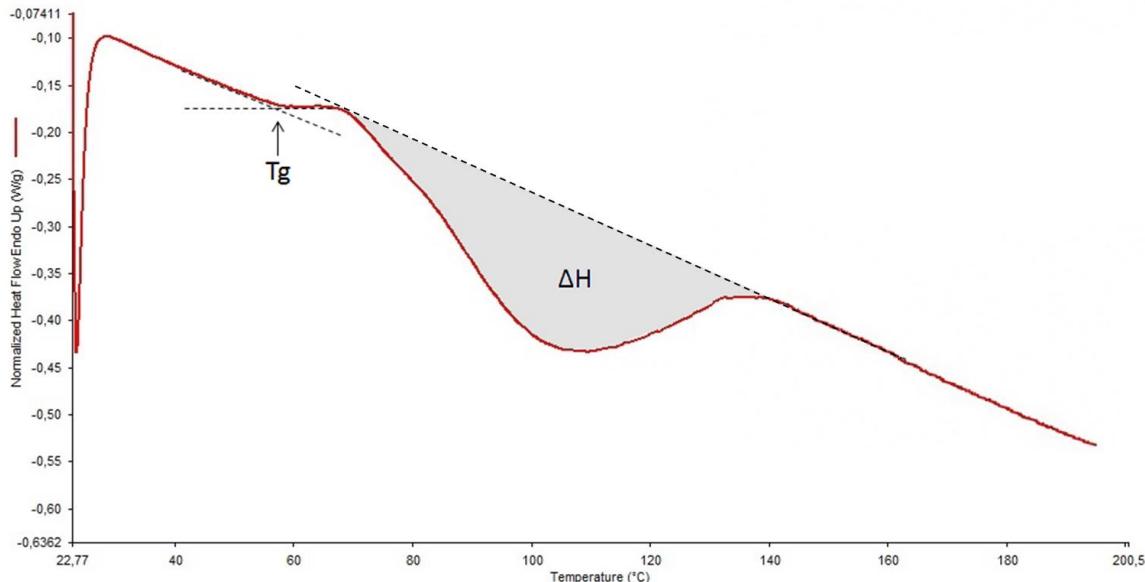


Figure II-XVIII DSC thermogram showing the determination of the T_g and the reaction enthalpie (ΔH).

II-4.3.2 Fourier transform infrared spectroscopy (FTIR)

ATR-FTIR was carried out in order to verify the chemical degradation (mainly hydrolysis) of the polyester resin during ageing in water. FTIR spectra were accessed using a Bruker IFS66 spectrometer (Golden gate reflexion system). Scans were collected for each measurement over the $4000\text{-}400\text{ cm}^{-1}$ spectral range with a 2 cm^{-1} resolution.

II-4.4. Mechanical testing

II-4.4.1 Uniaxial tensile tests

Simple tensile tests were carried out on composite specimens in order to access the elastic modulus and the ultimate (stress and strain) properties of glass and flax fibre composites. Two different set-ups were employed here based on the precision demanded for each measurement.

The elastic modulus was assessed with a Zwick testing machine (model B Z010/TH) equipped with a 10kN capacity load cell featuring an accuracy of 0.1 N and a clip-on extensometer providing an accuracy of 10^{-4} mm. The crosshead displacement was fixed at 1 mm/min for all composites according to the standard ISO EN 2747. The elastic modulus was calculated at the interval of 0.05-0.15% of strain for flax fibre composites instead of 0.05% - 0.25% stipulated in the standard ISO 527 dedicated to the tensile modulus measurements of plastic reinforced composites. This point will be discussed in details in Appendix 2. The reproducibility was evaluated on 5 samples.

The ultimate tensile properties of composite specimens were assessed with a MTS testing machine (model Criterion C45.105) equipped with a 100kN 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 strain was accessed by using a no-contact optic measurement based on the digital image correlation of the speckled surface of composite samples (see Figure II-XIX). The reproducibility was evaluated on 5 samples.

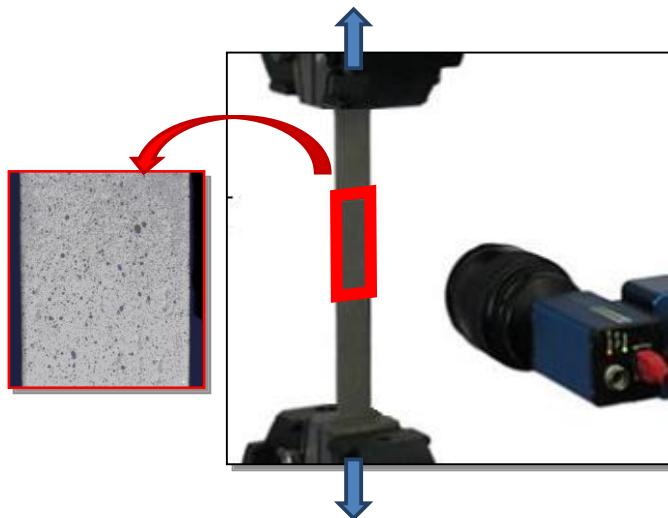


Figure II-XIX No-contact optic measurement based on the digital image correlation of the speckled surface of composite samples.

II-4.4.2 Interlaminar shear strength

The interlaminar shear strength measurements were realized on notched tensile samples based on the standard ISO14130 (see Figure II-XX). The specimens were 120 mm long and 25 mm wide, with a variable thickness for glass and flax fibres. The distance between notches is 20 mm. A MTS testing machine (model Criterion C45.105) equipped with a 10kN capacity load cell is used in tensile configuration for a crosshead displacement rate of 1mm/min.

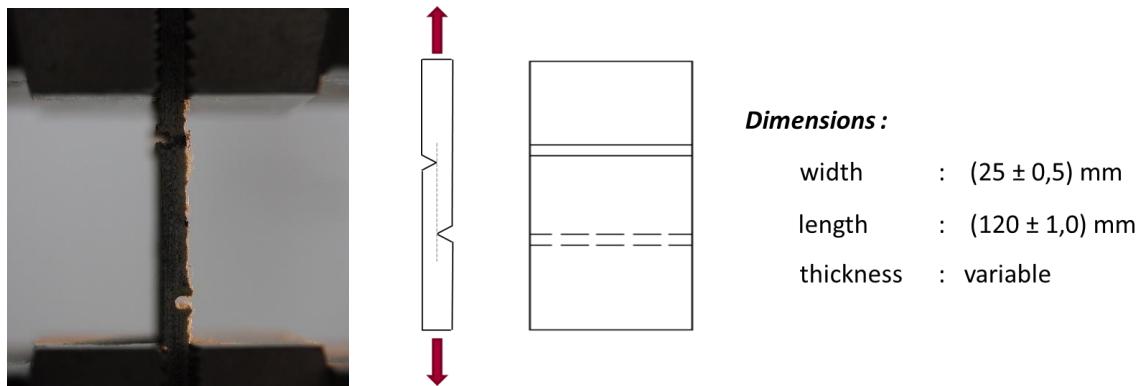


Figure II-XX Representation of the notched tensile samples used for ILSS tests.

The interlaminar shear strength is calculated by Equation II-IV:

$$\tau = \frac{F}{b \cdot d} \quad \text{Equation II-IV}$$

where τ - shear strength, in MPa;

F - maximum force at break, in N;

b - width, in mm

A calibration was realised by employing two gauge lengths (25 and 50 mm). The longer gauge length (50mm) was found to create stresses out of the interlaminar fracture plan and presented higher variation of the results compared to 25mm (4% compared to 7% respectively). So, the gauge length of 25mm was chosen for the further ILSS analysis.

Results and discussion

The materials and methods presented in the last chapter will be applied to study the ageing behaviour of biocomposites. The experimental results will be discussed and correlated to aspects addressed in the bibliographic section of this manuscript.

The first part of Chapter III consists in a preliminary study of materials and processing.

Flax fibres fabrics from different manufacturers are compared to select the more suitable one for performing the ageing study. The selection was based on mechanical tests performed both on textile fabrics and on composites.

The thermal behaviour of the polyester resin is then analysed through differential scanning calorimetry (DSC) in order to characterize the resin polymerisation degree.

Composites are then processed through two processing techniques: vacuum infusion and thermos-compression. The second part of Chapter III discusses the influence of processing conditions on the mechanical and the morphological properties of composites.

Then, the Chapter IV aims to study the ageing behaviour of composites. In the first part of this chapter, glass and flax fibre composites are immersed in water and their evolving behaviour is characterized until and after water saturation. In the second part, the samples are then dried in order to verify the reversibility of mechanical properties after hydrothermal ageing.

The third part concerns the hydro-thermo mechanical coupling behaviour of biocomposites. The impact of the mechanical ageing is verified by imposing a creep solicitation to biocomposites immersed in water.

The fourth and last part discusses the modelling of hydrothermal flax fibre reinforced biocomposites behaviour. A multi scale approach is proposed to take into account the flax fibre heterogeneous dispersion in the polyester matrix.

Chapter III. Preliminary characterisation of biocomposites

This chapter aims to provide a preliminary characterisation of the glass and flax fibres physical and mechanical properties. This step before impregnation with the unsaturated polyester matrix will be referenced as “fabric scale” in this work. Once fibres have been impregnated with the matrix, the properties of the composites are investigated at “composite scale”. The influence of the thermal cycle on the properties of physicochemical and mechanical properties of the unsaturated polyester resin is also investigated here. At the end of this chapter, one flax fabric and one resin post-curing condition will be selected to be used thereafter for long-term ageing tests detailed in the next section of this chapter (part III-2 - Influence of biocomposite processing conditions on their mechanical and morphological properties).

Chapitre III – Caractérisation préliminaire des biocomposites

Ce chapitre a pour objectif de fournir une première caractérisation des propriétés physiques et mécaniques des composites renforcés par des fibres de verre et par des fibres de lin. Les fibres sont testées avant imprégnation, dans une configuration référencée comme « échelle du tissu » dans ce travail. Une fois que les fibres ont été imprégnées par la résine, les propriétés du composite sont investiguées à l'« échelle du composite ». L'influence du traitement thermique (post-réticulation) sur les propriétés physicochimiques et mécaniques de la résine polyester insaturé est également investiguée dans cette partie. Trois tissus de fibre de lin (issus de différents fournisseurs) sont testés et, à la fin de ce chapitre, un tissu de fibre de lin et un cycle de traitement thermique seront sélectionnés pour être utilisés dans les essais de vieillissement à long terme présentés dans la deuxième partie de ce chapitre (part III-2 - Influence of biocomposite processing conditions on their mechanical and morphological properties).

III-1. Characterisation and selection of the basic constituents

An inventory of the first results obtained for the characterisation of glass and flax fibre reinforced composites is presented here.

In the first part, unidirectional flax fabrics supplied by three different manufacturers were tested at a “fabric scale” with the objective of comparing their mechanical and dimensional aspects to glass fabrics. Then, the properties of flax fibre composites compared to glass fibre composites at a “composites scale”. The second part concerns the polymeric matrix used to produce composites: an unsaturated isophthalic polyester resin. The matrix curing and post-curing conditions are detailed by comparing the influence of the thermal cycle on their mechanical and physical-chemical properties.

Glass fibre composites were elaborated at the laboratory of the Ecole des Mines d’Alès (Alès, France) using the same materials (resin and fibres) and the same processing conditions as those employed by the company Outremer (La Grande Motte, France) for boat components fabrication.

III-1.1. The choice of the flax fabric

Before starting the ageing tests, the first decision concerns the choice of flax fibres. Three flax fabric suppliers were chosen for their capacity to furnish good quality flax fibres in sufficient quantity for the production of full scale boat components. The companies Biorenforts (Longvic), Chomarat (Le Cheylard) and FRD (Fibres Recherche Developpement - Troyes), all located in France, are able to supply two types of flax fabrics: unidirectional and triaxial flax fibre fabrics. Unidirectional fibres are used in this study to produce composites at laboratory scale. In this case, composites are reinforced unidirectionally in order to simplify the experimental study and the modelling of the composites diffusion behaviour. Triaxial fabrics are considered as a way to explore a future scaling up to boat components. The flax fibre supplier must be able to ensure this transition from laboratory to the shipyard.

The methodology applied to this chapter is to analyse the flax fibres behaviour at fabrics and composites scale aiming to choose the flax fabric presenting the best performance once processed into composites.

III-1.1.1 Characterization at the “Fabric scale”

a. *Physical properties*

The visual aspect (Figure III-I) and technical databased (Table III-I) of the flax fabrics consist in a first approach, to analyse the differences between them. The reference is the glass fabric supplied by Chomarat with 0.4 mm of thickness and 416 g/m² of areal weight (408 g/m² in weft direction and 8 g/m² in warp direction). The flax fabric supplied by Biorenforts is thicker than the others, which might lead to thicker composites after processing. Another basic difference between the three fabrics is noted for Chomarat fabric: flax fibres are assembled using transverse glass fibres and a polyester substrate in a so-called “UD hybrid” configuration. Biorenforts and FRD flax fabrics are made with unidirectional flax fibres linked together by cotton fibres in the warp direction.

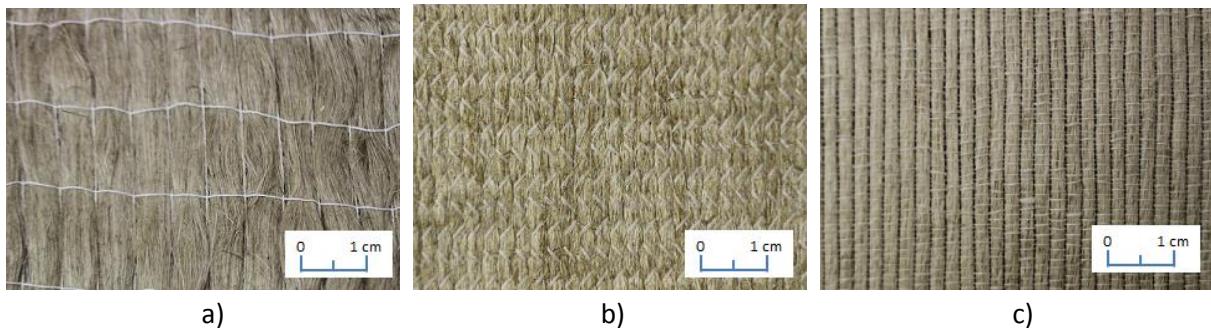


Figure III-I Flax fabrics supplied by: a) Biorenforts ; b) Chomarat and c) FRD.

Table III-I Flax fabric technical database compared to glass fabric (informed by the suppliers).

Type	Fibres Orientation	Supplier	Weight (g/m ²)	Thickness (mm)
Glass	UD	Chomarat	416	0.4
	UD	Biorenforts	400	1.4
Flax	UD "hybrid"	Chomarat	670	0.5
	UD	FRD	360	0.4

The total weight of fabrics was determined by isolating and weighing the fibres in the warp and weft direction by using a precision balance (precision of 10^{-4} g). A total of five samples ($50 \times 50 \text{ mm}^2$) were analysed for each fabric. The areal weight (in grammes per square meters) informed by the suppliers was experimentally determined. The fibre concentration in weft and warp direction was moreover evaluated (Table III-II). Concerning glass fibres a good agreement with the database was obtained. Concerning flax fabrics, results show that FRD flax fibres have 9% of fibres in warp direction while Biorenforts flax fibres have 4%. Therefore FRD fabrics could be classified as quasi-unidirectional fabrics because of their relatively high concentration of fibres in warp direction (about 10%). Concerning Chomarat fabrics, a significant proportion of their total weight is composed by glass fibres in the weft binding yarn and the polyester substrate (about 19%), which may result in a complex material to study and model.

Table III-II Weight of flax fabrics determined experimentally in weft and warp direction.

Type	Fibres Supplier	Total weight (g/m ²)	weight (weft) (g/m ²)	weight (%)	weight (warp) (g/m ²)	weight (%)	Substrate (g/m ²)	Substrate (%)
Glass	Chomarat	416±11	408±17	98%	8±1	2%	-	-
	Biorenforts	446±17	429±19	96%	17±4	4%	-	-
Flax	Chomarat	825±8	676±12	82%	23±2	3%	128±2	16%
	FRD	369±14	335±11	91%	34±2	9%	-	-

b. Mechanical properties

Flax fabrics were analysed in uniaxial tensile tests to determine the fabrics breaking strength. The distance between the jaws has an important role in the determination of the fabrics fracture mechanism. Tensile testing of yarns is widely employed by the textile industry as a way of controlling yarn quality. The tests are realised with relatively large gauge lengths (standard is 250 or 500 mm ;

ASTM D2256; ISO2062), and the results reflect therefore long-range behaviour where fibre-fibre friction is a essential factor. A short-range behaviour was found to approximate the properties of the fibres, while long-range yarns generates fibre-fibre frictional forces [70].

In this work, three gauge lengths were tested: 22 mm, 53 mm and 106 mm. A distance of 22 mm between jaws (Figure III-II-a) leads to a sharp fabric fracture where the major mechanism is identified as the breaking of the technical fibres. Increasing the distance between the jaws (106 mm - Figure III-II-b) induces to an important change in the fabric rupture mechanism: the flax fibres slips against each other. This mechanism is called disentanglement, a progressive mechanism that modifies considerably the aspect of the curve load vs displacement after the maximum force (the curve is more fluctuating at 106mm compared to 22mm).

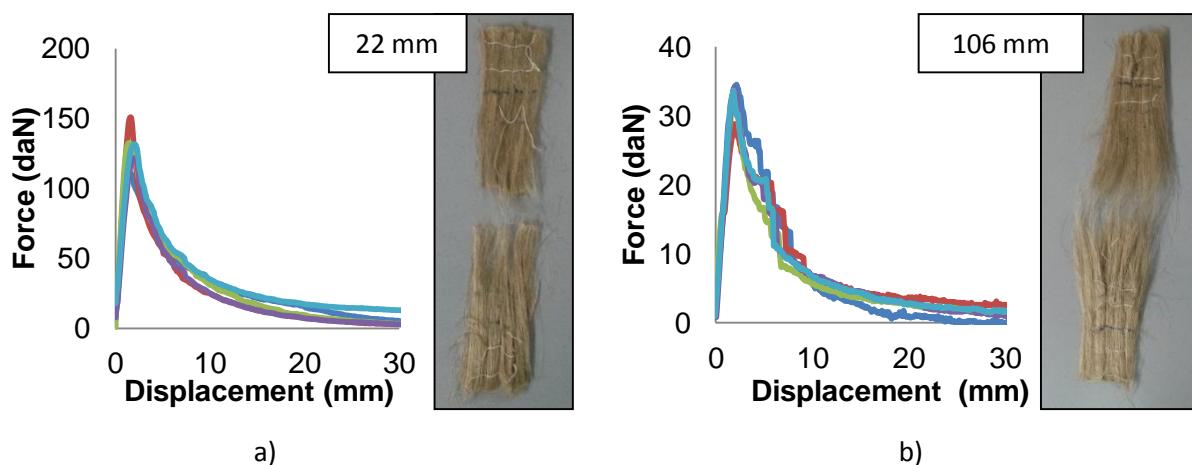


Figure III-II Fracture mechanisms of Biorenforts flax fabrics during uniaxial tensile test: a) a fabric sharp break and b) the fibres disentanglement mechanism.

The slope of the yield curve and the maximum tensile force (Figure III-III) can be determined as well. It can be observed that the slope and maximum load decrease with the increasing gauge length. This effect is linked to the length of the fibres, which can explain the lower sensitivity to gauge length displayed by glass fibres compared to flax fibres. The probability to have the endings of the fibre clamped on both extremities of the jaws are higher for glass fibres because of their longer fibres. The analyse of the fracture surface confirmed that fibres breaking is the major mechanism of glass fabrics even if some disentanglement was also observed. Concerning the flax fabrics, the disentanglement mechanism explained above is confirmed here by the decrease of the maximum tensile force with the gauge length.

At equal gauge length, it can be noted that the Chomarat fabric displayed the higher values of maximum load but the lower results of slope between the flax fabrics. These results are probably related to the fact that flax fibres are supported by the polyester substrate and glass fibres in warp direction, which promote the consolidation of the flax fabric in the weft direction mainly when exposed to high loads. The FRD fabric shows intermediate values of maximum load, while the Biorenforts flax fabrics display the lower values compared to other flax fabrics probably because their yarns are not twisted. For this reason, we observe a higher disentanglement, which means that flax fibres slippage is the main mode of failure instead of fibres breakage.

Even if it is tempting to make conclusion about the fibres properties, some caution needs to be taken when analysing the tensile characterisation of a flax fabric. This characterisation is influenced by

other parameters than the fibre properties, such as the gauge length and the fabric weaving process conditions. The latter can alter the mechanical behaviour of the flax at a fabric scale. However, Liu and Hughes [175] highlighted that the fracture behaviour and toughness (K_{IC}) of flax composites was found to be not influenced by the weave type. The authors concluded that toughness in composites is dominated by the properties of the fibre (and the fibre volume fraction), rather than the reinforcement architecture. However a superior balance of stiffness, strength and toughness can be achieved by improving the yarn and fabrics design.

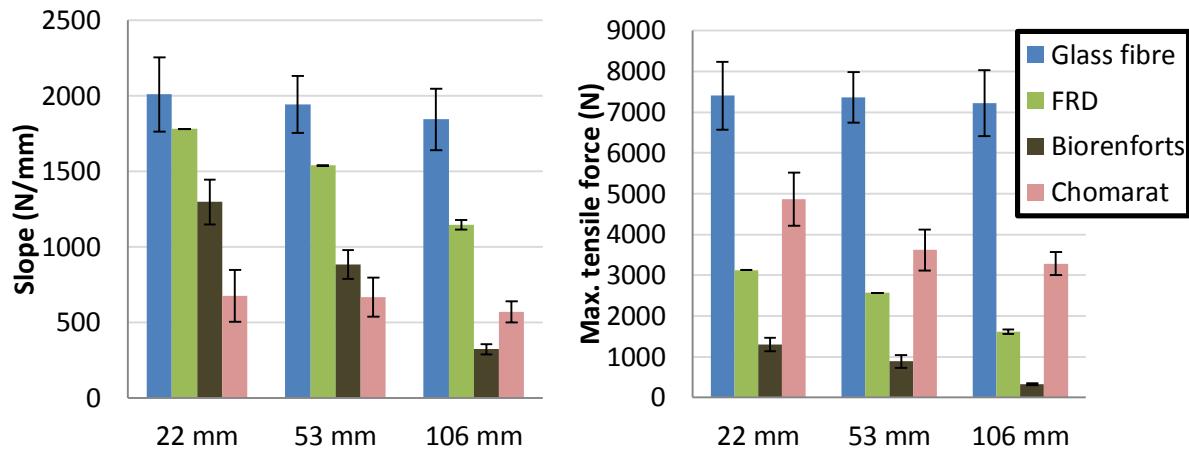


Figure III-III Slope of the yield curve and maximum tensile force of different flax fabrics compared to glass fibres as a function of the distance between yaws.

From this part of the characterization of the flax fibres behaviour at a “fabric scale” it can be concluded that the FRD fabric is a good candidate because of its low thickness, and relative good mechanical properties compared to the two other flax fabrics tested in this work. The Chomarat flax fabric could be an interesting candidate, but its heterogeneous composition could make the experimental and model study more complex at the composites scale.

III-1.1.2 Characterization at the “Composites scale”

a. Physical characteristics

Biocomposites are produced so that the same areal weight as glass fibre composites (six layers of 400 g/m² each layer) is obtained. Six layers of Biorenforts and FRD flax fabrics, and four layers for Chomarat flax fabrics are used to obtain a total areal weight of 2400 g/m². Composites thickness, and therefore fibre content, depends on flax fabrics arrangement. This dependency is clearly demonstrated in

Table III-III : six layers of Biorenforts fabrics produce composites with 5.61 ± 0.31 mm of thickness while six layers of FRD fabrics produce thinner composites (4.86 ± 0.14 mm of thickness). Fibre content increases for thinner composites (for a same fabric weight): fibre volume content increases from 26.3% \pm 1.9 % for Biorenforts composites, to 31.1% \pm 0.4 % for FRD composites. Fibre content for Chomarat composites is not defined since it consists in hybrid fabrics (glass and flax fibres).

Table III-III Thickness, density and fibre volume content values for flax composites reinforced by diverse flax fabrics.

Composite	Layers	weight	Thickness	Density	Mass*	Fibre vol. content
	<i>units</i>	(g/m ²)	(mm)	(g/cm ³)	(g)	%
GFRC	6	416	1.70 ± 0.11	2.08 ± 0.04	20.20 ± 0.53	61.0 ± 0.6
FFRC (Biorenforts)	6	400	5.61 ± 0.31	1.27 ± 0.01	43.70 ± 1.33	26.3 ± 1.9
FFRC (Chomarat)	4	670	4.16 ± 0.15	1.34 ± 0.01	33.92 ± 0.61	-
FFRC (FRD)	6	360	4.86 ± 0.14	1.27 ± 0.01	37.83 ± 1.05	31.1 ± 0.7

*Mass values correspond to tensile specimens (250 mm x 25 mm).

The Figure III-IV shows the visual aspect and the microscopic images of the studied three FFRC. The high variability in thickness for Biorenfort composites is confirmed by cross-section pictures. The other cross-section pictures show a more constant thickness of the samples. Moreover MEB pictures show that flax yarns distribution within the composites changes according to the fabrics design. The yarns are more readily visible into the matrix for Chomarat and FRD composites, arranging itself in a rectangular configuration for Chomarat (Figure III-IV-b) and in an elliptical configuration for FRD composites (Figure III-IV-c). In Figure III-IV-b, glass fibers appear in white in the transverse direction.

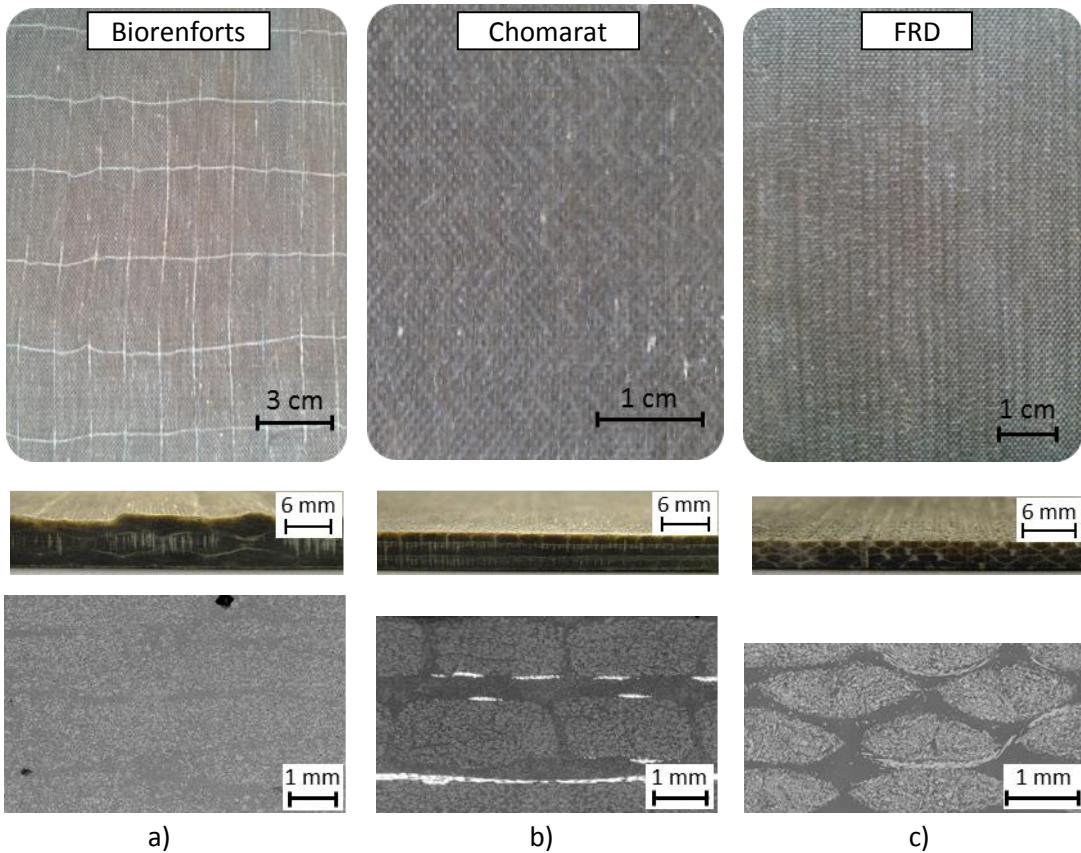


Figure III-IV Visual aspects (top and middle pictures) of the surface and of the cross-section of vacuum infused composites; and electronic microscopy observations (bottom pictures) of flax fibre composites reinforced by: a) Biorenforts, b) Chomarat and c) FRD flax fabrics.

Looking closer at the microscopic images, a qualitative and quantitative morphological analysis lead to some conclusions about the composites:

- Composite final thickness depends on yarn dimensions and its capacity to deform under pressure (for the same processing conditions – 100 mbar of vacuum pressure). In this case, composites fibre content can be improved by employing adequate designed fabrics. It consists in changing weaving parameters to obtain more compact and deformable flax fabrics;
- The yarn dimensional parameters when impregnated into composites are described in Table III-IV, and its arrangement into the polyester matrix is shown in Figure III-V. It can be noted that the Biorenforts yarns possess an aspect ratio (width/height) much higher than the two other yarns and a better dispersion into the polyester resin. The other yarns (FRD and Chomarat) presented a squared and ellipsoidal respectively, and matrix rich zones surrounding the yarn. The characterisation of the yarn dimensions will assist the understanding of the experimental results and the creation of the diffusion model based on the realistic biocomposites microstructure.

The yarn dimension measurements was realised by analysing the MEB images using the *Gimp* software.

Table III-IV Yarn dimensions for Biorenforts, Chomarat and FRD flax fibre composites.

Composites	Yarn dimensions	
	width (mm)	height (mm)
FFRC (Biorenforts)	8.62 ± 0.23	1.15 ± 0.19
FFRC (Chomarat)	2.68 ± 0.09	1.23 ± 0.12
FFRC (FRD)	2.18 ± 0.12	0.72 ± 0.17

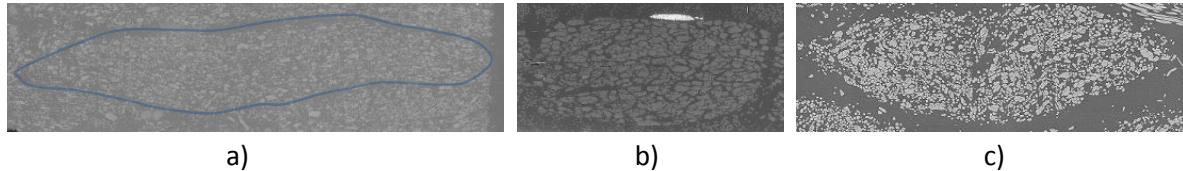


Figure III-V Dimensional aspect of flax yarns for: a) Biorenforts; b) Chomarat and c) FRD composites

The dimensional aspects (fibres diameter and shape factor) of the unitary flax fibres when impregnated into a polyester matrix under vacuum pressure are presented in Table III-V. No difference can be noted because of the high standard deviation (about 30% for fibres diameter and 20% for fibres shape factor). It can be also observed that FRD composites (Figure III-VI-c) presents a higher concentration of unitary fibres dispersed in the polyester matrix than Chomarat (Figure III-VI-b) and Biorenforts composites (Figure III-VI-a). Chomarat in particular presents a higher concentration of bundles that remains connected after processing.

The diameter and the shape factor measurements were realised by analysing MEB images using the Aphelion software.

Table III-V Unitary flax fibre dimensions for Biorenforts, Chomarat and FRD flax fibre composites.

Flax fibre supplier	Diameter	Shape factor
Biorenforts	$18.0 \pm 4.8 \mu\text{m}$	1.39 ± 0.22
Chomarat	$18.3 \pm 5.4 \mu\text{m}$	1.54 ± 0.28
FRD	$19.5 \pm 5.7 \mu\text{m}$	1.51 ± 0.37

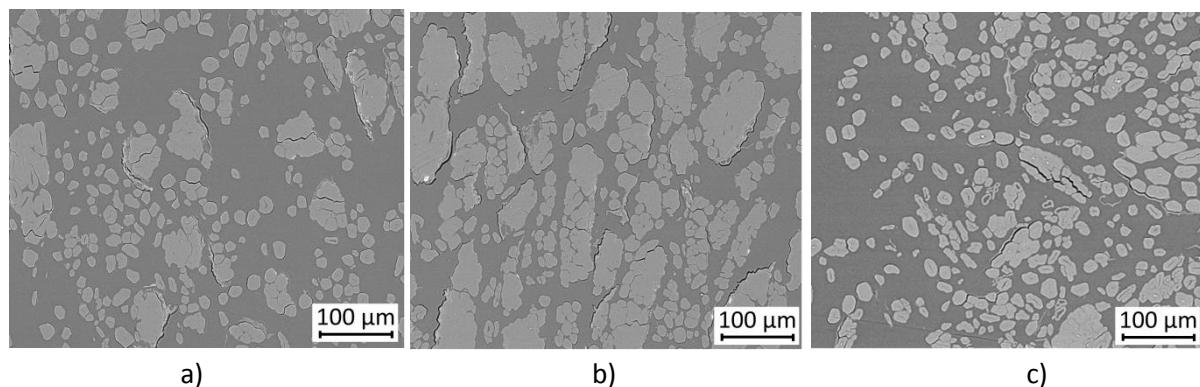


Figure III-VI Dimensional aspect of : a) Biorenforts ; b) Chomarat and c) FRD composites

b. Mechanical properties

Ultimate and elastic properties are determined for flax fibre composites (see Table III-VI). The Young modulus value for Biorenforts composite is equal to 14.7 ± 1.1 GPa (for a fibre content of $26.3 \pm 1.9\%$) while FRD composite show a value of 16.6 GPa (for a fibre content of $31.1 \pm 0.4\%$). However the ultimate tensile stress of Biorenforts composites is higher than those of FRD composites (195 ± 13 MPa compared to 167 ± 4 MPa). This result may be related to a better interfacial adhesion between Biorenforts fibres and the polyester matrix. Unfortunately, the results of impact tests highlight the influence of composites thickness on mechanical properties: the vacuum infusion process does not allow to control the thickness of the composite whereas this test allows comparison if based on the same section. The high values of impact resilience observed for Biorenforts composites are related to a structural aspect (higher thickness compared to the others flax fibre composites). Caprino et al. highlighted the dependency of the absorbed energy during impact tests with the fibre volume fraction and the thickness of hemp fibre reinforced epoxy composites. Sanadi et al. [176] reported a value of 21.5 KJ/m² in a *Izod* notched test for a uniaxial hemp polyester composite with a fibre volume content of 24%, while Albuquerque et al. [177] reported a *Izod* impact strength of 84.2 KJ/m² for jute polyester composites

Table III-VI Ultimate and elastic mechanical properties of FFRC's reinforced by diverse flax fabrics.

Composite	Thickness (mm)	Fibre vol. content %	Young Modulus GPa	Ultimate tensile stress MPa	Ultimate tensile strain %	Charpy impact resilience KJ/m ²
FFRC (Biorenforts)	5.61 ± 0.31	26.3 ± 1.9	14.7 ± 1.1	195 ± 13	1.34 ± 0.12	70 ± 4
FFRC (Chomarat)	4.16 ± 0.15	-	19.2 ± 2.0	201 ± 5	1.04 ± 0.37	53 ± 5
FFRC (FRD)	4.86 ± 0.14	31.1 ± 0.4	16.6 ± 1.3	167 ± 4	1.12 ± 0.1	54 ± 4

The rule of mixture can be used to determine a theoretical longitudinal Young's modulus of the unidirectional composites according to Equation III-I:

$$E_{\text{composite}} = E_{\text{fibre}} V_{\text{fibre}} + E_{\text{matrix}} V_{\text{matrix}} \quad \text{Equation III-I}$$

where

E_x : Young modulus of the component x ; ($E_{\text{fibre}} = 59$ GPa and $E_{\text{matrix}} = 3.4$ GPa)

V_x : Fibre volume content of the component x .

The value of the matrix modulus was experimentally determined, while the fibre modulus was reported in the literature as the average of the values described by Lamy and Baley [178].

The theoretical Young modulus takes into account real parameters for its calculation. It consists in a fairly good estimation of the composite properties, even if the model assumes that the composite contain no porosity. Biorenforts and FRD composites present results for experimental Young modulus close to the values determined by the rule of mixture (Table III-VII). The theoretical Young modulus for the Chomarat composite was not determined because of its hybrid configuration (flax and glass fibres).

Table III-VII Theoretical (rule of mixtures) and experimental Young modulus of flax composites reinforced by diverse flax fabrics.

Composite	Thickness	Density	Fibre vol. content	Young modulus	
	(mm)	(g/cm ³)	%	<i>Experimental</i>	<i>Theoretical</i>
FFRC (Biorenforts)	5.61 ± 0.31	1.27 ± 0.01	26.3 ± 1.9	14.7 ± 1.1	18.1 ± 0.9
FFRC (Chomarat)	4.16 ± 0.15	1.34 ± 0.01	-	19.2 ± 2.0	-
FFRC (FRD)	4.86 ± 0.14	1.27 ± 0.01	31.1 ± 0.4	16.6 ± 1.3	20.7 ± 0.3

The analysis of the fracture surface of composites after tensile tests (Figure III-VII) shows that fibres present a brittle fracture mechanism when impregnated by a polyester matrix for all composites in this study. It is interesting to note that polyester matrix penetrates into flax fibre from surface to the core of the fibre (Figure III-VIII). All fibre walls and also the lumen are impregnated by polyester matrix which means that fibres behaviour and morphology before processing are not the same after being processed. Mohanty and al. [179] reported the filling of the lumen by the polymer matrix during compounding and processing of WPC (Wood Polymer Composites) as the key in optimising the composites properties. Other studies reported a similar phenomenon [180] [181], in particular Hepworth et al. [182] proposed a treatment to increase the penetration of an epoxy resin into the cell walls of plant fibres. This treatment was found to increase the stiffness of flax fibre epoxy reinforced composites. The fact that the flax fibres were impregnated by the polyester resin in this work can explain the low difference found between the experimental and theoretical composite stiffness.

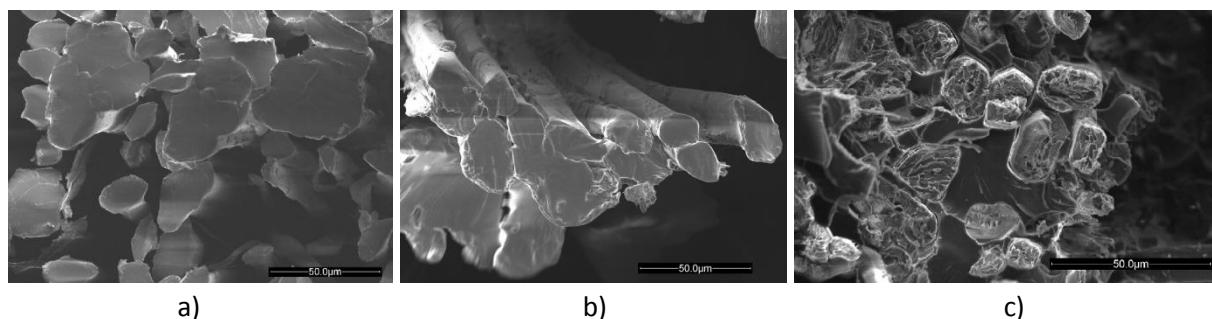


Figure III-VII Fibre fracture mechanism when impregnated by a polyester matrix for : a) Biorenforts ; b) Chomarat and c) FRD composites.

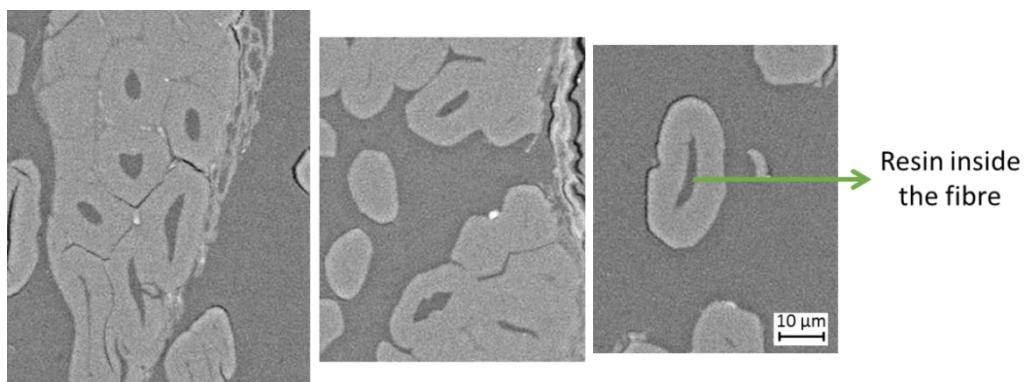


Figure III-VIII The presence of the UP matrix inside the lumen of flax fibres (magnification of 500X).

The flax fabric which provides better composites mechanical properties with higher fibre content is the unidirectional flax fabrics supplied by FRD. The flax fabric supplied by Chomarat shows good results but its assembly of materials (flax plus glass and polyester fibres) could make the experimental study of composites mechanical and diffusion behaviour more complicated.

III-1.2. Characterization and selection of curing and post curing conditions of the polyester resin

In some shipyards, the boat hulls remain exposed to outdoor conditions for about 5 months before launching in water. During this time the hulls harden at ambient temperature (post-curing behaviour) related to an incomplete polymerisation of the polyester matrix during processing (Figure III-IX).



Figure III-IX Curing and post-curing steps of boat hulls before launching in water.

Therefore it is suggested in this part to determine the polymerisation degree of the polyester resin using differential scanning calorimetry. The resin viscoelastic properties are then studied through dynamic mechanical analysis. The objective here is to determine the crosslinking degree of the polyester matrix after post-curing during 5 months at ambient temperature and to propose a post-curing treatment using an oven in the laboratory

a. Crosslinking rate

Six thermal cycles are investigated (Table III-VIII). The first cycle is the reference of a polyester resin tested immediately after curing (without post-curing treatment). The second cycle corresponds to the polyester resin post-crosslinking at outdoor conditions during 5 months. Then, cycle 3 to cycle 6 are realized using an oven in laboratory with a variation in post curing time (between 16h to 72h) and temperature (40°C and 60°C).

Table III-VIII Thermal cycles investigated for polyester matrix post-curing.

Materials	Thermal cycle	
	Curing	Post-curing
Cycle 1.	24h / 23°C	-
Cycle 2.	24h / 23°C	5 months / 23°C
Cycle 3.	24h / 23°C	16h / 40°C
Cycle 4.	24h / 23°C	24h / 40°C
Cycle 5.	24h / 23°C	72h / 40°C
Cycle 6.	24h / 23°C	24h / 60°C

Results for the glass transition temperature (first and second heat) and crosslinking degree are shown in Figure III-X. Polyester resin cycle 1 (cured without post-curing treatment) presents a crosslinking rate of $77.7 \pm 0.7\%$. After post curing an increase in the crosslinking rate is observed with values varying between 86.8% and 88.6% . The same behaviour is obtained for the glass transition temperature, which increases with the exposure time to thermal treatment (from 59.6°C to values varying between 64.6°C and 67.0°C). The T_g for the cycle 1 at the first heating cannot be determined due to the superposition of the beginning of the crosslinking reaction and the T_g . Then, the evolution of the cycle 1 compared to the other cycles was realised by analysing the second ramp of heating. For the post-curing cases, the values were found to range between $59^\circ\text{C} - 67^\circ$ in the first heating, and $96.9^\circ\text{C} - 99.7^\circ\text{C}$ in the second heating. Perrot [9] observed a similar behaviour for unsaturated polyester and vinyl ester polymers exposed to different thermal cycles. The author reported a glass transition temperature between $57.8^\circ\text{C} - 62.7^\circ\text{C}$ at the first heating, and $103.7^\circ\text{C} - 101.2^\circ\text{C}$ at the second, for a unsaturated polyester resin post-cured at 40°C during $16\text{h} - 48\text{h}$, respectively. The crosslinking rate ranged from $88.9\% - 90.9\%$.

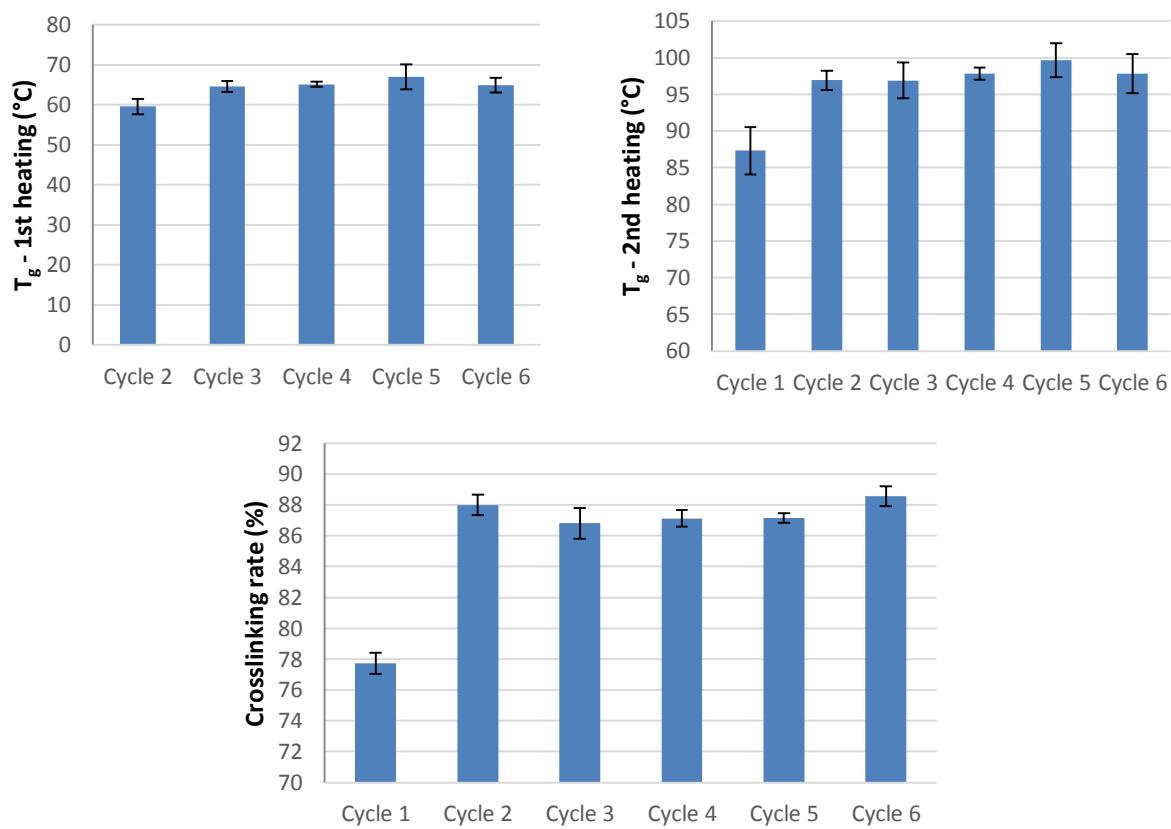


Figure III-X Glass transition temperature (first and second heating) and crosslinking rate for the polyester resin exposed to different thermal treatments.

The evolution of the glass transition temperature as a function of the post-curing time (for the same post-curing temperature of 40°C) (Figure III-XI) seems to follow a linear trend (the variation in temperature of less than 5°C is too small to confirm this trend). However, the value of the T_g without post-curing treatment (around 64°C for the T_g value extrapolated to zero time) do not correspond to the T_g determined experimentally for the polyester resin before post-curing treatment ($T_g=59.6^\circ\text{C}$). This may means that the evolution of the polyester's T_g do not present the same kinetics during the thermal treatment duration.

Concerning the evolution of the polymer's crosslinking ratio, the trend was found to be not linear with a stabilisation observed between 24 and 72 hours. It could be more interesting here to observe the evolution of the crosslinking ratio during the interval between zero and 16 hours to identify a complete evolution of the crosslinking rate with the thermal cycle.

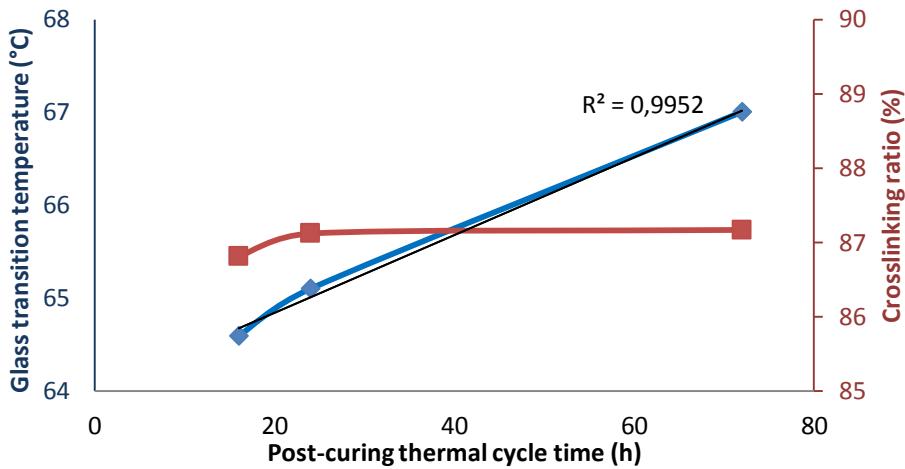


Figure III-XI Evolution of the glass transition temperature (first heating) and the crosslinking rate in function of the post-curing time (at the same temperature of 40°C).

b. Mechanical properties

The Figure III-XII presents the evolution of the polyester viscoelastic mechanical properties as a function of temperature (tests were performed at 10°C/min at a frequency of 5 Hz and a deformation of 10^{-2} mm). The peak of $\tan \delta$ observed around 140°C corresponds to the mechanical relaxation of the polyester resin associated to the glass relaxation temperature ($T\alpha$).

The mechanical tests realised with the only cured (but not post cured) resin (cycle 1) highlight the presence of two peaks of damping: the first peak at 98°C (Figure III-XII-a) disappears when polyester resin undergoes a post-curing treatment (Figure III-XII-b). This behaviour is related to the presence of partially crosslinked zones into the polyester resin before post-curing treatment. The effect of thermal treatment is to increase the tridimensional state of molecules and hence homogenize their crosslinking degree. Fraga et al. [48] associated this phenomena to an instability in the measurement. Visco et al. [183] suggested that the presence of two peaks of loss factor can be attributed to a partially cured network, while a single peak reveals the presence of a fully cured network, and therefore, a single glass transition region.

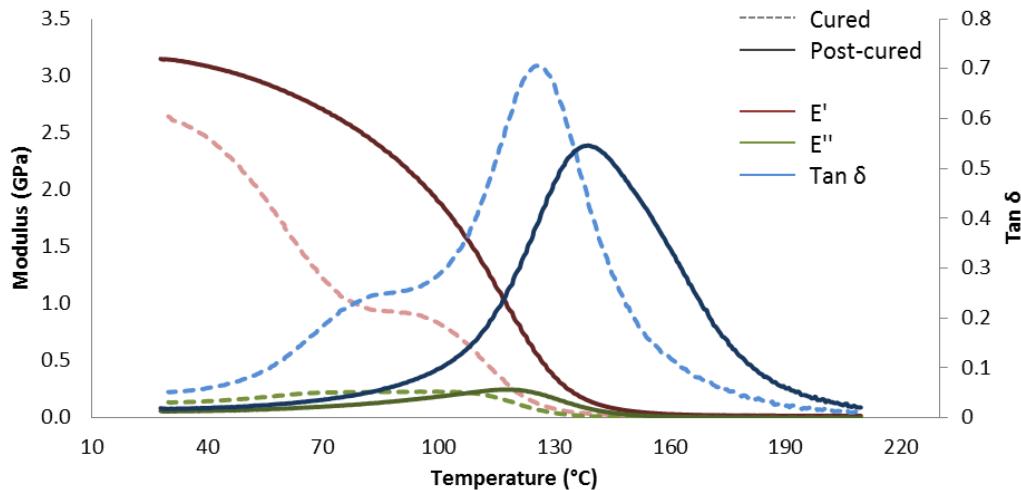


Figure III-XII Dynamic mechanical analysis of cured polyester resin compared to post-cured with cycle 1 (5 months at 23°C).

Polyester resin hardens and increases stiffness with crosslinking rate. The Figure III-XIII highlights the increase of the Young modulus with the post-curing treatment (Cycle 2 to 6) compared to the under-cured samples (Cycle 1). Post-crosslinking the polyester resin led to a decrease of its damping and therefore the loss factor, tan δ. It can be noted that the duration of the thermal treatment had little impact on the polyester modulus by comparing the cycles realised at 40°C (Cycles 3, 4 and 5). Greene [184] showed a similar behaviour for an unsaturated polyester resin cured during 24 hours at 23°C and post-cured at 100°C. Young modulus was found to increase from 3.6 GPa to 4.8 GPa with the post-curing treatment, but the duration of post-curing did not change the Young modulus. Indeed, in this work the temperature was found to have a higher impact on the modulus for the same treatment duration (by comparing the cycle 4 to cycle 6).

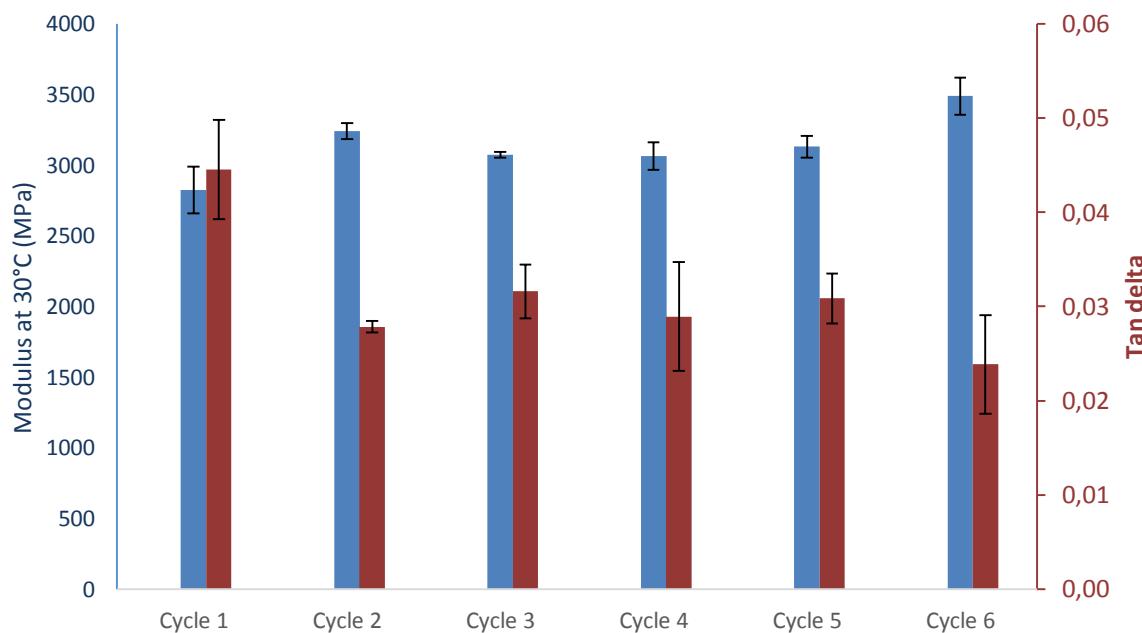


Figure III-XIII Young modulus and damping (measured at 30°C) for polyester resin exposed to different thermal treatments.

This section confirms that a post-crosslinking treatment realized in the laboratory can reach the curing state of the polyester resin that crosslinks at outdoor conditions during 5 months.

III-1.3. Conclusions

This first section shows experimental results for the selection of the flax fibre and the thermal cycle of the polyester resin to produce composites for nautical application. The objective is to replace glass by flax fibres using the same resin and processing technique. The unidirectional flax fabric provided by FRD presents good dispersion in the polyester matrix and allows to reinforce composites at 31% of fibre volume content. The mechanical properties are interesting compared to Biorenforts composites (Chomarat composite were reinforced by hybrid flax-glass fabrics).

A statistical analysis was performed to choose the thermal treatment that best fits the results of the resin exposed to ambient temperature during 5 months. The following parameters were taken into account: glass transition temperature, crosslinking rate, Young modulus and damping. The thermal cycle that found to be the most similar was the thermal cycle 5 : 24h at 60°C. The polyester resin showed a crosslinking rate of 78% after curing, while the post-cure treatment realised at 60°C during 24 hours (cycle 5) was found to improve the crosslinking rate from 78% to 88%. This value corresponds to a similar value of the polyester resin that crosslinks at ambient temperature during five months: period during which boat components remain exposed to outdoor conditions before being launched in water. A crosslinking rate of 88% means that polyester resin will probably continue to post-cure during ageing in water. This behaviour will be investigated in section IV-1.1.2 (page 126).

Furthermore, the flax fibre composites reinforcement content of 31% is lower than the fibre content of 61% obtained for glass fibre composites. Increasing reinforcement content in composites means change materials (especially flax fabric) or processing technique.

In the next section of this manuscript, the influence of processing on composites properties will be investigated by using the materials and procedures defined in this first chapter: a unidirectional flax fabric supplied by FRD is impregnated with an unsaturated polyester resin. Curing is performed at ambient temperature during 24h, and then a post-curing is realized at 60°C during 24h. The influence of processing on mechanical and morphological properties of composites will be explored by employing vacuum infusion and compression moulding techniques.

III-2. Influence of biocomposite processing conditions on their mechanical and morphological properties

Processing composite materials is an important step to create and design structures. In the marine industry, glass-fibre reinforced materials are mostly manufactured using vacuum infusion technique. This technique has some advantages compared to other techniques including the possibility to produce large-sized composites exhibiting low porosity. One of the disadvantages of this technique is that composite thickness is mainly controlled by the arrangement of the fabrics. It means that the composite thickness, and the subsequent fibre content, cannot be controlled without changing fabrics design (for a given vacuum pressure). Indeed producing composites with different fibres by the same technique could lead to different fibre content. This is particularly significant when comparing glass to flax fibre composites. Fibres morphology and their arrangement into fabrics influence the compaction state of fibres into composite.

In this chapter, the density, fibre content and mechanical properties were analysed for composites manufactured by two different techniques: vacuum infusion and compression moulding. Composites produced by compression moulding have an advantage compared to vacuum infusion composites which is the control of the thickness and consequently the fibre content. At the end of this chapter we will be able to answer the following question: Does we degrade composites when increasing their fibre content?

III-2.1. Generalities

Glass fibre reinforced composites were fabricated using vacuum infusion technique and flax fibre reinforced composites were manufactured using vacuum infusion and compression moulding techniques. Four and six layers of flax fibres were used to produce composites in each technique. The higher values of pressure imposed on composites using compression moulding technique leads to an increase in fibre content. However fibres compacted by compression moulding may be degraded during processing which results in lower mechanical properties than infusion technique (comparing composites with similar fibre contents). One possibility to assess the composites degradation (mainly fibres) during processing is to compare experimental results to the values obtained by the rule-of-mixtures. If experimental and theoretical values are close, it means that there is no damage on composite phases: matrix, fibres and interface. Another assumption made in the rule-of-mixtures is that there is no porosity or inclusions [99]. A corrected version of the rule-of-the mixtures that include composite porosity content [185] is also employed in this chapter.

Another issue concerns the fibre content of composites manufactured by vacuum infusion. It was demonstrated in the previous chapter that glass and flax fibres are dispersed differently in the polyester matrix: glass fibres are dispersed quasi-homogeneously while flax fibres (and bundles of fibres) are gathered into yarns. For same processing conditions (mainly vacuum pressure), glass fibre composites were found to be lighter than flax fibre composites, even if glass fibre possess a higher density compared to flax fibres (2.5 g/cm^3 compared to 1.45 g/cm^3 respectively). The difference

observed in weight displayed by these two composites is due to the fact that GFRC presented a lower thickness compared to FFRC. The compression moulding technique reduces the matrix content by employing higher compaction pressure than vacuum infusion (characteristic pressure values of vacuum infusion and compression moulding are less than 1 bar and 50 bars respectively). A shim is employed here to obtain the same thickness in two processing techniques (around 3mm). This strategy is part of the study of the influence of processing technique on mechanical properties but it also aims to decrease the composites final weight.

III-2.2. Composites density and fibre content

Composites morphological and dimensional aspects are exposed in Table III-IX. Comparing GFRC to FFRC, both fabricated by infusion technique using six layers of fabrics, is clearly visible that an equivalent fibre content cannot be achieved (61% to GFRC compared to 31% to FFRC). The low value of fibre content exhibited by infused flax fibre composites is the consequence of an increase in composites thickness, which means that the polyester matrix occupies more volume in infused flax composites than glass composites. The thickness increases from 1.7 mm for GFRC to 4.9 mm for FFRC. At the same time, density values decreases from 2,08 g/cm³ for GFRC to 1,27 g/cm³ for FFRC which leads to a composite mass increase of 87% (37,8 g for FFRC compared to 20,2 g for GFRC).

Table III-IX Density and fibre content values for GFRC and FFRC fabricated by vacuum infusion and compression moulding techniques.

Materials	Processing technique	Layers	Thickness	Density	Mass*	Fibre content
		units	mm	g/cm ³	g	%
Glass FRC	Infusion	6	1,7 ± 0,1	2,08 ± 0,04	20,2 ± 0,5	61,0 ± 0,6
	Infusion	4	3,1 ± 0,2	1,27 ± 0,01	23,8 ± 0,8	32,3 ± 1,5
	Infusion	6	4,9 ± 0,1	1,27 ± 0,00	37,8 ± 1,0	31,1 ± 0,7
	Compression moulding	4	2,8 ± 0,1	1,29 ± 0,00	21,1 ± 0,3	38,5 ± 1,7
		6	2,9 ± 0,1	1,35 ± 0,00	23,1 ± 0,6	62,0 ± 1,2

*Mass values correspond to tensile specimens (250 mm x 25 mm).

The number of flax fabric layers was found to not affect the performance of infusion process: 4 or 6 layers lead to similar density or fiber content. Besides linking the increasing fibre content to physical properties of the composites, it is also important to investigate the arrangement of fibres into the polymer matrix. A closer look at composites' morphology allows us to investigate the overall stacking of glass and glass fibres into the polyester matrix.

III-2.3. Morphological analysis

III-2.3.1 Dispersion of fibres in the polyester matrix and dimensional aspects

Flax and glass fibres are dispersed differently into the polyester matrix (Figure III-XIV). Glass fibres are cylindrical particles, mono-diameter and relatively well dispersed into the matrix (Figure III-XIV-a).

On the other hand, flax fibres are polygonal particles that can be found unitarily dispersed into matrix or forming clusters, called bundles for the case of natural fibres (Figure III-XIV-b).

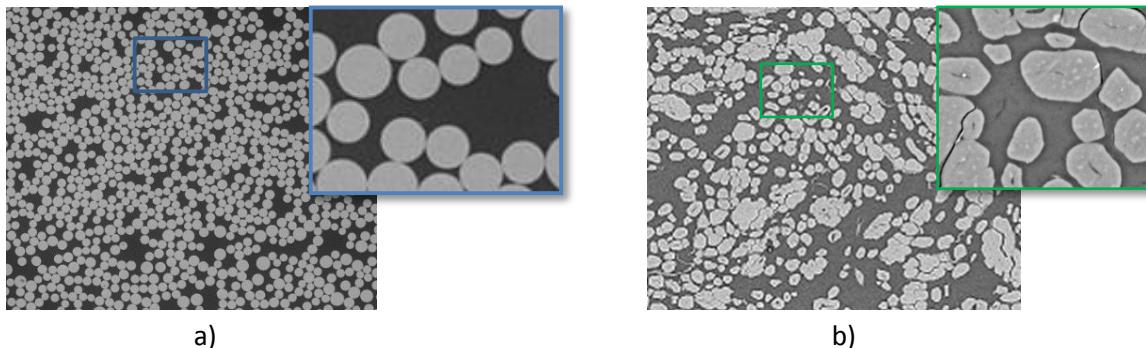


Figure III-XIV Morphological analysis of vacuum infused flax and glass fibre reinforced composites.

Dimensional measurements of glass and flax fibres dispersed into vacuum infused composites are disposed in Table III-X. Cylindrical glass fibres present an average diameter of $17 \mu\text{m}$ and a shape factor very close to 1, while flax fibres presents different dimensional values if unitary dispersed into matrix or forming clusters (bundles of fibres).

Table III-X Dimensional aspects of flax and glass fibres into vacuum infused composites.

Fibre type	dispersion state	Diameter	Shape factor
Glass	unitary fibres	$16.9 \pm 1.9 \mu\text{m}$	0.99 ± 0.02
Flax	unitary fibres bundles	$19.5 \pm 5.7 \mu\text{m}$ $76.4 \pm 26.9 \mu\text{m}$	1.51 ± 0.37 1.88 ± 0.56

Unitary fibres and bundles are dispersed into yarns within a scale that will be called intra-yarn scale in this work (Figure III-XV-b). At this scale, it is possible to distinguish unitary fibres, bundles, the matrix and eventually some porosity. Looking further, it is possible to distinguish the yarn distribution, the matrix and porosity in an upper scale called yarn scale (Figure III-XV-a).

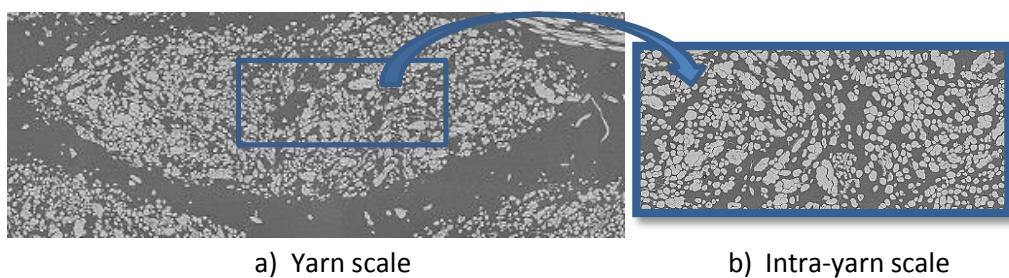


Figure III-XV Flax individual fibres and bundles dispersed into flax yarns (vacuum infused composite).

Figure III-XVI presents the morphology of composites fabricated by vacuum infusion and compression moulding techniques at yarn scale. Comparing the morphology of composites fabricated with 4 flax fabric layers by vacuum infusion (Figure III-XVI-a) and compression moulding (Figure III-XVI-b), no substantial differences were observed but a higher porosity content can be noted. The similar morphology obtained here can be explained by the fact that compression moulded composites had their thickness imposed by a metallic shim of 3 mm thick. Otherwise, morphology changes for composites fabricated with 6 flax fabric layers by compression moulding technique (Figure III-XVI-d) compared to 6 layer fabric vacuum infused composites (Figure III-XVI-c). The space between yarns

occupied prior by matrix, is reduced to create a new morphology where yarns are closer to each other. Replacing matrix by yarns makes it possible to increase the composites fibre content using compression moulding technique.

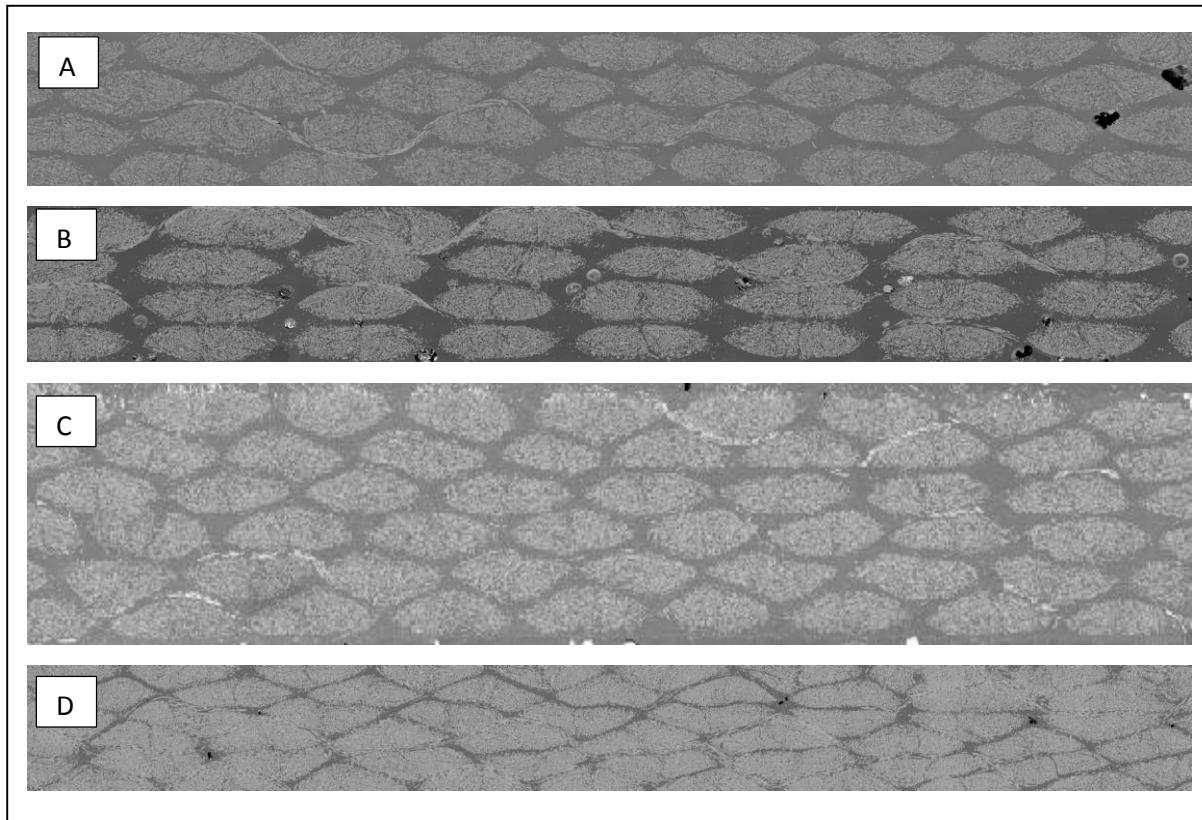


Figure III-XVI Microscopy analysis of the yarns dispersion into polyester matrix for: A) Vacuum infusion – 4 layers ; B) Compression moulding – 4 layers ; C) Vacuum infusion – 6 layers ; D) Compression moulding – 6 layers.

III-2.3.2 Porosities

The morphological analysis of composites cross-section highlights the presence of porosities in the composite. These porosities are preferentially located in the polyester matrix and in between yarns, as shown in Figure III-XVI. Madsen et al. [67] identified four types of porosity in plant fibre composites: fibre porosity, interface porosity, impregnation porosity and matrix porosity. In this work, the X-ray tomography (3SR, Grenoble, France) technique was employed to obtain more information about the porosities distribution into the composite. This technique was found to demonstrate excellent correlation with the microscopic measurements in measuring manufacturing defects in composite materials [186]. Figure III-XVII-a shows the flax fibre distribution into the polyester matrix, and Figure III-XVII-b shows the porosity distribution for the same sample. It can be noted mainly the presence of one type of porosity: matrix porosity, which is identified by air bubbles entrapped in the polymer matrix during processing.

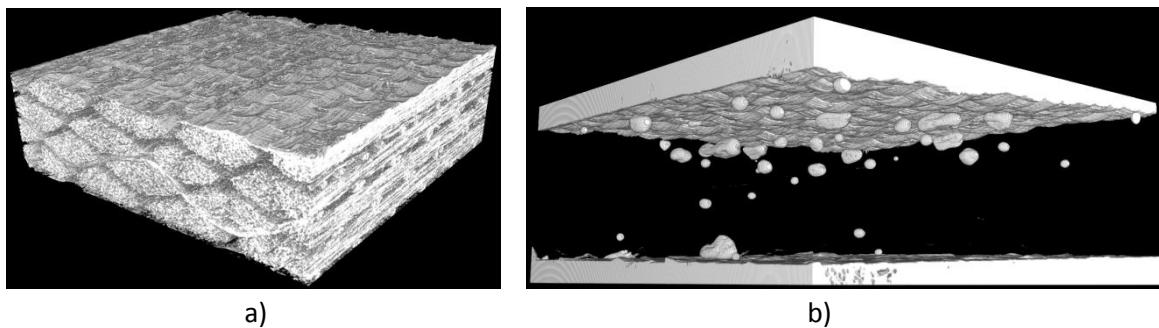


Figure III-XVII X-ray tomography analysis of (a) fibres and (b) porosity distribution into a vacuum infused flax fibre composite.

A closer look on the x-ray tomography images (Figure III-XVIII) confirms the presence of porosities in the matrix rich regions identified to be external to the flax yarns. The resolution of the x-ray tomography measurements ($8.75 \mu\text{m}/\text{pixel}$) did not allow further analysis about the porosity content in the fibres lumen (lumen's diameter was found to be around $8 \pm 5 \mu\text{m}$ measured by image analysis).

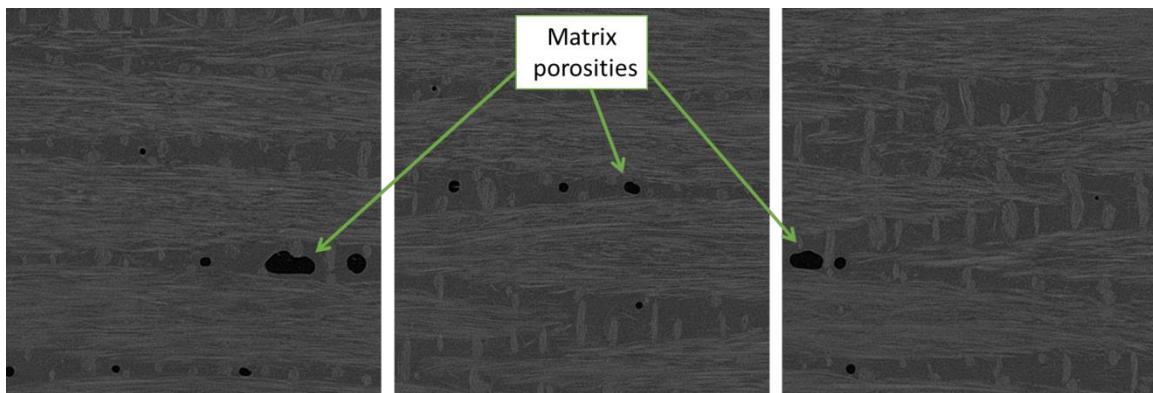


Figure III-XVIII X-ray tomography analysis of porosity distribution in a vacuum infused flax fibre composite.

By analysing the results in the literature, it can be noted that vacuum infusion technique produces biocomposites with low fibre content and low porosity while composites manufactured by compression moulding present higher fibre content, therefore higher mechanical properties, but higher porosity content [179][66]. In this work, the porosity content was identified for the vacuum infused and compression moulded composites (Table III-XI) and found to be related to the processing technique but also to the fibre content. The porosity content of the 4 layers compression moulded composites was found to be higher than the vacuum infused composites presenting the same number of layers ($3.6 \pm 0.8\%$ compared to $1.6 \pm 0.6\%$, respectively). This result is in agreement with Mwaikambo and Ansell [66] that shown an increasing void content with the processing pressure of compression moulded hemp fibre reinforced composites. In this work, the porosity level was assessed by analysing the cross-section images (minimum of 3 samples by reference).

However, the porosity dependency on the processing technique of composites reinforced by 6 layers did not follow the same behavior. It was previously showed in this work that only matrix porosity was observed in flax fibre composites. For this reason, it is expected that increasing fibre content might lead to reduce the zones rich in matrix, and therefore, to decrease the porosity level because the porosity is located in the matrix. The fact that this behavior was only observed for compression

moulded composites confirms this hypothesis: the fibre content of vacuum infused composites remained constant with the number of flax fabric layers ($32.3 \pm 1.5\%$ compared to $31.1 \pm 0.7\%$ for 4 and 6 layers, respectively), while the compression moulded composites increased their fibre content from $38.5 \pm 1.7\%$ to $62.0 \pm 1.2\%$ with the increasing number of flax fabric layers.

Table III-XI Porosity content for GFRC and FFRC fabricated by vacuum infusion and compression moulding techniques.

Materials	Processing	Layers units	Fibre content %	Porosity %
GFRC	Infusion	6	61.0 ± 0.6	1.5 ± 0.9
	Infusion	4	32.3 ± 1.5	1.6 ± 0.6
	Infusion	6	31.1 ± 0.7	2.1 ± 0.6
FFRC	Compression moulding	4	38.5 ± 1.7	3.6 ± 0.8
	Compression moulding	6	62.0 ± 1.2	2.2 ± 0.9

III-2.4. Elastic and ultimate mechanical properties

III-2.4.1 Elastic properties

Table III-XII shows the results of static and dynamic tests carried out for glass and flax fibre composites. The mean value of the elastic modulus of GFRC was 45 GPa, which is higher compared to all other FFRC fabricated by vacuum infusion or compression moulding technique. Damping factor values for glass composites are lower in all cases (found to be around 0.24). Concerning FFRC, the viscoelastic properties (Young's modulus and damping factor) display different trends according to the processing technique: vacuum infused composites present the same elastic properties using either 4 or 6 flax fabric layers. This result can be related to the identical fibre content exhibited by these composites. In the case of compression moulded flax composites, the elastic properties increase with the number of flax fibre plies (as well as the fibre content increases with the number of layers). In general, the Young modulus of compression moulded composites is higher than infused composites (comparing composites with the same number of layers).

It is interesting to note a gap between the dynamic and the elastic modulus for the FFRC (clearly observed for the 6 layers compression moulded flax composites) which does not exist for GFRC. This gap could be explained by the viscoelastic behavior of FFRC. Tests achieved by dynamic mechanical analysis (DMA) highlighted the fact that FFRC show an elastic modulus dependence on the imposed frequency. The results of this study are covered in Appendix 2.

Table III-XII Elastic mechanical properties for GFRC and FFRC fabricated by vacuum infusion and compression moulding techniques.

Materials	Processing	Layers	Fibre content	Dynamic Young Modulus	Static Young Modulus	Damping
			units	%	GPa	
GFRC	Infusion	6	61.0 ± 0.6	45.0 ± 0.9	45.0 ± 0.9	0.24 ± 0.01
		4	32.3 ± 1.5	20.3 ± 0.6	19.2 ± 0.8	1.00 ± 0.06
		6	31.1 ± 0.7	19.4 ± 0.6	20.0 ± 1.3	1.00 ± 0.09
	Compression moulding	4	38.5 ± 1.7	20.3 ± 0.4	19.7 ± 2.5	0.73 ± 0.02
						0.65 ± 0.01

In this part, the rule of mixtures is employed to determine fibre modulus from experimental composites properties. The higher processing pressure imposed to compression moulded composites can lead the fibre degradation. The porosity was taken into account in the rule-of-mixtures by the Equation III-II developed by Mackenzie [187] :

$$E_p = E_d(1 - V_p)^2 \quad \text{Equation III-II}$$

where E_d is the modulus of the fully dense material and E_p the modulus of the porous material.

In Table III-XIII it can be noted that fibre Young modulus for infused composites is higher than compression moulded composites. This interesting result confirms that increasing fibre content by higher processing pressure leads to composites degradation. This trend is more obvious in Figure III-XIX. The results for compression moulded composites were found to be lower than those calculated by the rule of the mixtures. Otherwise, vacuum infused composites presented values for the Young modulus very close to those calculated from the rule of mixtures, which means that flax fibres are not degraded during processing.

The modulus of the FRD fibres were determined experimentally by a specific vibration analysis and found to be 57.6 ± 51.4 GPa. The large standard deviation observed in the measurements of the flax fibre modulus was also reported by Joffe et al [91].

It is interesting here to discuss about composites evolving behavior during processing, more specifically, the changes occurring in the matrix, the fibre and in the fibre/matrix interface. Concretely, the polyester matrix is in a liquid state at the beginning of processing. It impregnates fibres and can adapt its volume into the composite by its low viscosity. The excess is expelled from the composites volume by the processing pressure (coming from mechanical pressure for compression moulded composites, and by atmospheric pressure for infused composites). This way, it is supposed that polyester matrix is not degraded in either case. It isn't the same case for flax fibres. The fibres are flexible and deformable materials, which mean that its dimensional aspects can change with the processing pressure. Besides the dimensional aspects and so the mechanical properties can be influenced by processing conditions. Comparing experimental properties to *rule-of-mixtures-properties* could give an indication about the degradation state of flax fibres. The difference observed between experimental and rule-of-mixtures results can be explained by the flax fibres degradation, or

by the presence of porosity that is not taken into account in the theoretical model. The issue here is to decouple fibre and interface degradation, and take into account the porosity in the calculation of the *rule-of-mixtures*. This issue will be discussed in the next section of this chapter.

Table III-XIII Composites Young modulus determined by the rule of mixtures compared to experimental results for: Glass fibres composites and flax fibre composites produced by vacuum infusion and compression moulding techniques.

Materials	Mise en œuvre	Layers units	Fibre content	Composites Young modulus	Fibre Young modulus
			%	GPa	GPa
GFRC	Infusion	6	61,0 ± 0,6	45.0	73.8
	Infusion	4	32,3 ± 1,5	19.2	59.4
	Infusion	6	31,1 ± 0,7	20.0	66.2
	Compression moulding	4	38,5 ± 1,7	19.7	51.7
	Compression moulding	6	62,0 ± 1,2	28.3	51.0

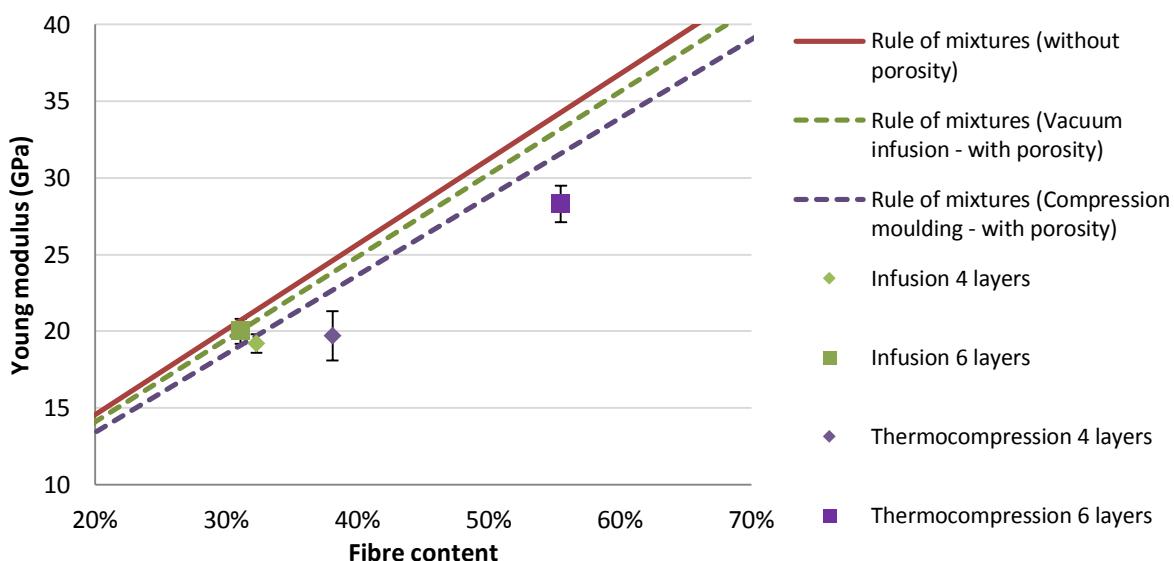


Figure III-XIX Young modulus versus fibre content showing the experimental results compared to the rule of mixtures (model with porosity and without porosity).

III-2.4.2 Ultimate tensile properties

Table III-XIV show ultimate tensile properties for glass and flax FRC. Ultimate properties follow the same trend as Young modulus: GFRC ultimate stress is higher than all FFRC. The difference consists in the fact that ultimate properties are more sensitive to the fibre content than elastic properties (for the same processing technique). The ultimate tensile strength of compression moulded composites was found to be higher than those of vacuum infusion composites as an effect of the increasing in fibre content with the processing pressure applied to composites. A similar behaviour reported in the literature for a kenaf fibre reinforced polyester composite[188]. The samples subjected to pressure in the mould (manufactured by RTM technique) presented higher tensile strength compared to the non-pressurised ones.

Table III-XIV Ultime tensile properties for GFRC and FFRC fabricated by vacuum infusion and compression moulding.

Materials	Processing	Layers	Fibre content	Ultimate tensile strength	Ultimate tensile strain
		units	%	MPa	%
GFRC	Infusion	6	61,0 ± 0,6	587 ± 15	1,62 ± 0,06
	Infusion	4	32,3 ± 1,5	163 ± 4	1,19 ± 0,06
	Infusion	6	31,1 ± 0,7	167 ± 5	1,12 ± 0,10
FFRC	Compression moulding	4	38,5 ± 1,7	240 ± 21	1,66 ± 0,15
	Compression moulding	6	62,0 ± 1,2	303 ± 17	1,57 ± 0,04

III-2.4.3 Fracture surface observation

The fracture surfaces were analysed by ESEM (Figure III-XX). The presence of peeled fibres in composites indicates a good resistance to shear at interface or a poor resistance to peel (Figure III-XX-a). The good resistance to shear can be physically explained by a mechanical friction between fibres and matrix (the two parts are hold together by compression of one part against the other), or chemically explained by a good adhesion at interface. This resistance to shear avoid fibres to slip along matrix, which is highlighted by a short revealed length (Figure III-XX-b). Finally, the fibre fragile fracture behaviour (Figure III-XX-c) confirms the low strain values observed in tensile tests for flax composites. The fracture surface observation was conducted for vacuum infused and compression moulded composites. The images presented here concerns only the vacuum infused composites because the mechanism of rupture of the composites manufactured by the two techniques was found to be very similar.

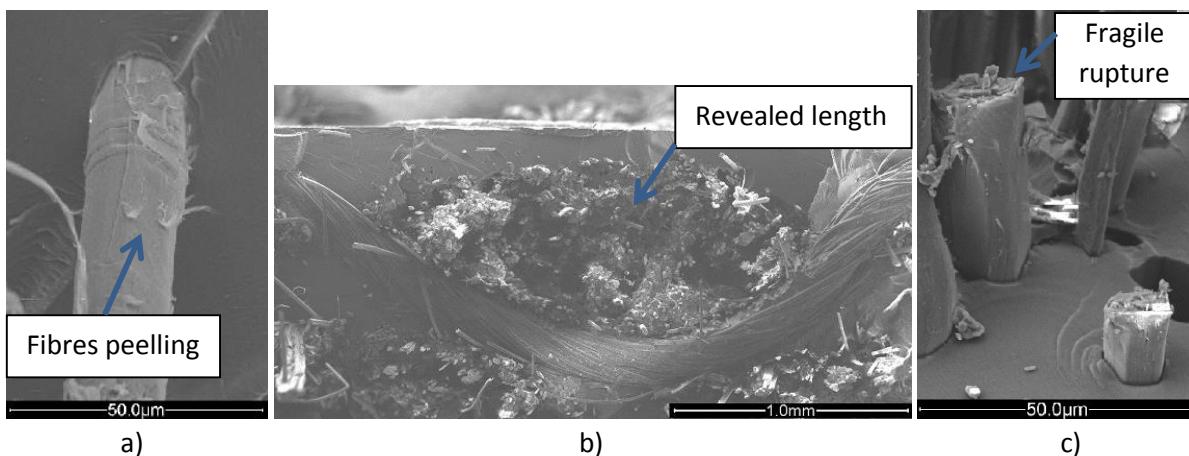


Figure III-XX Fracture surface analysis of flax fibre composites: A) and C) at fibre scale B) at yarn scale.

III-2.5. Analysing the fibre/matrix interface resistance to shear

The degradation observed on flax fibre composites manufactured by compression moulding technique may be related to fibre degradation or degradation of the interface between fibre and

matrix. In this section, interlaminar shear tests were realized to verify the shear adhesion between fibre and matrix for composites manufactured by vacuum infusion and compression moulding. The results are shown on Table III-XV.

It can be observed that resistance to interlaminar shear is higher for flax fibres composites than for glass fibre composites. It confirms that flax fibres present a good mechanical adhesion because of its rougher surface finish than glass fibres (also discussed in the last section: fracture surface analysis of flax composites). The results observed for interlaminar shear strength are close to the results obtained by Munikenche Gowda et al (1998) for a polyester-jute composite fabricated by hand lay-up. An interlaminar shear strength of 10.0 ± 0.6 MPa is observed for ILSS tests.

Concerning flax fibre composites, it also interesting to observe that flax fibre composites fabricated by compression moulding show lower interlaminar shear strength than vacuum infused composites. This confirms that the higher values of maximum strength observed for thermopressed composites are only related to fibre content (ref. De Albuquerque 2000). It is seen that infused composites presents higher interlaminar shear resistance than compression moulded composites even if the latter presents higher fibre content. Furthermore the shear resistance increases with fibre content for the same processing technique.

Another important aspect concerns the correlation between shear strength and the composites voids content. Olivier et al. (1995) describes a shear strength dependency on the void content for carbon/epoxy composites. Composites presenting higher void content show lower shear strength: composites lose 20% of shear strength when void content increase for 1% to 4%. This correlation can explain the lower shear strength obtained for compression moulded composites compared to infused ones.

Table III-XV Interlaminar shear tests for GFRC and FFRC fabricated by vacuum infusion and compression moulding.

Materials	Processing	Layers	Fibre content	Interlaminar shear strength	
			units	%	MPa
GFRC	Infusion	6	61,0 ± 0,6	8,61 ± 0,36	
		4	32,3 ± 1,5	13,73 ± 0,85	
		6	31,1 ± 0,7		
	Compression moulding	4	38,5 ± 1,7	9,87 ± 1,11	
		6	62,0 ± 1,2	10,92 ± 0,09	

III-2.6. Conclusions

Glass fibre composites present higher fibre content than flax fibre composites fabricated by the same technique (61% for glass composites compared to 31% for flax composites both fabricated by vacuum infusion technique). The fibre content and composite density of vacuum infused composites remained constant whatever the number of flax layers used, while composites weight increases of 87% because of thickness increase. The yarns distribution into polyester matrix was found to determine the

composites thickness, and therefore its morphological and mechanical properties. Concerning the mechanical properties, Young modulus and ultimate tensile strength have not changed with the increasing number of flax fabric layers for vacuum infused composites.

An alternative is to change processing pressure conditions by using compression moulding technique. Indeed, flax fibre content increased from 31% for vacuum infused composites to 62% for compression moulded ones. The porosity content was found to be dependent on the processing technique and the fibre content, and the mechanical properties increased up to 64% for Young modulus and up to 81% for maximum strength. However flax fibres composites can degrade during processing because of the considerable pressure applied to composite sheets. Comparing experimental properties to the *rule-of-mixtures*-might give an indication about the degradation state of flax fibres. The difference observed between experimental and rule-of-mixtures results can be explained by the flax fibres degradation. The effect of interface was observed by interlaminar shear tests: flax fibre composites processed by compression moulding showed lower interlaminar shear strength than vacuum infused composites. It could be interesting here to introduce a term linked to the interface in the *rule-of-mixtures*.

Finally, vacuum infusion technique produced relatively low fibre content composites presenting good mechanical properties and low porosity. The work in the design of flax fabrics is an interesting way to improve its dispersion into matrix and therefore increase fibre content for flax fibre composites. This could lead to the production of better-performing biocomposites.

Chapter IV. Ageing of flax fibre reinforced unsaturated polyester biocomposites

The purpose of this chapter is to present and discuss the mechanisms involved in the ageing of flax fibre unsaturated polyester composites. The methodology and materials previously introduced and discussed in the last chapters will be applied here to analyse the physico-chemical and mechanical evolving behaviour of biocomposites immersed in water.

This chapter is divided into three parts: the hydrothermal ageing of flax and glass fibre composites, the reversibility of properties after ageing and the mechanical-hydrothermal coupling behaviour.

The first part focuses on analysing the biocomposites evolving behaviour during ageing by comparing to conventional glass fibre reinforced composites. The evolution of the morphological, physico-chemical and mechanical properties are addressed in this part.

The second part concerns the reversibility of properties after water removal from composites. The objective here is to observe the occurrence of damage (irreversible phenomena) during hydrothermal ageing tests.

Finally, the effect of mechanical loadings during ageing is investigated by applying a creep stress on flax fibre composites under a controlled atmosphere (thermomechanical tests) and immersed in water (mechanical-hydrothermal tests). The evolution of creep and of the elastic modulus during ageing are reported in this study.

Chapitre IV – Vieillissement des composites à matrice polyester insaturé renforcés par de fibres de lin

Le but de ce chapitre est de présenter et discuter les mécanismes de vieillissement des composites à matrice polyester insaturé renforcés par des fibres de lin. La méthodologie et les matériaux introduits dans les chapitres précédents seront utilisés ici afin d'analyser l'évolution du comportement physicochimique et mécanique de biocomposites immersés dans l'eau.

Ce chapitre est divisé en trois parties : le vieillissement hydrothermique, la réversibilité des propriétés après vieillissement et le couplage hydrothermo-mécanique.

La première partie se concentre sur l'analyse du comportement évolutif des biocomposites dans l'eau et sur la comparaison de ce comportement à celui des composites traditionnels renforcés par des fibres de verre. L'évolution de la morphologie et des propriétés mécaniques et physicochimiques de ces composites est décrite dans cette partie.

La deuxième partie concerne la réversibilité des propriétés après que l'eau a été retirée du composite. L'objectif ici est d'observer l'occurrence d'endommagements (phénomènes irréversibles) pendant le vieillissement hydrothermique.

Finalement, l'effet des sollicitations mécaniques pendant le vieillissement dans l'eau est investigué en appliquant des contraintes de fluage aux biocomposites en atmosphère contrôlée (essais thermomécaniques) ou immersés (essais hydrothermo-mécaniques). L'évolution du fluage et du module élastique au cours du vieillissement est présentée dans cette partie.

IV-1. Hydrothermal ageing of flax and glass fibre reinforced composites

This main objective of this experimental study is to analyse the effects of water ageing on physico-chemical, morphological and mechanical properties of flax and glass fibre reinforced composites. Composites are immersed into water at different temperatures (30, 50 and 70°C) and their behaviour is followed until water saturation. Different chemical treatments applied at the surface of the flax fabrics (a silane based one, called MPS for methacryloxypropylmethoxysilane, a butyl methacrylate (BMA)/MPS copolymer and a styrene (S)/MPS copolymer) are proposed aiming to reduce the hydroscopic behaviour of flax fibres composites.

The results will be presented in five parts: physico-chemical modification, dimensional stability, microstructural analysis, viscoelastic behaviour and mechanisms of rupture.

The water uptake is followed and related to physico chemical modifications, mainly resin post-cross linking and plasticisation. Then, the presence of water within composites leads to a change in the microstructural configuration that is observed at a macroscopic scale by swelling measurements and at a microscopic scale by image analysis of cross-sections of the samples. Finally, the physical and chemical modifications observed during ageing are associated to the mechanical evolving behaviour (viscoelastic and ultimate properties) of flax and glass fibre composites during ageing.

IV-1.1. Physico-chemical evolving behaviour

The most relevant physical effect for composites materials immersed in water is the weight uptake. This effect is especially important for hydroscopic materials, such as natural fibre reinforced composites. The presence of water within a composite induces physical and chemical modifications of their components that behave differently regarding to water exposure. Water diffuses slowly in polyester matrix while diffusion in fibres depends on their nature (hydrophobic for glass fibres and hydrophilic for flax fibres).

IV-1.1.1 Water sorption

a. Flax and glass fibre composites, and the unreinforced polyester resin

Figure IV-1 presents the water uptake behaviour of glass and flax-fibre composites compared to the polyester resin at 30°C, 50°C and 70°C as a function of ageing time. The results confirm the hydrophobic behaviour of glass fibres and the hydrophilic behaviour of flax fibres when impregnated with an unsaturated polyester matrix. The temperature was found to accelerate the water diffusion and led to a higher water uptake at saturation. A similar influence of temperature was related by Regazzi [97] for flax/PLA composites immersed in water at different temperatures.

The unreinforced polyester resin presents a water uptake of $0.90\% \pm 0.07\%$ (after an ageing duration of 3600 hours and at 30°C) while flax fibres composites exhibit $5.94\% \pm 0.41\%$ and glass fibre

composites $0.40\% \pm 0.06\%$ of water uptake for the same ageing conditions. Assarar et al. [4] reported a higher water uptake of 13.5% and 1.0% for glass and flax/epoxy composites immersed in water for 40 days at room temperature, respectively. The higher reinforcement volume fraction (nominal value of 0.40) could explain the higher diffusion parameters showed by the authors.

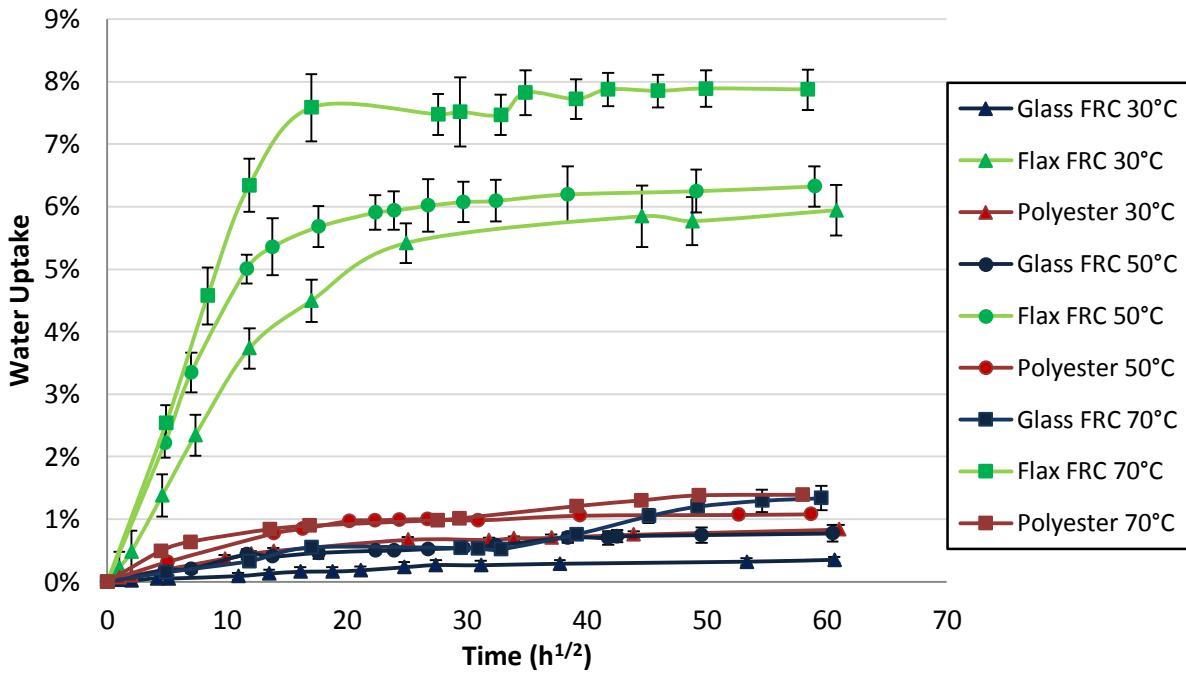


Figure IV-1 Water uptake as a function of ageing time for polyester resin, glass and flax-fibre composites immersed in water at 30°C, 50°C and 70°C.

Let us analyse the shape of the water absorption curves for the three materials.

As concerns flax fibre composites, the water sorption appears to be Fickian, with a linear initial part and a saturation plateau. The results for the diffusion coefficient (D), the corrected coefficient (D_c) and water concentration at saturation (M_m) are displayed in Table IV-I, and were calculated by the equations described in (section I-1.3.1 – page 13). It can be noted that the water concentration at saturation depends on the ageing temperature for all the materials. A published study on the hydrothermal ageing of flax/epoxy composites at different temperatures shows a similar trend for the influence of temperature on moisture absorption [69]. The authors reported a M_m of 4.1% and 6.9%, and a D of $5.5 \times 10^{-13} \text{ m}^2/\text{s}$ and $1.1 \times 10^{-12} \text{ m}^2/\text{s}$ for samples aged at 20°C and 40°C, respectively.

Table IV-I Equilibrium water uptake (M_m), diffusion coefficients (D) and corrected coefficients (D_c) for glass and flax fibre reinforced composites compared to unreinforced polyester resin.

Materials	M_m (%)			$D \times 10^{-12} (\text{m}^2\text{s}^{-1})$			$D_c \times 10^{-12} (\text{m}^2\text{s}^{-1})$		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
Polyester resin	0.90	1.08	1.38	1.28	2.29	1.62	0.55	1.18	1.15
Glass FRC	0.40	0.54	1.34	0.10	0.39	0.30	0.09	0.34	0.26
Flax FRC	5.94	6.20	7.89	1.64	2.91	2.09	1.26	2.27	1.65

If the weight changes are evaluated by calculating the the water sorption of the polymer matrix in the composite by the rule-of-mixtures (based on the water sorption of the unreinforced polymer)

(Table IV-II), it is observed that the water uptake relative to the polyester content in GFRC is very close at 30°C (0.41% for the polyester matrix in the GFRC compared to 0.40% for the GFRC observed experimentally), but an effect of temperature is remarkable. It was reported a phenomenon of water absorption at the fibre/matrix interface for glass fibre reinforced PET composites [189], related to a relative water sorption higher in the matrix in the composites compared to the unreinforced polymer. In this work, the effect of the water sorption at the interface can be related to the increasing temperature. However, this “interface-dominant” water sorption effect is difficult to calculate for unsaturated polyester composites because the GFRC weight loss due to matrix dissolution, which could “mask” the effect of water sorption at the interface. This mechanism of matrix dissolution in water during ageing will be discussed later in the sub-chapter IV-2 (page 147). Furthermore, the levels of porosity in the composite might also explain the faster diffusion [28], but it was shown in the last chapter that void content was found to be low (less than 2%).

Table IV-II Equilibrium water uptake (M_m) for glass FRC compared to that of the polymer matrix in the composite (calculated by the rule-of-mixtures).

Materials	M_m (%)		
	30°C	50°C	70°C
Glass FRC	0.4	0.54	1.34
Polymer matrix in the composite	0.41	0.49	0.62

The diffusion coefficient obtained for flax fibre composite first increased with increasing temperature then decreased between 50°C and 70°C. This phenomenon was generalized for all the studied materials. The fact that this behaviour was observed for all the materials suggests that it is a mechanism related to the polyester matrix. The mechanism of interaction between the polymer matrix and the water molecules can be described by different models, such as the model of Carter and Kibler [34] that describes the existence of free and bonded water molecules in the polymer network, or the model of Jacobs and Jones [190] that describes the presence of two independent diffusion phenomena. The latter model is based on the assumption that there are two regions of moisture uptake dominated by a more or less dense phase; This model is called “two phase Fickian diffusion”.

As concerns polyester resin and glass fibre composites, a closer observation of the water uptake behaviour reveals a non Fickian behaviour at 70°C (see Figure IV-II). Indeed, the use of a Fickian diffusion model to describe a non-Fickian diffusion behaviour is controversial. Le Duigou et al. [123] highlight that describing diffusion by a Fickian model in materials presenting substantial differences in D is questionable. The water profiles within heterogeneous materials, mainly composites, are visibly very complex. The term heterogeneous used here concerns the composite as a multi-component material, but also the polyester matrix as a heterogeneously crosslinked material. The approach used in this work, as it has been in previous studies on biocomposites [191] [192], was limited to a global trend of the rate of samples water uptake.

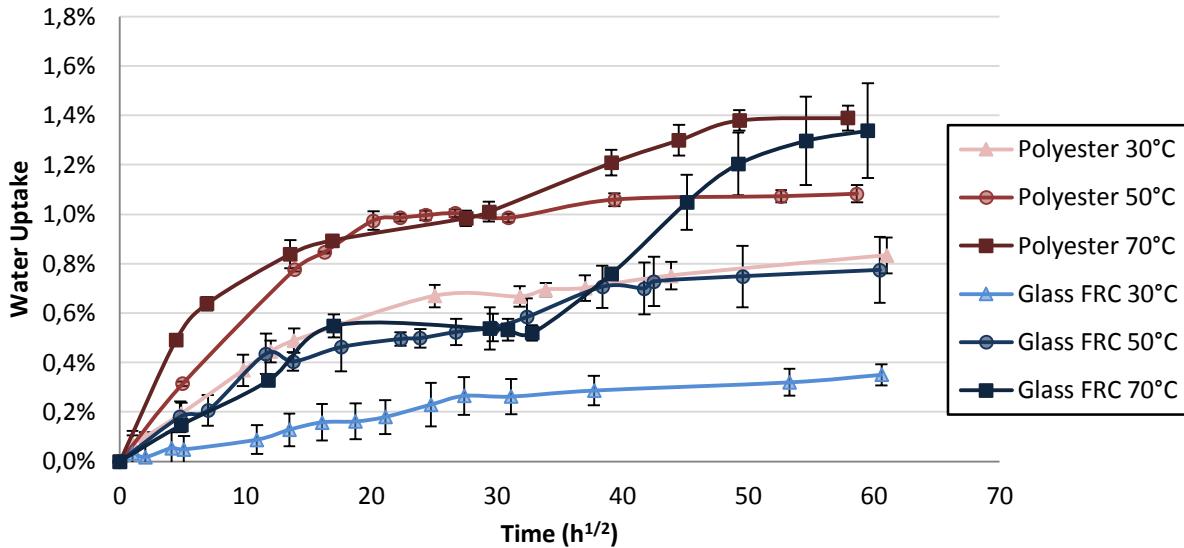


Figure IV-II The non-Fickian diffusion behaviour of glass fibre composites and unreinforced polyester resin immersed in water at 30°C, 50°C and 70°C

Furthermore, the water sorption may lead to a modification of the microstructure, such as the formation of microcracks which influence the water diffusion behaviour. In the literature, values of $\ln D$ are plotted against the reciprocal temperature $1/T$ in order to apply an Arrhenius relationship. Instead of a linear trend that is expected for an Arrhenius behaviour, in this work a non-linear relationship suggests that materials changes its diffusion behaviour with the ageing temperature (see Figure IV-III). Other authors [53] suggest that the initial free volume contained into materials samples expands with increasing temperature, which could possibly account for a higher proportion of the absorbed water.

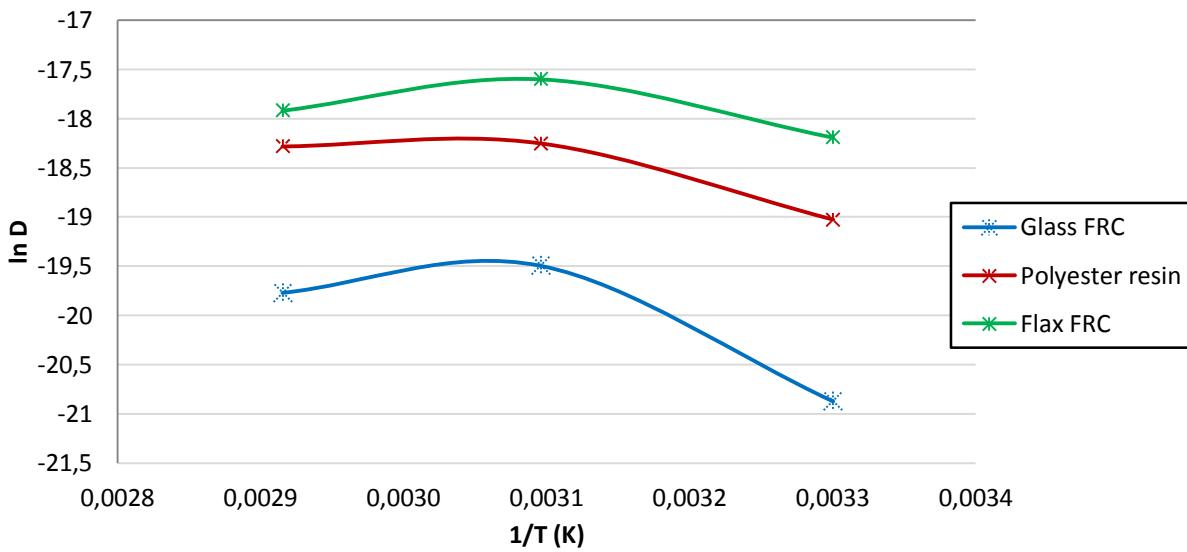


Figure IV-III Relationship between the diffusion coefficient and the ageing temperature.

b. Treated flax fibre composites

Different chemical treatments were applied onto flax fabrics aiming to improve their water resistance when impregnated in unsaturated polyester composite. Fibres were treated using a

methacryloxypropylmethoxysilane (MPS), a Butyle methacrylate (BMA)/MPS copolymer and a styrene (S)/MPS copolymer.

b1. Visual behaviour of treated flax fabrics towards a water droplet

Before proceeding to fibres impregnation in a polyester matrix, the effect of the treatment was verified on the flax fabrics by depositing a drop of water on the surface and following its absorption over time. The untreated flax fibres absorbed instantaneously the drop of water while the treated ones took a longer time to absorb water (see Figure IV-IV). This procedure was repeated five times in different places of the flax fabric in order to verify if the treatment is uniformly spread throughout the fabric.

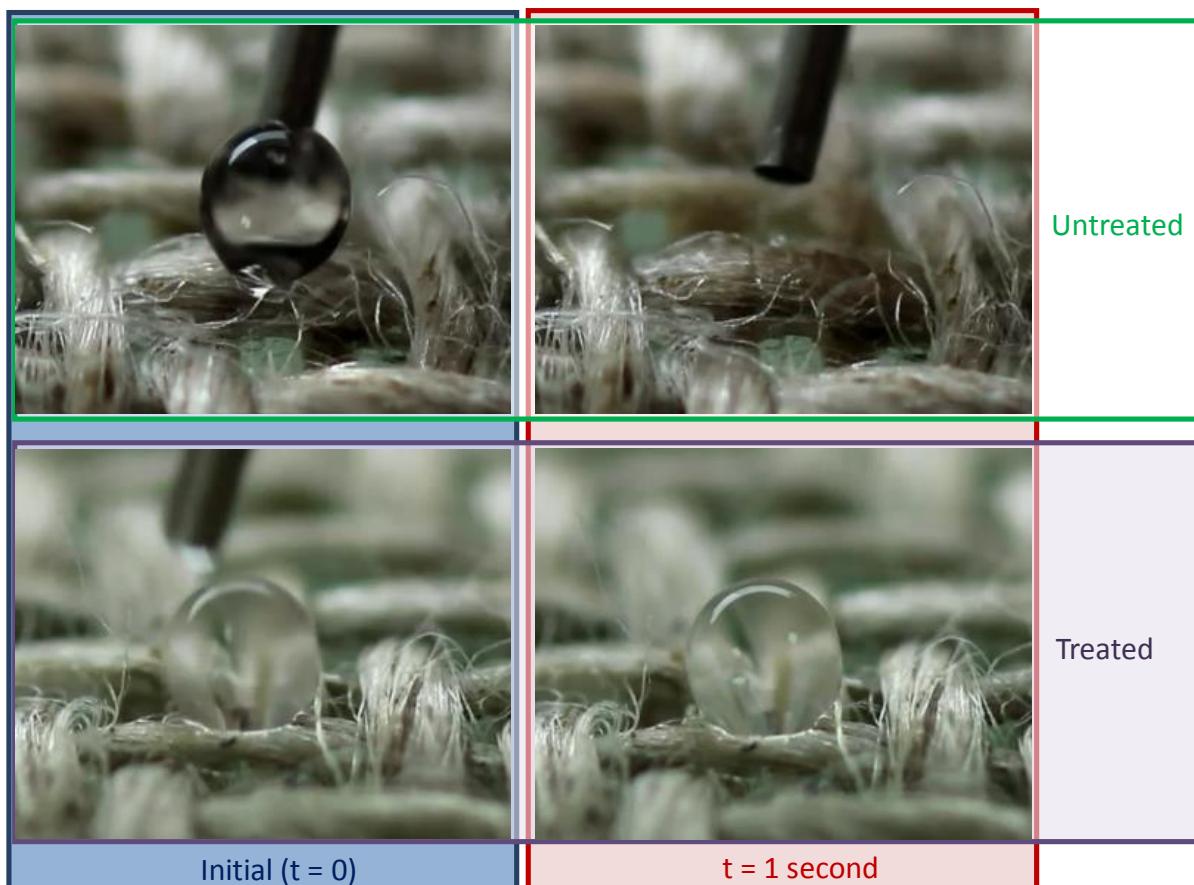


Figure IV-IV Observation of the effect of fibres treatment by depositing a drop of water on the flax fabric.

The time elapsed between the deposition of the drop of water and its absorption highlights the effect of the treatment on the fibres water resistance. The results are shown in Table IV-III.

Table IV-III Time elapsed between the deposition of the drop of water and its absorption by flax fibres

Flax fibres	Time elapsed until absorption
Untreated	Instantaneously
MPS	Instantaneously - 27 minutes
BMA/MPS	19 - 30 minutes
S/MPS	16 - 29 minutes

The values presented in this table may vary according to the location of the drop of water in the flax fabric. The zones presenting more compacted fibres typically show faster water absorption. Hence this method gives an indication about the fibres treatment efficiency without providing a quantitative result of the fibres water resistance.

It was noted that the flax fabrics treated with MPS exhibit a higher variability (about 30 min) compared to those treated with BMA/MPS and S/MPS copolymers (about 10 min).

b2. Analysis of the homogeneity of the treatments onto the flax fabrics

The homogeneity of the treatments onto the flax fabrics was analysed through scanning electron microscopy coupled with an energy dispersive X-ray spectroscopy (SEM/EDX) analysis (Figure IV-V). Five images were analysed in different zones of the treated composite. It was observed the presence of smoothed surface fibres and roughened surface fibres. These zones were analysed by EDX to verify the existence of silicon elements that indicates the presence of treatment molecules. The results are shown in Table IV-IV. The presence of untreated and treated fibres on the flax fabrics confirms the inhomogeneity of the MPS treatment shown earlier by the water drop test.

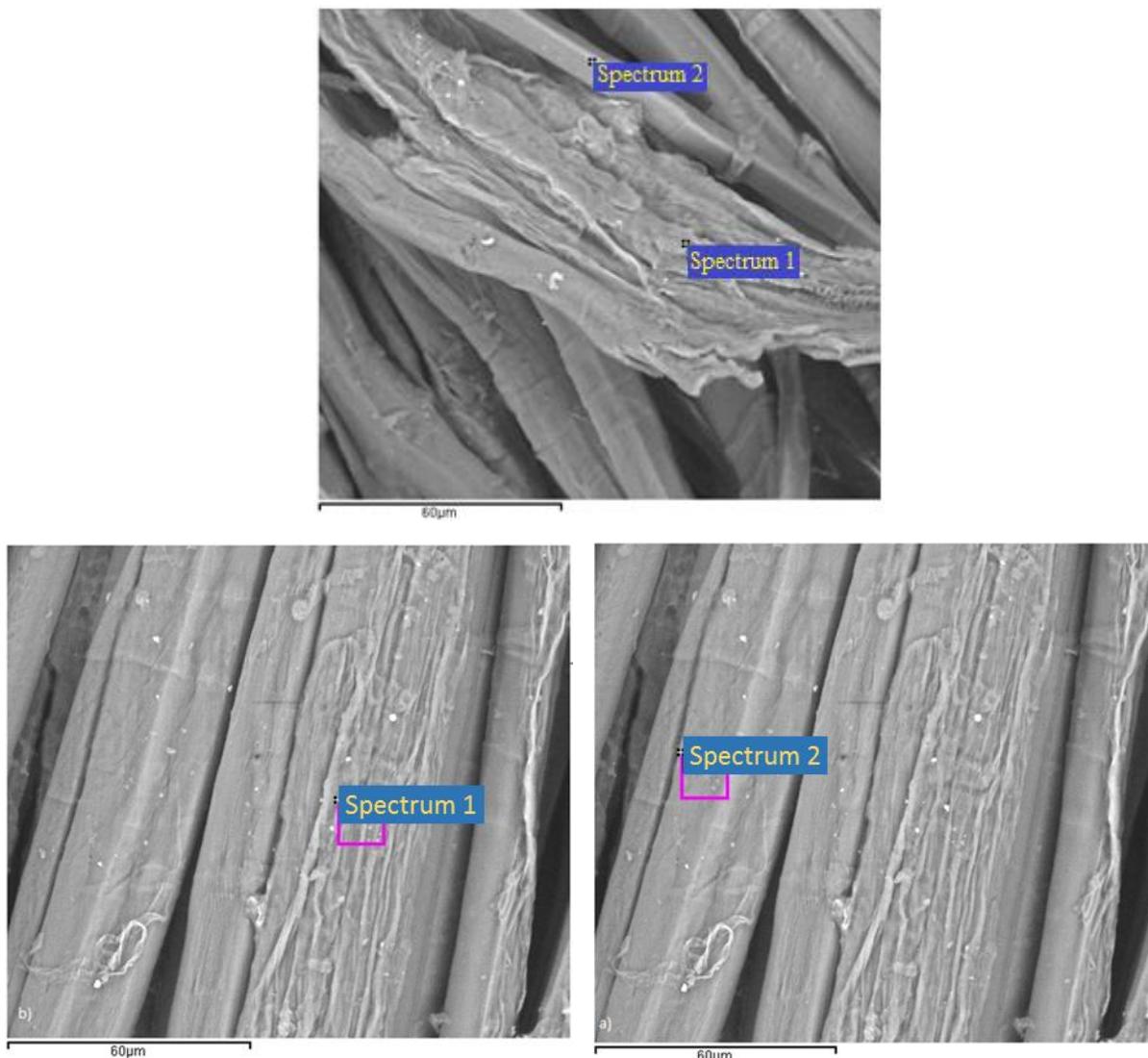


Figure IV-V SEM images of MPS treated flax fibres showing the formation of agglomerates.

Table IV-IV SEM/EDX spectrum of MPS treated flax fibres.

Spectrum 1 (treated fibre)			Spectrum 2 (untreated fibre)		
Element	% Mass	% Atomic	Element	% Mass	% Atomic
C	59.16 ± 2.44	67.07 ± 2.29	C	63.15 ± 2.65	69.72 ± 2.45
O	36.40 ± 3.09	30.98 ± 2.63	O	36.12 ± 3.14	29.94 ± 2.54
Si	1.55 ± 0.21	0.75 ± 0.15	Si	0.14 ± 0.08	0.07 ± 0.04

The EDX spectrum was also analysed for the BMA/MPS (Table IV-V) and the S/MPS (Table IV-VI) treated fibres. However, the low content of silicon indicated that the treatment molecules did not remain attached to fibres after washing step.

Table IV-V SEM/EDX spectrum of BMA/MPS treated flax fibres.

Element	% Mass	% Atomic
C	61.35 ± 2.11	67.90 ± 2.09
O	38.08 ± 2.98	32.01 ± 2.54
Si	0.12 ± 0.09	0.05 ± 0.04

Table IV-VI SEM/EDX spectrum of S/MPS treated flax fibres.

Element	% Mass	% Atomic
C	63.22 ± 2.14	69.77 ± 2.38
O	36.18 ± 3.22	29.88 ± 2.44
Si	0.18 ± 0.10	0.09 ± 0.05

Regarding the results of the water drop test on flax fabrics treated with both copolymers, no differences were observed through this qualitative test.

b3. Water uptake behaviour

Water uptake behaviour is exhibited for untreated and treated flax fibres when impregnated in composites (see Figure IV-VI). As all treated fibres were washed before being impregnated by the polyester resin, the influence of washing alone were analysed for untreated flax fibres composites. The results show a slight increase for about 5% ($M_s=6.3\%$ for untreated and washed FFRCs compared to 5.9% for untreated samples) in water uptake at saturation. This is probably linked to the removal of certain hydrophobic surface components of the flax fibres such as waxes. The removal of waxes from the flax fibre surface was also reported by Alix et al [151] to increase composites water uptake.

The BMA/MPS treated composites show an unexpected saturation water uptake of 10% compared to about 6% for the untreated fibres. The S/MPS treated composites present a slower kinetics of diffusion than the untreated composites, but the same saturation water uptake. Finally, the MPS treated composites present a reduction in the water uptake of around 8% ($M_s=5\%$ compared to 5.9% for the untreated composites) during the ageing test.

The influence of the manufacturing process on the treatment applied on fibres should be also taken into account here. Indeed it is supposed that the vacuum infusion technique and especially the presence of styrene in the unsaturated polyester resin alters either the surface of untreated fibres by removing components such as waxes and pectins, or the surface of treated fibres by removing the treatment molecules themselves. A similar behaviour was found by Feuillade et al. [193] that showed a solubilisation of the glass fibre sizing treatment by styrene during composites processing. The affinity

of the molecules treatments towards styrene in flax fibre reinforced unsaturated polyester composites should be evaluated to know their respective removal effectiveness.

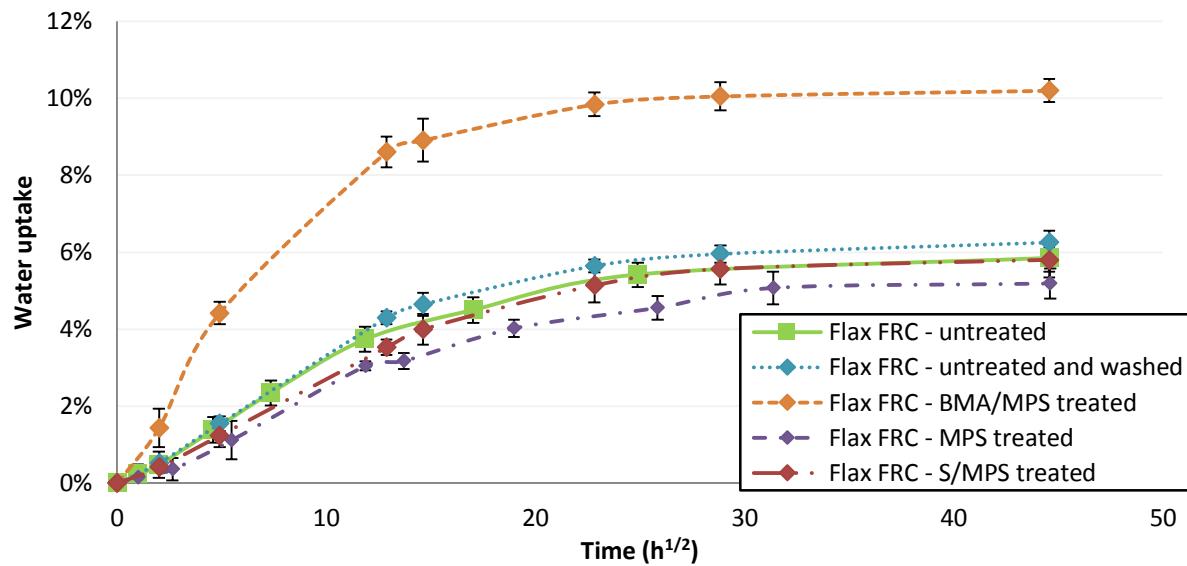


Figure IV-VI Water uptake behaviour of flax fibre reinforced unsaturated polyester composites (treated and untreated) immersed in water at 30°C.

IV-1.1.2 Resin post-crosslinking

Differential scanning calorimetry (DSC) is a highly sensitive technique to investigate the thermal properties of polymers. The evolution of the polymer's cross-linking degree when exposed to ageing conditions can reveal post-cure mechanism through an irreversible increase in the enthalpy.

It was shown in Figure III-X (page 101) that polyester resin attains a crosslinking degree of 78% after curing and 88% after a post cure treatment. Even after a thermal treatment, the degree of crosslinking of 100% is never obtained, which means that the degree of crosslinking of the polyester resin can evolve during ageing in water. It is well known that water diffusion induces both plasticization effect that leads to a decrease in mechanical properties (because of higher macromolecular chain mobility) and post-crosslinking that on the contrary leads to higher mechanical properties. These two phenomena are in competition during ageing.

The polyester resin post-crosslinking has been analysed separately from the plasticising effect by enthalpy measurements using DSC. Polyester resin degree of crosslinking was monitored during ageing in water at 30°C. The degree of crosslinking was found to increase from 88% before immersion to 96% at saturation for samples immersed in water at 30°C during 3600 hours (see Figure III-XI).

The crosslinking evolution behaviours of the polyester resin only cured (but not post-cured) and the polyester resin post-cured during 5 months at room temperature were compared to the polyester resin post-cured in an oven at 40°C during 16 h. It can be observed that polyester samples show different degree of crosslinkings before ageing but water ageing tends to homogenise the crosslinking degree beyond 200 hours ageing. It can be concluded that the presence of water in under-cured polyester resins accelerates the post-crosslinking kinetics. Zhou and Lucas [139] report that the evolution of the polymer properties (such as water uptake and the T_g) when exposed to hydrothermal ageing does not

depend solely on the water absorbed but also on the hygrothermal history of the materials and the time/temperature of exposure.

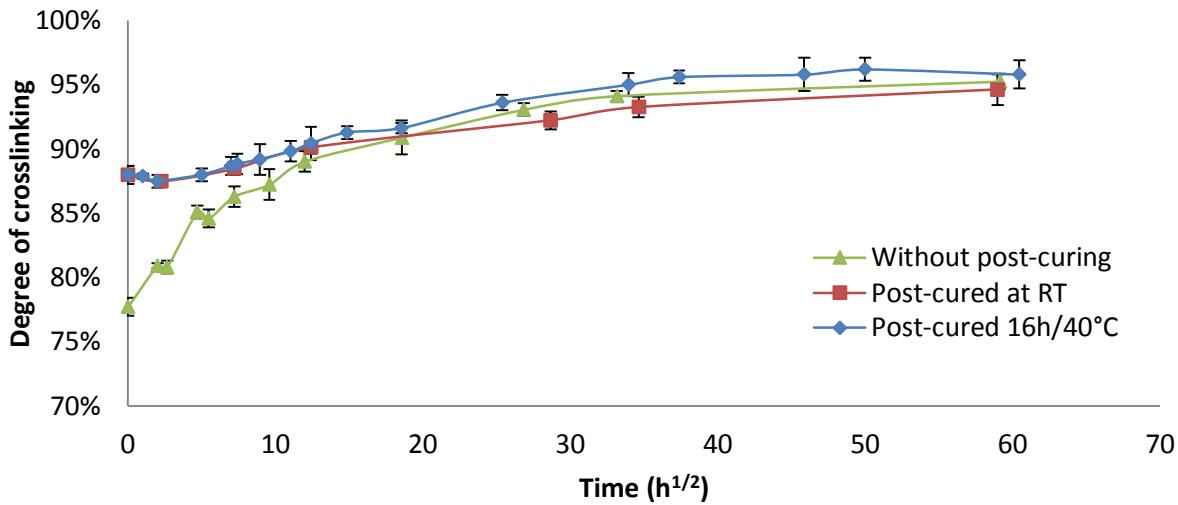


Figure IV-VII Degree of crosslinking evolution as a function of ageing time for polyester resin immersed in water at 30°C.

After immersion in water at 30°C, 50°C and 70°C for 3600 hours, the degree of crosslinking of the unsaturated polyester resin was measured at saturation (see Figure IV-VIII). Samples exposed to water ageing at 50°C and 70°C exhibit a degree of crosslinking similar to that of the samples aged at 30°C. Perrot [9] showed a similar trend for the degree of crosslinking of polyester resins in which the thermal energy transferred to the polyester samples by water leads to a resin degree of crosslinking of 95% after 9 months immersed in seawater at 40°C. The post crosslinking kinetic is found to be high at the beginning of the ageing period and slows progressively until the time to reach the degree of crosslinking of 100% becomes infinitely long. Weitsman [42] states that the water absorption of a polymer resin depends on the polarity of its molecular structure, but also on its crosslinking tridimensional structure. From this statement it can be concluded that the water uptake of polymer materials slows down with the increasing degree of crosslinking during ageing.

Furthermore, it should be noted that the plasticising effect related to the absorption of water in polymer is not observed here. The plasticisation mainly influences the T_g measurement while the post-cure observed during ageing impacts the polymer degree of crosslinking.

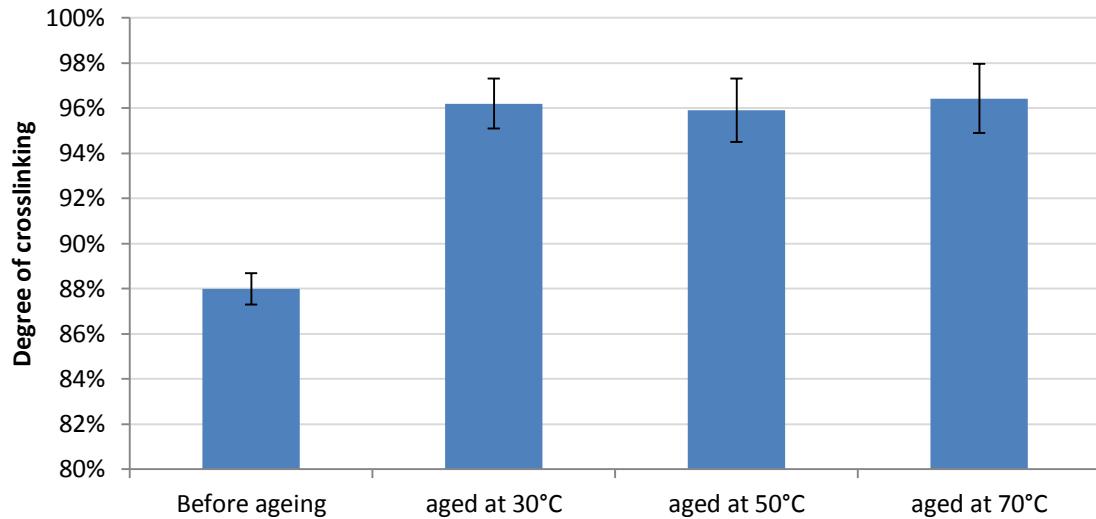


Figure IV-VIII Degree of crosslinking of polyester resin aged in water at 30°C, 50°C and 70°C for 3600 hours compared to the initial property before ageing.

IV-1.1.3 Resin Plasticising

The polyester resin absorbs water during ageing which is associated with an increase in the separation between molecular chains. This phenomenon, called plasticisation, enhances chain mobility and can be characterised by a decrease in the glass transition temperature for the wet polymer [42]. Typically, the plasticisation process is thermodynamically reversible.

Figure IV-IX shows the glass transition temperature evolution for the polyester resin during ageing in water. It can be noted that polyester's T_g decreases from 60°C to 56°C after 3600h immersed in water at 30°C, which is in agreement with the experimental results of Fayolle and Verdu [33] for epoxyde polymers exposed to 95% HR at 70°C during 500h. The decrease in polyester's T_g is associated here to the plasticising effect of water.

This experimental result was compared to the values obtained by using the rule of Simha-Boyer that takes into account the volume of water absorbed by the polyester resin and its glass transition temperature following the Equation I-X (page36). The two curves seem to follow similar tendencies for the decrease of the T_g during ageing. However, the experimental curve increases from 60°C to 62°C during the first hours of water immersion probably due to the post-crosslinking behaviour of polyester resin that is not taken into account by the rule of Simha-Boyer. Then, it is noted a constant gap between the two curves confirming that the increase of crosslinking during ageing does not influence the evolution of T_g during ageing.

The fact that the polyester resin plasticises while the post-crosslinking effect is still active complexifies the study of the polymer matrix evolving behaviour during ageing. The next subchapter "IV-2 - Reversibility of properties after hydrothermal ageing" (page 147) will approach the reversibility of properties by comparing the polyester thermal behaviour in a wet and in a dry state. Only after drying it will be feasible to distinguish the plasticisation effect (reversible) from the cross-linking behaviour (irreversible).

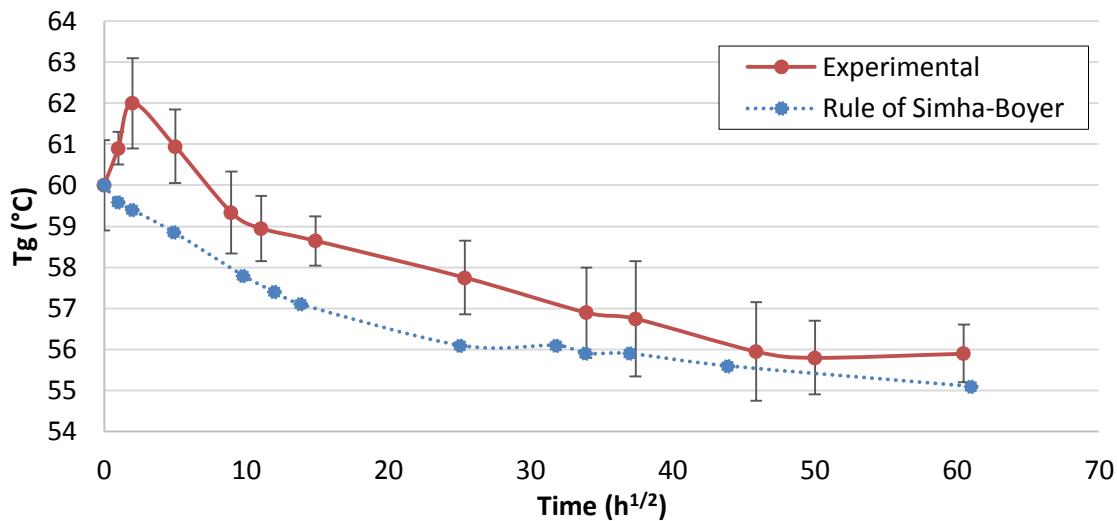


Figure IV-IX Evolution of the polyester T_g as a function of time for samples immersed in water at 30°C compared to the results obtained using the rule of Simha-Boyer.

The polyester resin was also exposed to other water ageing temperatures of 50° and 70°C. The results at saturation are compared to the initial ones in Table IV-VII.

It is shown that glass transition temperature decreases with increasing of the ageing temperature. The results at 30°C and 50°C are very similar, but a higher decrease is observed for the polyester resin aged at 70°C. This can be related to a plasticising effect of water, but also to the fact that the temperature of ageing was superior to the polymer's T_g . Indeed, the water uptake of the polyester samples aged at 30°C and 50°C were found to be very similar (0.9% and 1.0% respectively) while samples aged at 70°C absorbed 1.4%. The results obtained by using the rule of Simha-Boyer display a similar trend.

Table IV-VII Glass transition temperature of polyester resin immersed in water at 30°C, 50°C and 70°C for 3600 hours compared to the T_g before ageing.

Testing conditions		Glass transition temperature (°C)			
		Experimental		Rule of Simha-Boyer	
Unaged	Initial	60	±	1.1	-
	30°C	55.9	±	0.7	54.8
Water immersion	50°C	55.5	±	1.1	54.2
	70°C	52.2	±	1.1	51.9

Zhou and Lucas [139] report that an increase in T_g with increasing ageing temperature can be observed. The authors outline the influence of two types of bound water on the polymer T_g . Type I bound water breaks the initial interchain Van der Waals forces and hydrogen bonds acting as a plasticiser causing a large drop in T_g . In contrast, Type II bound water narrows the extent of T_g depression in the water saturated materials as a result of secondary crosslinking. The experimentally determined T_g values represent then the combined effects of the two mechanisms. Therefore, the increase in the T_g observed during the first hours of ageing this present work might be related to the resin post-crosslinking induced by the presence of Type II bonded water in the polymer network.

IV-1.1.4 Resin degradation

The variation of the infrared absorbance spectrum is obtained for polyester resin samples aged in water at 30°C and 70°C (see Figure IV-X). Three specimens of each reference were dried before measurement in order to subtract the reversible mechanisms linked to presence of water. The analysis of the spectra shows that no substantial change was found for samples aged in water compared to the unaged reference. It seems that the hydrolysis is not activated at the temperatures studied in this work. The hydrolysis of the polyester resin was indicated by Fraga et al. [48] as a peak appeared around 1670-1530 cm⁻¹ due to the carboxylate group which was produced through hydrolysis of the resin. However, in the present work this peak was not observed.

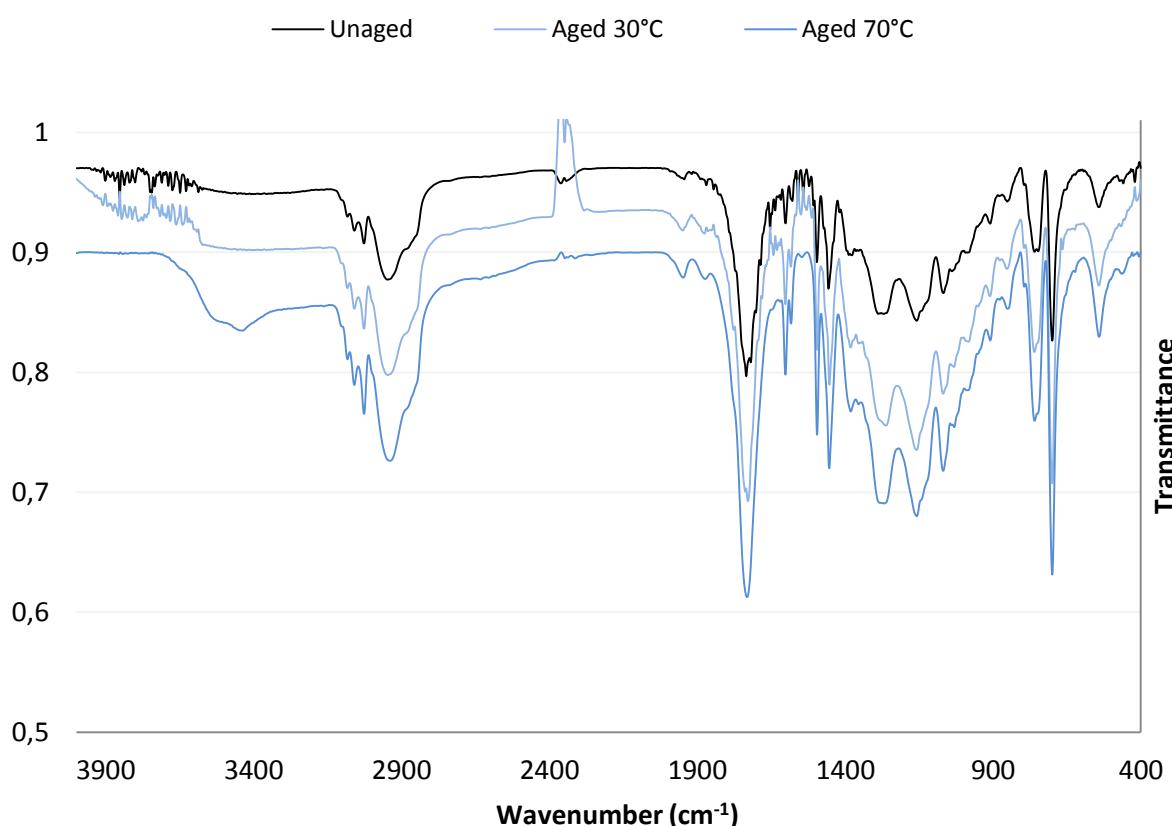


Figure IV-X FT-IR spectra of unsaturated polyester samples immersed in water at 30°C and 70°C compared to the unaged resin.

Peaks at 3600 cm⁻¹ and 3450 cm⁻¹, corresponding to anti-symmetric and symmetric vibrations of the hydroxyl group, confirm the presence of water in the polyester resin after ageing. In Fig. IV-XII, the absorption peak at 3530 cm⁻¹ may be interpreted as the antisymmetric vibration of the OH and the peak at 3440 cm⁻¹ refers to symmetric vibration of the OH. It can be noted from Figure IV-XI that these peaks appeared at a temperature of 70°C. Kawagoe et al. [194] reported an absorption peak at 3630 cm⁻¹ corresponding to water existing in a state near the gaseous state, probably being adsorbed to the ester group of the polyester matrix. A lower wavenumber peak at 3440 cm⁻¹ was also reported indicating the presence of clustered water near liquid state. The authors also analysed samples after drying and the same peaks (presenting lower amplitudes) were observed, which highlights the presence of bonded water molecules within the polymer samples even after drying.

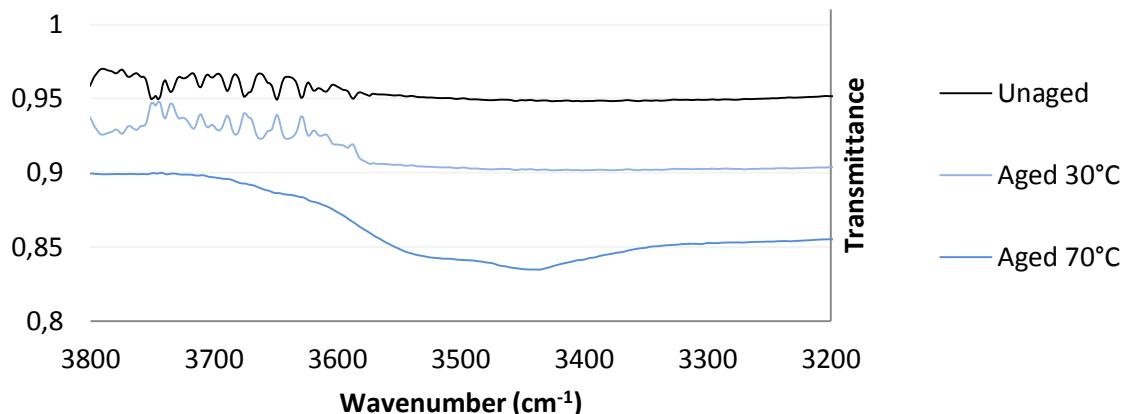


Figure IV-XI FT-IR spectra of absorbed water in unsaturated polyester samples immersed in water at 30°C and 70°C compared to the unaged resin.

IV-1.1.5 Extractibles removal during ageing

The biocomposites samples exposed to water ageing conditions were observed to change in the form of colour fading. Figure IV-XII shows a flax fibre reinforced composite before ageing and after ageing at 30°C for 3600 hours. This modification in the colour of composite samples may indicate a morphological evolving behaviour of flax fibres during ageing in water. Beg and Pickering [195] reported the leaching of lignin and water soluble products from wood/PP composite samples during ageing. The leaching of lignin was apparently responsible for the yellowing of composite samples.

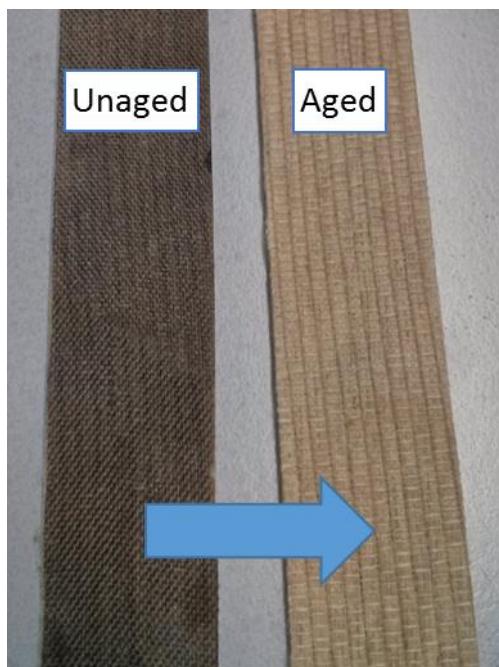


Figure IV-XII Flax fibre composite samples before and after ageing in water at 30°C for 3600 h.

Water bath was recovered and evaporated to analyse residues by SEM. It can be seen from Figure IV-XIII that a fibreous substance were removed during ageing. The SEM-EDX analysis shows that this substance is mainly composed by carbon and oxygen such as flax fibres. However it is difficult to confirm the location in the fibres structure that these components came from.

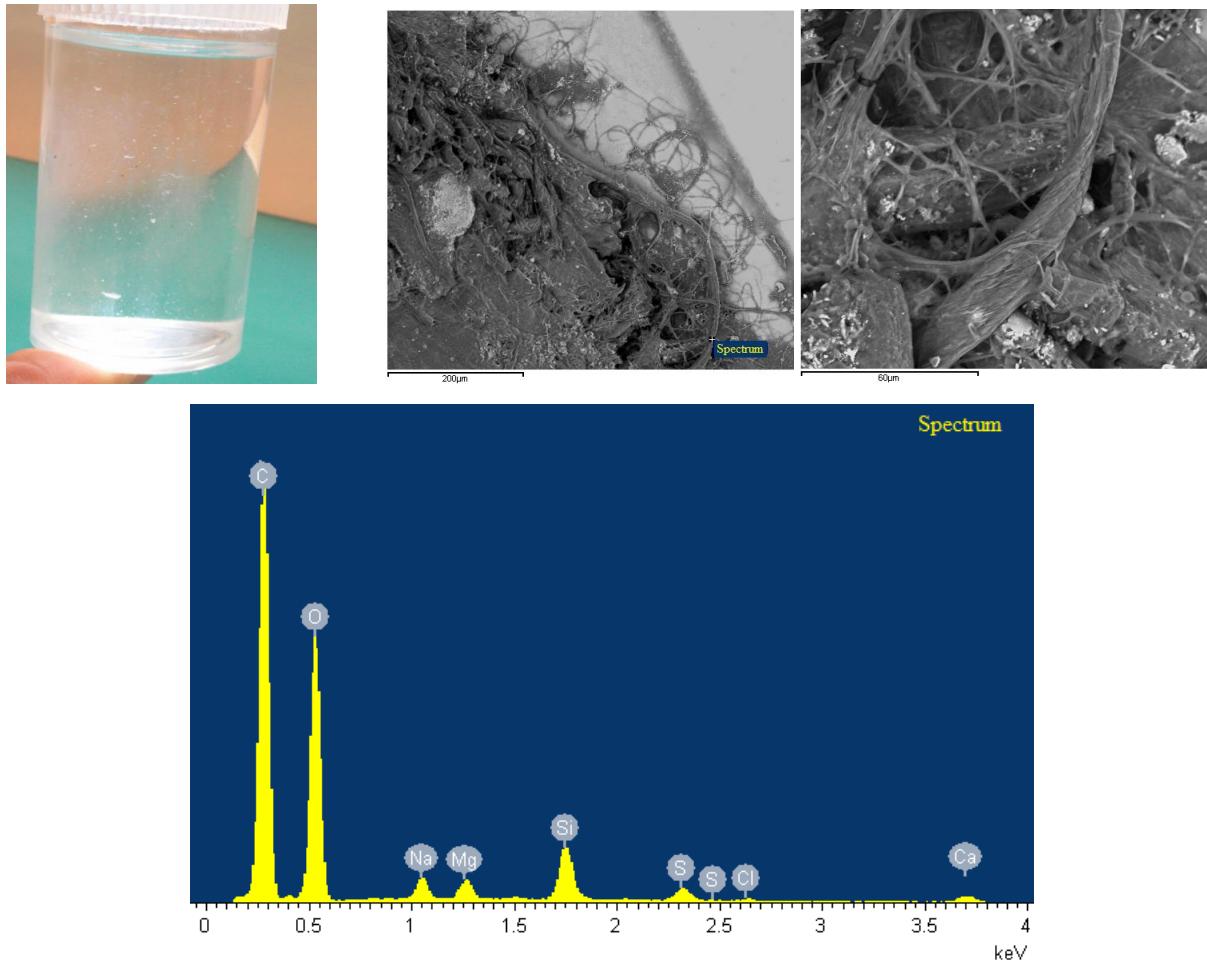


Figure IV-XIII EDX-SEM analysis of water extractable fibreous substance during biocomposites water ageing.

Besides fibres leaching, some authors report the release of unsaturated polyester resin into the water bath. Mouritz et al. [196] showed that the ester groups of the unsaturated polyester resin can be hydrolysed during ageing. This reaction generates alcohol and acid groups that lead to a lixiviation of certain components of the polymer matrix and result in a composite weight loss. In certain cases, a drop in the water uptake behaviour can be observed for long-term ageing tests, which is related to a release of polymer chemical components into water [25].

The evolution of the composites weight during water ageing is then a complex phenomenon that involves the water absorption (in free and bound forms) but also the release of certain components of fibres and matrix. These mechanisms take place at the same time and can lead to a misinterpretation of the water uptake measurements.

The analysis of the fibre extractables and the water used to age samples by FT IR technique should be performed in order to determine the nature of the released components. Otherwise, the percentage of components removed during ageing will be addressed in section IV-2.2.1 (page 148) when composites are dried and the water uptake is no longer taken into account.

IV-1.2. Dimensional stability

Composite materials presented a dimensional behaviour that evolved with the presence of water. Based on the hypothesis that the water absorption of composite materials is governed by a diffusion controlled process that leads to swelling, it is important to understand the swelling mechanisms that take place during hydrothermal ageing [53].

The water sorption undergone by polyester/flax composites generates swelling on specimens which is more or less pronounced depending on the water sorption behaviour of the fibres and the temperature. It was shown in the last section (see *Figure IV-I* – page 120) that flax fibre composites absorb more water than the glass fibre composites. A similar trend is noted for their swelling behaviour (see Figure IV-XIV): flax fibres composites thickness and width increase by more than $8.4\% \pm 1.2\%$ and $1.1\% \pm 0.24\%$ respectively, while glass fibre composites increase their thickness and width by about $1.8\% \pm 0.8\%$ and $0.1\% \pm 0.1\%$ respectively (during water ageing at 70°C). The length variation was observed to be around $0.1\% \pm 0.3\%$ for GFRC and around $0.2\% \pm 0.4\%$ for FFRC. In unidirectional composites, the higher swelling values are developed transversely to the fibre direction and in the smallest dimension, i.e. the thickness in this case, which confirms the results observed in this work. Moreover, the transversal direction in composites is not isotropic by considering the fibre volume content, which can also explain the difference observed here.

Furthermore, the swelling behaviour of composites can be related to the nature of their components and their behaviour in the presence of water. The work of Rassmann et al. [188] brings to light a similar behaviour for kenaf fibre reinforced polyester composite laminates immersed for 4 weeks in water at room temperature. Biocomposites display a thickness increase of about 6%, a width increase of about 0.3% and a length increase of 0.4%. The most pronounced composites length increase reported by the authors is probably due to the smaller length of samples (composites length of 50mm compared to 250mm of samples in this present work).

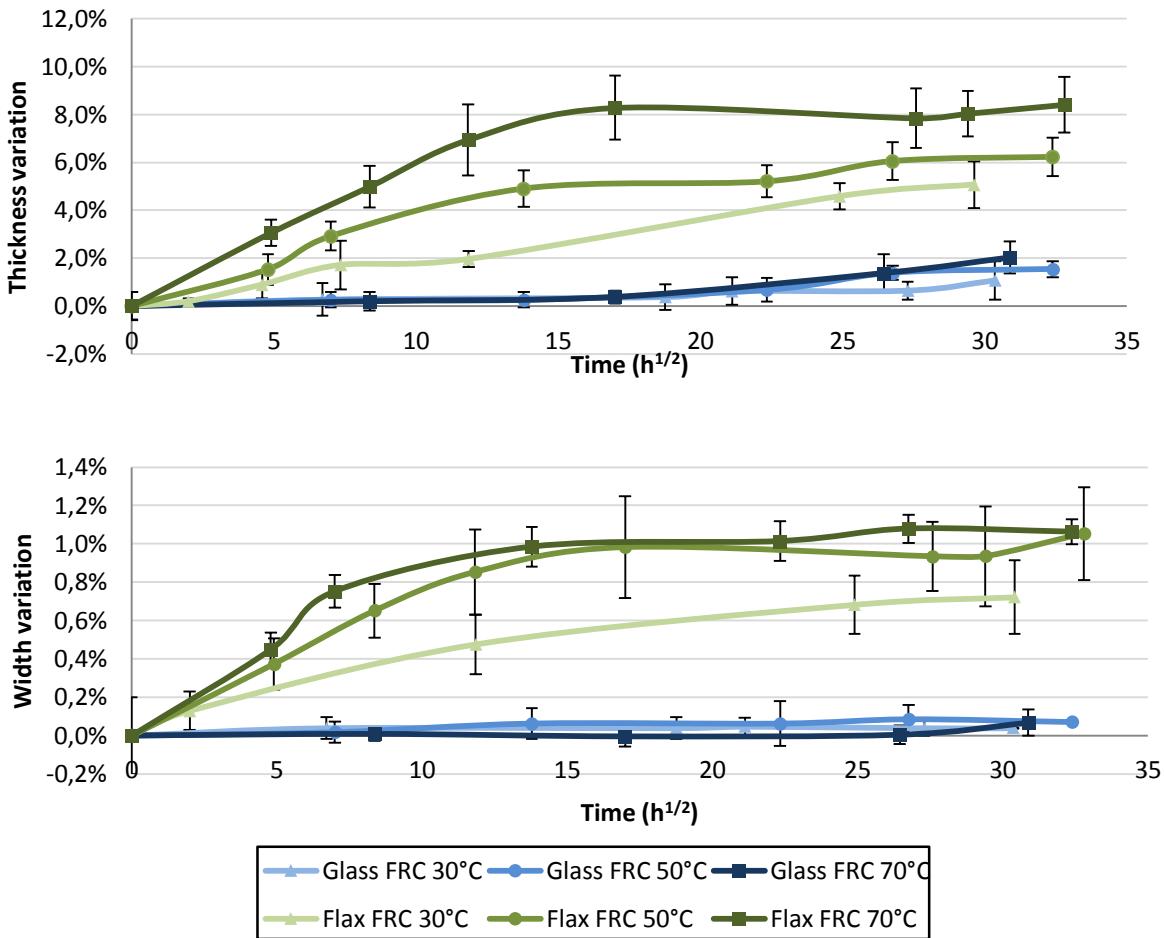


Figure IV-XIV Thickness and width variations as a function of ageing time for glass and flax fibre composites immersed in water at 30°C, 50°C and 70°C.

Glass fibres are hydrophobic materials presenting a high dimensional stability during ageing in water. The dimensional changing behaviour experienced by glass fibre composites can be associated to the swelling of the polyester matrix. Some authors report a swelling behaviour of the amorphous part of polymers due to the sorption of water [197]. The bound water was related to be responsible for polymer swelling by increasing the interchain bond length as free water enters through free volume existing between polymer chains [198]. In this case, the increase of swelling can be interpreted by the theory of the free volume, which asserts that the available volume between molecules increases with temperature [199].

Furthermore, the higher swelling values observed for flax fibre composites could be interpreted by analysing the fibre structure: flax fibre is a composite material by itself and presents a hydrophilic behaviour because of its cellulose cells. The water molecules penetrate into the fibre by forming hydrogen bonds between cellulose microfibrils. This allows more water to enter and swell the walls [182].

All the results for thickness, width and height of composite and polyester resin samples are presented in Table IV-VIII. It is interesting to note that the glass fibre composites swell more than the unreinforced polyester resin. It is expected that the polyester resin swells more than GFRC if only the water uptake behaviour is taken into account. However, the presence of materials displaying

differential swelling deformations when exposed to water uptake can generate internal stresses in the composite, particularly through thickness since the highest stress gradients will develop in the smallest dimension [198]. In the case where matrix swells without cracking, a composites swelling is verified but no additional water uptake is observed. The appearance of cracks in composites during ageing will be investigated in the next section IV-1.3 (page 136).

Table IV-VIII Measurements of thickness, width and height variation (at saturation) for unreinforced polyester resin, glass and flax fibre composites during into water.

Dimension (at t= 3600h)	Polyester resin			Glass FRC			Flax FRC		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
Thickness	0.39%	0.56%	1.49%	1.30%	1.54%	1.79%	5.07%	6.23%	8.42%
Stand. Dev.	0.33%	0.13%	0.52%	1.06%	0.30%	0.82%	1.00%	0.87%	1.16%
Width	0.28%	0.24%	0.21%	0.04%	0.07%	0.07%	0.67%	1.06%	1.05%
Stand. Dev.	0.12%	0.12%	0.10%	0.02%	0.06%	0.05%	0.18%	0.06%	0.24%
Height	0.10%	0.07%	0.08%	0.10%	0.06%	0.08%	0.12%	0.13%	0.15%
Stand. Dev.	0.15%	0.12%	0.16%	0.42%	0.31%	0.27%	0.39%	0.33%	0.37%

It can be also observed that the swelling of polymer and polymer composites depends on the water concentration and temperature, which is confirmed by other authors [106] [200]. Figure IV-XV shows the relation between the water absorbed and the samples volume variation observed for flax fibre composites immersed in water at different temperatures. The volume increase of the composites during early ageing was found to be lower than that of mass represented on Figure IV-XV by the volume of water absorbed. For longer aging time, volume and mass uptake are similar. It is interesting to note that the delay between the water uptake and the swelling of samples decreases with the ageing temperature. This behaviour was previously interpreted as a mechanism of filling of the free volume with the absorbed water (see Figure I-XXII – page 38). Xiao and Shanahan [53] report a similar behaviour for the swelling of an epoxy resin during hygrothermal ageing. In the graph, the hypothetical volume change (Volume water absorbed/V₀) assumes that absorbed water retains its intrinsic density.

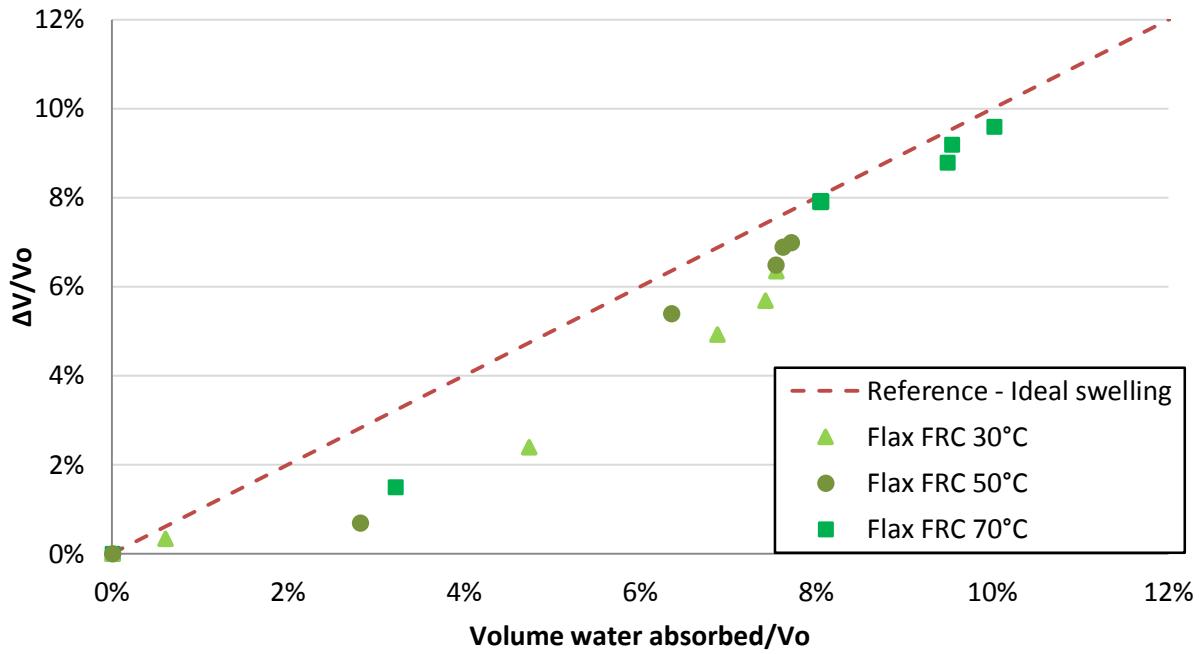


Figure IV-XV Swelling behaviour of flax fibre composites immersed in water at 30°C, 50°C and 70°C.

The swelling induced by hydrothermal ageing can be fully reversible or not depending on the damage processes experienced by the composites during ageing. The reversibility of the composites swelling behaviour will be addressed in the section IV-2.3 (page 151).

The next section will investigate the changes in composites microstructure related to water uptake. The microstructural analysis will give access to a characterisation of fibres swelling in the polyester matrix and potential cracking.

IV-1.3. Microstructural analysis of biocomposites

The differential swelling undergone by fibres and polyester matrix is likely to induce microcracking inside the composites during ageing in water. In the case of carbon fibre/epoxy composites, it was shown that interfacial cracks are developed when samples are immersed for 4300 hours in water at 75°C [201].

Cross-section images were taken after an immersion time of 3600h for glass fibre polyester composites aged at 70°C (Figure IV-XVI) and for flax fibre polyester composites at 30°C (Figure IV-XVII) and 70°C (Figure IV-XVIII). As concerns GFRC, no cracks were observed at the interface nor in the matrix rich areas after ageing samples at 70°C.

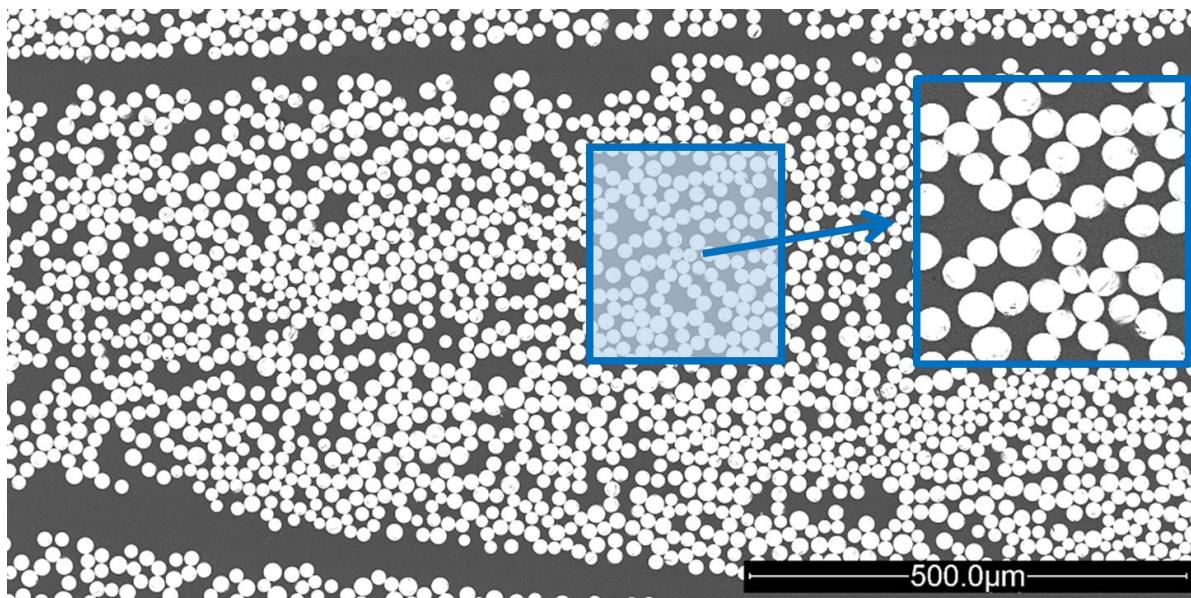


Figure IV-XVI SEM image of a glass fibre composite immersed for 3600 hours in water at 70°C.

A different behaviour was observed for flax fibres polyester composites. No changes in FFRC microstructure for samples aged in water at 30°C, but cracking is observed at 70°C.

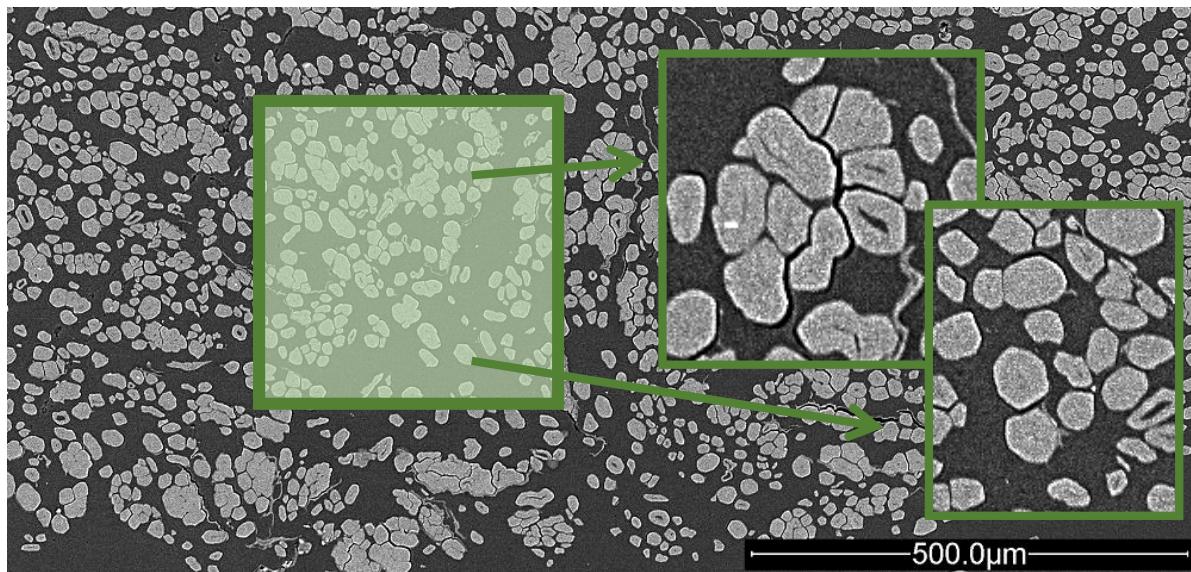


Figure IV-XVII SEM image of a flax fibre composite immersed for 3600 hours in water at 30°C.

Interfacial cracks are generated in samples immersed in water at 70°C preferentially located inside fibre bundles. In addition, decohesion is also observed at the matrix –unitary fibres interface. Another observation concerns the fibres degradation by the swelling of the free void at the center of the fibre (the lumen). Le Duigou et al. [157] report swelling and shrinkage of flax/PLLA biocomposites, where single flax fibres exhibit an enveloping cavity once immersed and dried compared to the unaged biocomposite samples. Furthermore, the cracks observed in the lumen after drying highlights the irreversibility of the fibres degradation during ageing.

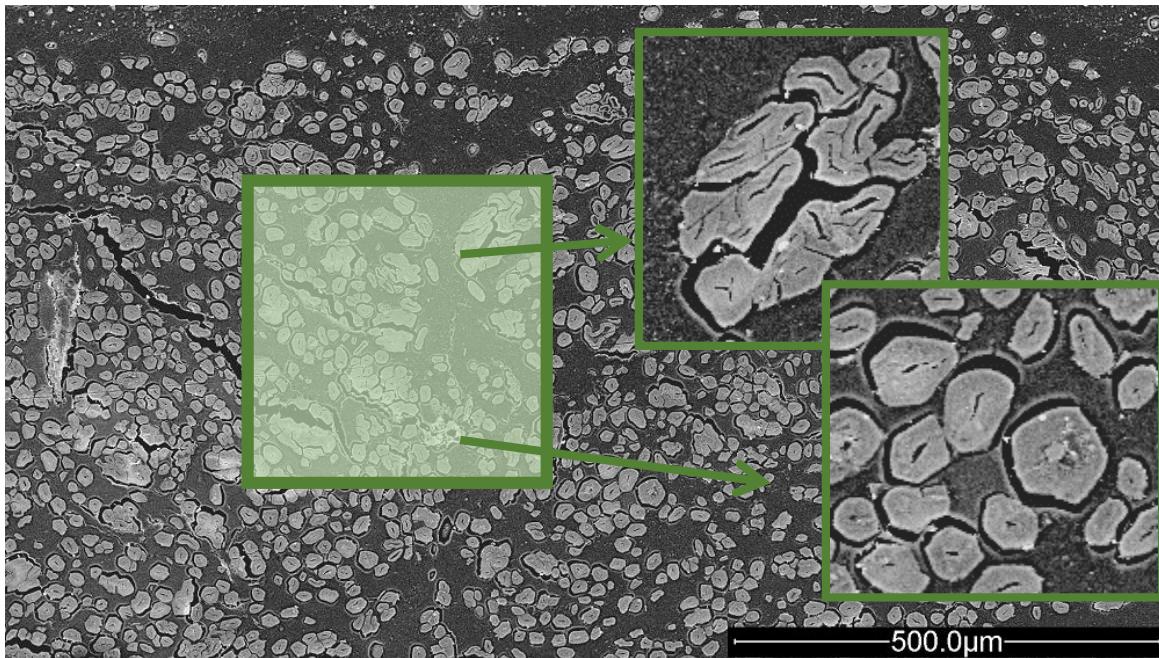


Figure IV-XVIII SEM image of a flax fibre composite immersed for 3600 hours in water at 70°C.

Madsen [70] has previously shown the appearance of cracks in hemp fibre reinforced polypropylene composites exposed to 85% RH. These cracks are located within the yarn fibre bundles and propagate along the periphery of fibres, i.e. at the fibre-matrix interface.

IV-1.4. Viscoelastic behaviour

The water uptake and swelling influence the evolution of composite elastic properties during ageing. The effects of the swelling on the properties of glass and flax fibre reinforced composites may include differential swelling and microcracking. The effect of water uptake may include plasticisation, hydrolysis and interfacial decohesion. All these phenomena led to a degradation of composites mechanical properties. However, water ageing can also lead to resin post-crosslinking that has beneficial consequences on the composites stiffness.

Figure IV-XIX presents the relative modulus evolution (the relative modulus value is the modulus of the aged sample divided by the modulus of the unaged one) of flax fibre composites compared to glass fibre composites and to the unreinforced polyester resin as a function of ageing time. Firstly, it can be noted that the loss in elastic modulus is greater for flax fibre composites than for glass fibre composites and polyester resin and the modulus loss is higher with increasing temperature.

The glass fibre composites present no change in modulus when immersed in water at 30°C for 3600 hours, while a slight decrease is obtained for polyester resin. On the other hand a 37% decrease with ageing time is depicted for FFRC.

It was reported in a previous section (see IV-1.1 – page 119) the competition between plasticisation and post-cure in polyester resin samples. The polyester T_g decreased during ageing showing that plasticisation was predominant. A similar behaviour was denoted for the elastic modulus since a decrease with ageing of flax fibre composites is observed. For GFRC both phenomena seem to induce equivalent effects on the stiffness.

For FFRC the water uptake is so important that plasticization phenomenon predominates. At 70°C a slight increase in glass fibre composite elastic modulus is observed denoting that post-cross linking phenomena predominate at high temperature. Indeed crosslinking is a thermally activated phenomenon that can be observed during the first hours of ageing for high temperatures (especially for temperatures higher than the polymer's T_g). This mechanism may also explain the increase in glass fibre composites modulus during the first 100 hours of ageing test. The elastic modulus of flax fibre composites displays a reduction of 41% and 45% (related to its initial modulus before immersion) at 50°C and 70°C respectively. The unreinforced polyester resin loses 4%, 6% and 7% of the elastic modulus for water exposure at 30°C, 50°C and 70°C respectively.

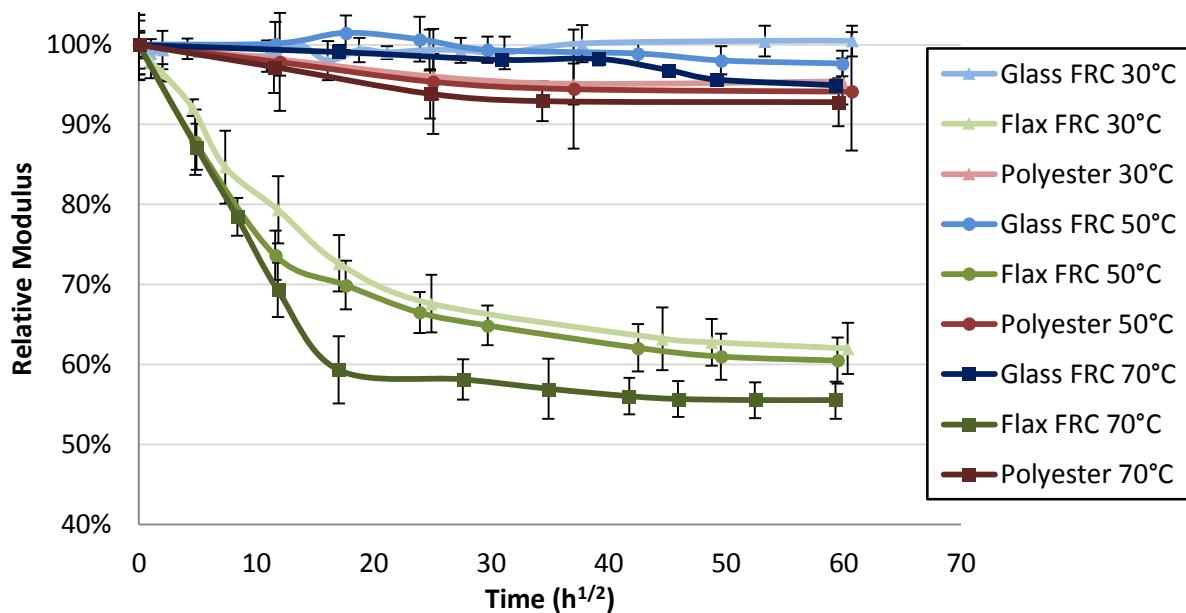


Figure IV-XIX Relative modulus (referenced to unaged samples) evolution as a function of ageing time for polyester resin, glass and flax-fibre composites immersed in water at different temperatures.

The relative modulus was plotted as a function of water uptake for flax fibre composites immersed in water at different temperatures (Figure IV-XX). For diffusional step, the elastic modulus of flax fibre composites was linearly dependant on the water uptake. A similar behaviour is described in the literature at both composite [127] and fibre [157] scale. The second phase is marked by a clear decrease of the stiffness when the composites reached the diffusional equilibrium state

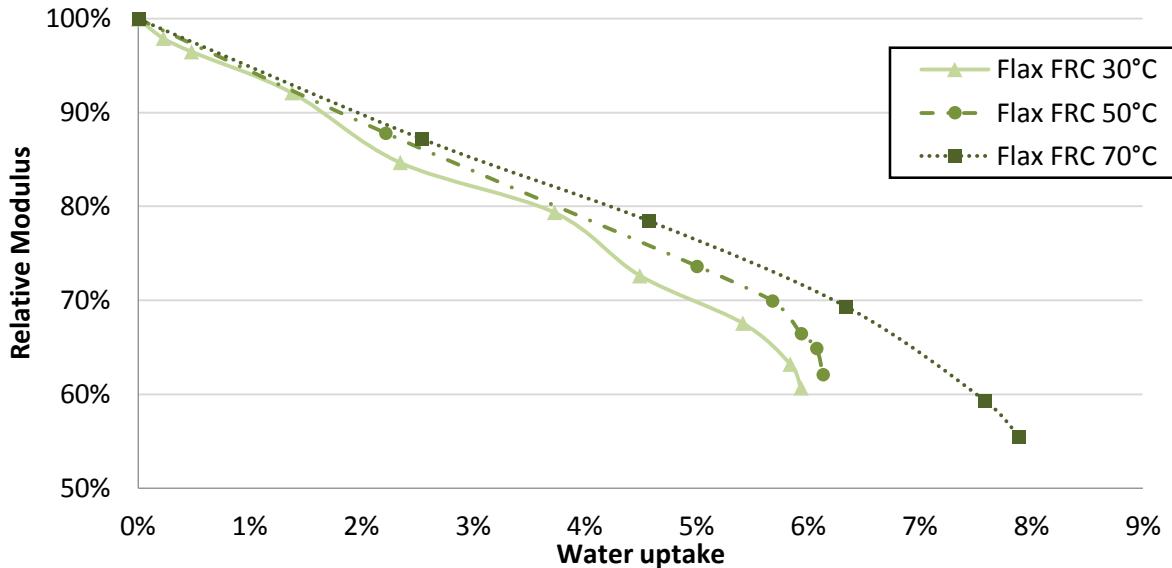


Figure IV-XX Correlation between the relative elastic modulus (reference to unaged samples) and the water uptake of flax fibre composites immersed in water at 30°C, 50°C and 70°C

To complete the study of the viscoelastic evolving behaviour of composites when exposed to hydrothermal ageing, the damping evolution of flax fibre composites compared to glass fibre composites as a function of ageing time is shown in Figure IV-XXI. The increase of FFRC's damping during immersion confirms that viscoelastic properties change with water uptake. This change is due to the flax fibre plasticisation in the presence of water [91]. GFRC's damping remains constant along the time confirming once more the hydrophobic behaviour of glass fibres. The polyester plasticisation in water was already observed in section IV-1.1.3 (page 128) by following the glass transition temperature during ageing using differential scanning calorimetry.

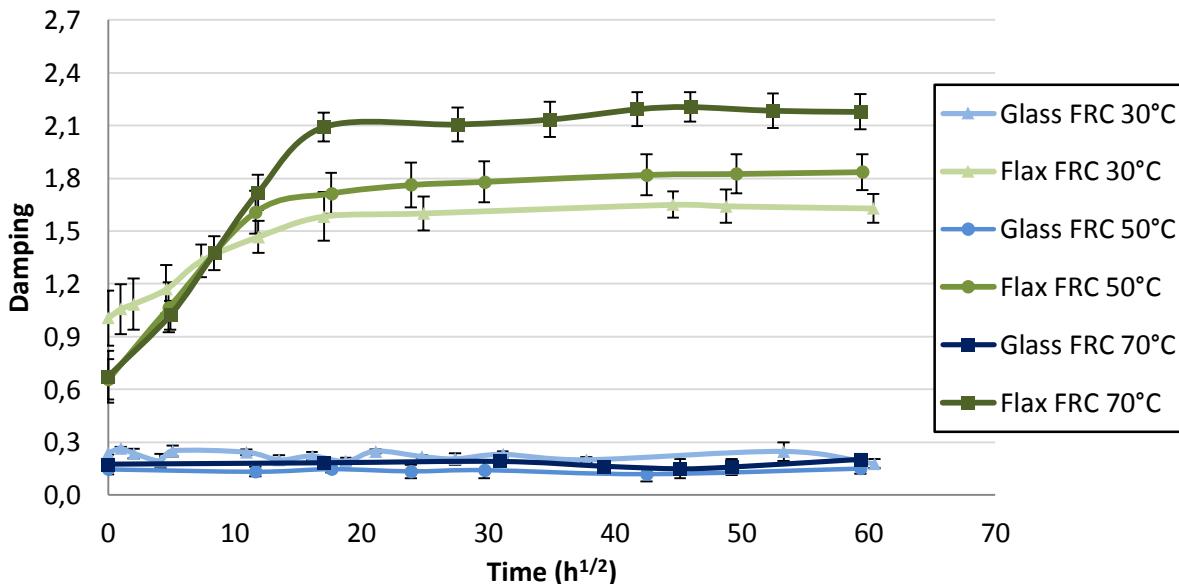


Figure IV-XXI Damping evolution as a function of ageing time for glass and flax-fibre composites immersed in water at different temperatures.

IV-1.5. Mechanisms of rupture

IV-1.5.1 Ultimate mechanical properties

Figure IV-XXII and Figure IV-XXIII exhibit the absolute and relative (reference to unaged samples) UTS and strain of composites in the initial state (before immersion) and at saturation at different ageing temperatures. The results show that GFRC tensile strength and strain are not affected by water uptake at 30°C and 50°C. However, a decrease of 36% and 43% in tensile strength and strain, respectively are observed for GFRC samples exposed to ageing at 70°C. The decrease in UTS at saturation may be explained by an interfacial debonding induced by differential swelling [202].

Concerning FFRC, despite a decrease in elastic modulus highlighted in the last section, it is noted an increase of the ultimate stress of 47% and 39% for samples immersed in water at 30°C and 50°C, respectively. A similar evolution for stress was reported in other studies [3]. Dhakal et al. attributed such increase in wet ultimate tensile stress to the fact that water causes fibres swelling and could fill the gaps between fibre and matrix. In this work, as shown in Figure IV-XVII (page 137), no gaps were observed for composites samples immersed in water at 30°C, and the increase of ultimate stress was probably due to a frictional effect caused by fibres swelling [203]. However, FFRC samples exposed to water ageing at 70°C were observed to present gaps between fibre and matrix (see Figure IV-XVIII – page 138), which can indicate interfacial decohesion.

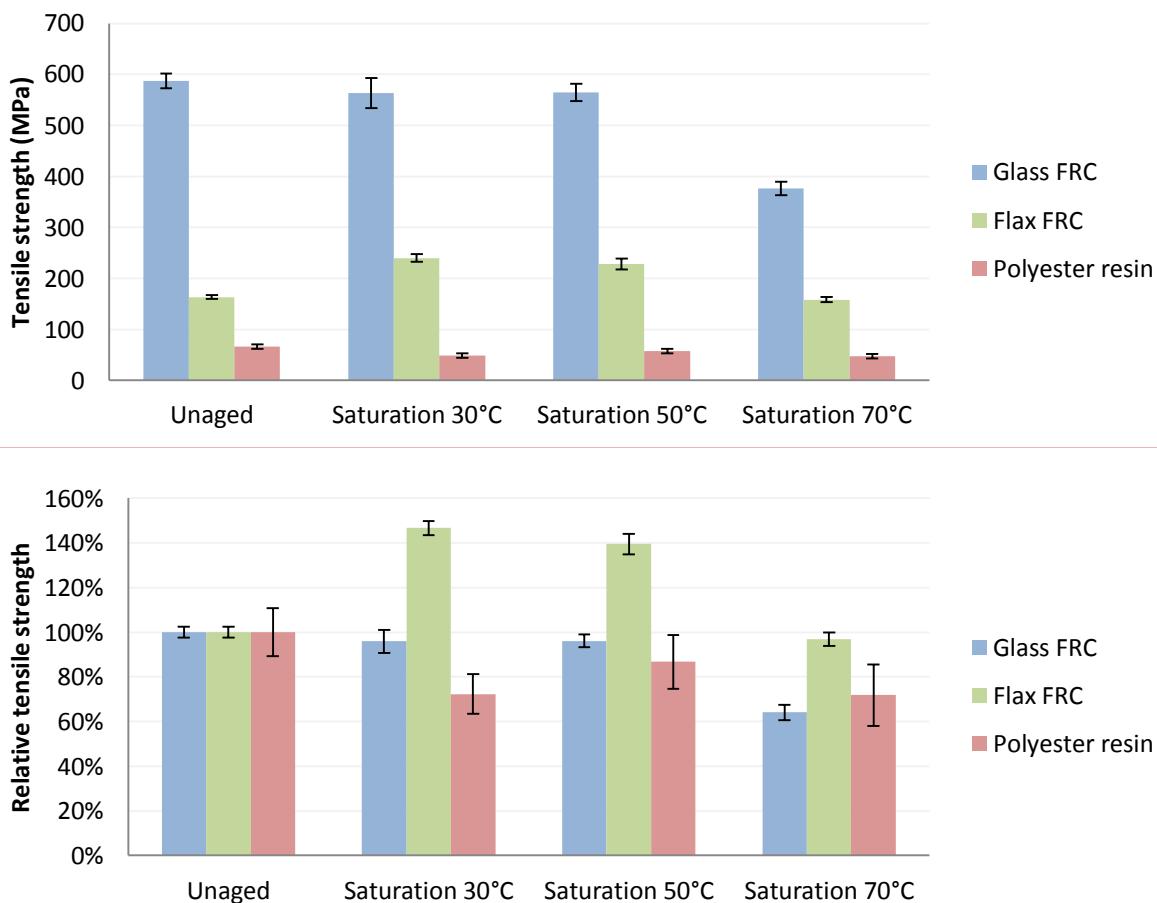


Figure IV-XXII Absolute (a) and relative (b) tensile strength (reference to unaged samples) of glass FRC, flax FRC and the polyester resin aged in water at 30°C, 50°C and 70°C.

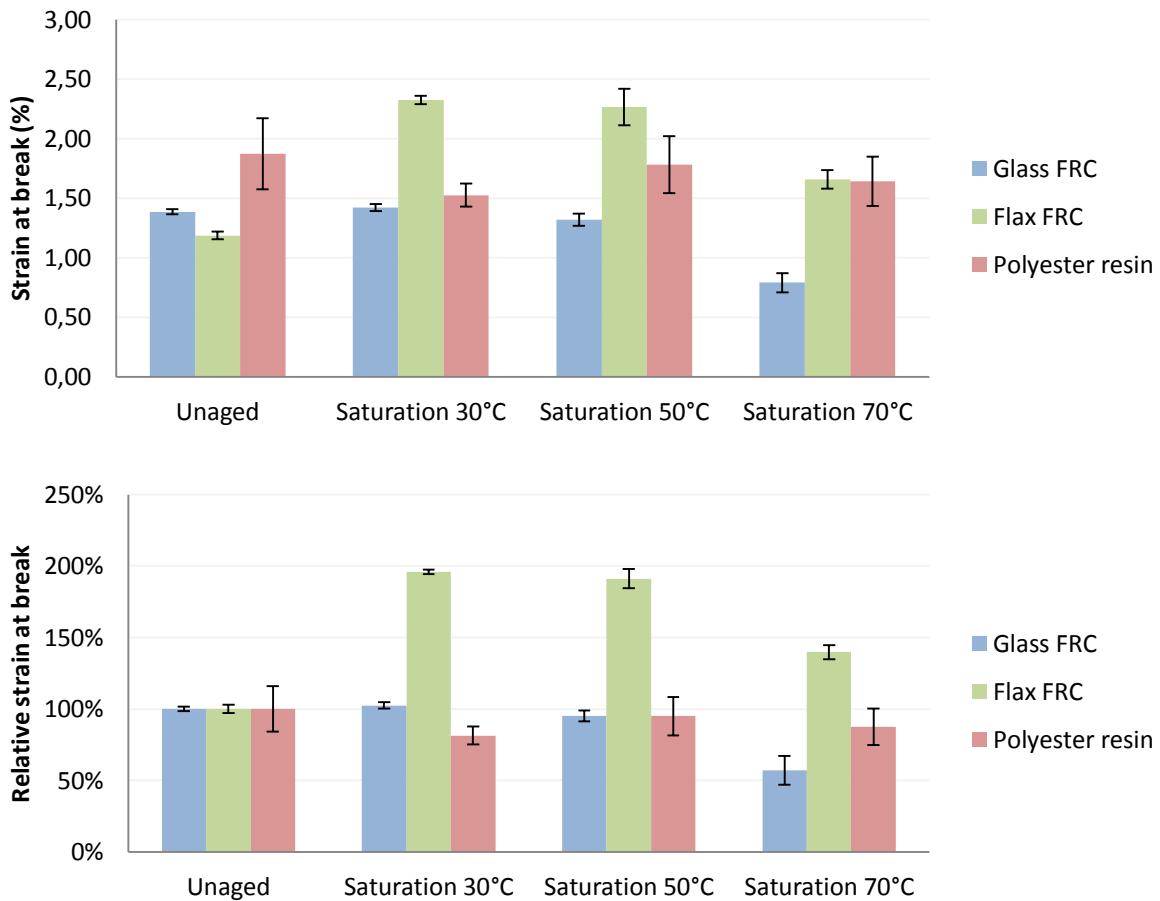


Figure IV-XXIII Absolute (a) and relative (b) tensile strain (reference to unaged samples) of glass FRC, flax FRC and the polyester resin aged in water at 30°C, 50°C and 70°C.

Some caution should be taken when characterising the fibre-matrix interface. The increase of the frictional effect caused by fibres swelling is mainly a physical mechanism while adhesion may involve physical (surface energy), mechanical (surface roughness) and chemical interaction. Indeed, the fracture surface analysis shows that surface debonding is already observed for samples aged at 30°C (see Figure IV-XXIV- A). This observation confirms that water generates fibres debonding, even if this is not visible by the cross-section image analysis because the empty space at the interface is hidden by fibres swelling.

Furthermore, debonding can lead to fibre slippage, which is highlighted by a longer revealed length (Figure IV-XXIV- B). Finally, the fibre ductile fracture behaviour after immersion (Figure IV-XXIV-C) confirms that fibre plasticisation is linked to the presence of water within composites.

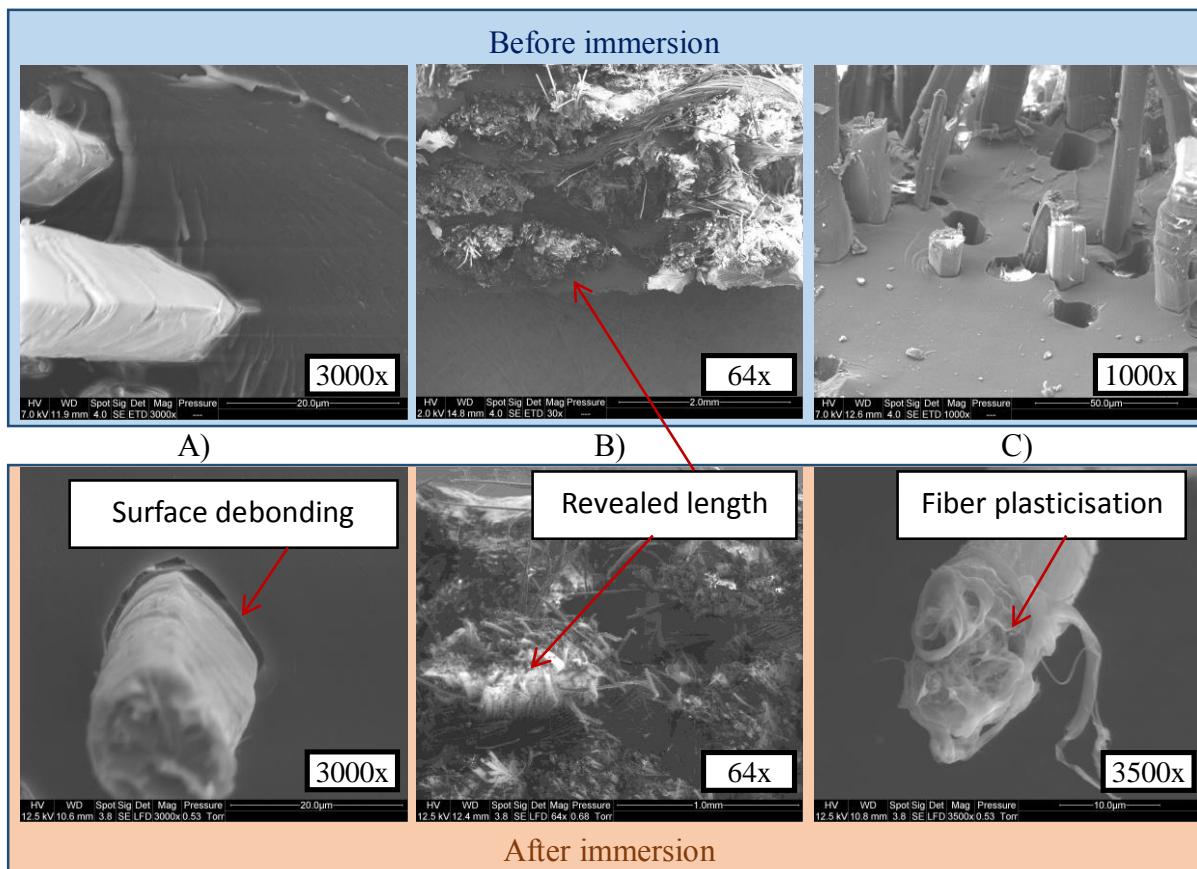


Figure IV-XXIV Fracture surface analysis of untreated FFRC before ageing and after ageing at saturation (immersion in water at 30°C).

IV-1.5.2 Interlaminar shear properties

The results for the relative interlaminar strength (reference to unaged samples) of flax and glass fibre composites at saturation are shown in Figure IV-XXV. It should be noted here that failure was occurred macroscopically through fibre–matrix debonding, hence allowing characterising the interlaminar shear strength by the ILSS measurements.

The glass fibre composites seem to be unaffected by the water ageing at 30°C and 50°C. However a decrease of ILSS is observed at 70°C that is probably due to the degradation at the fibre-matrix interface. This mechanism was also suggested to be responsible for the decrease in GFRC ultimate stress shown in the last section (see Figure IV-XXII – page 141).

The ILSS of flax fibre composites was found to be affected by water ageing for all ageing temperatures. It decreased by 8% at 30°C while a similar decrease of around 30% was observed at 50°C and 70°C. This observation is in accordance with the work of Assarar et al. [4], which suggests that the matrix interface weakening was the main damage mechanism of flax fibre epoxy composites aged during 20 days in water at room temperature.

Then it is noted that flax fibre composites have greater interlaminar shear strength than their counterparts glass fibre reinforced polymer. The geometry of flax fibres and their surface roughness undoubtedly contribute to this result.

The reversibility of the shear strength ageing in composites will be addressed in the next section.

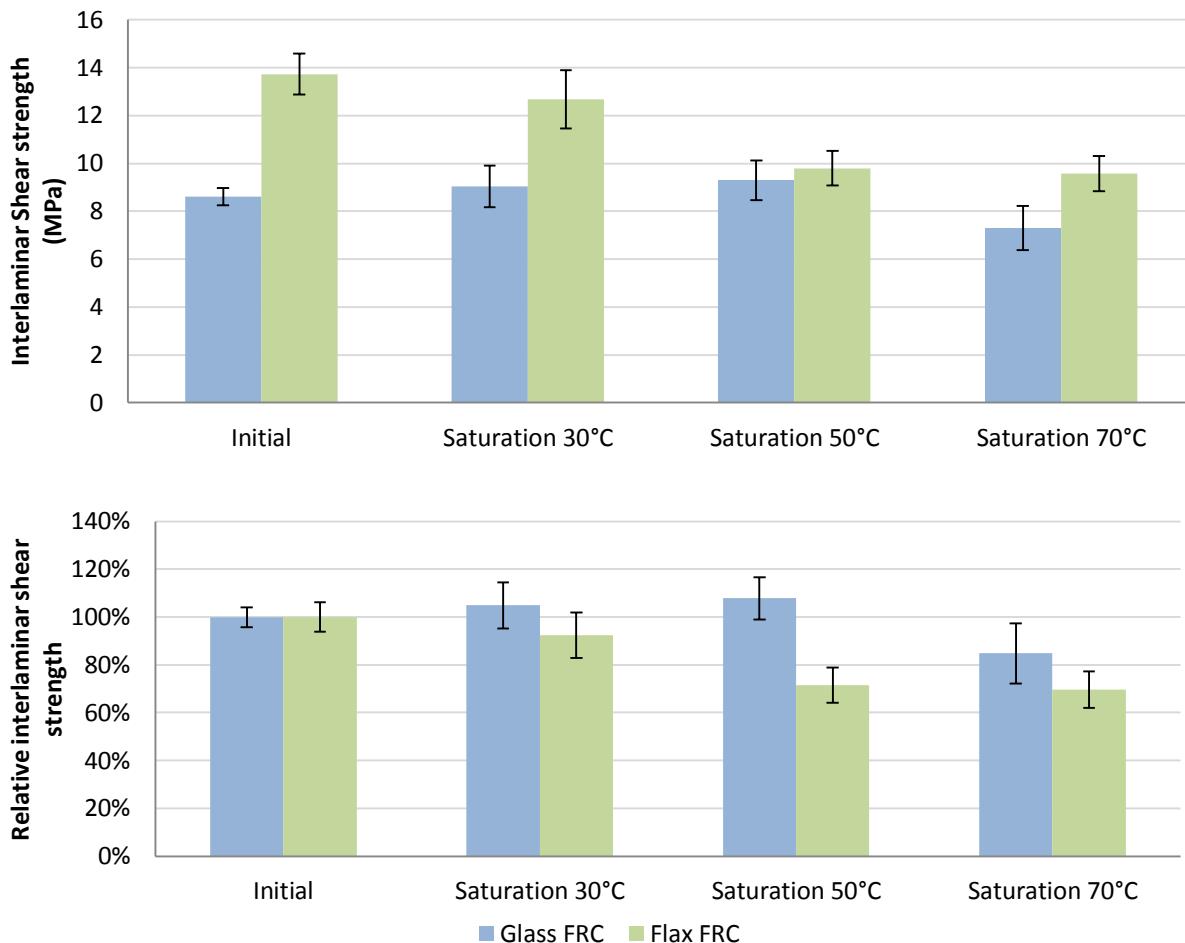


Figure IV-XXV Absolute and relative shear strength (reference to unaged samples) of glass (a) and flax (b) fibre composites saturated at 30°C, 50°C and 70°C.

IV-1.6. Conclusions

This section allowed the identification of the phenomena involved in the hydrothermal ageing of flax and glass composites. The glass fibre composites presented a hydrophobic behaviour when immersed in water contrasting with the hydrophilic behaviour of flax fibre composites. Different chemical treatments were applied to flax fibres aiming to improve their water resistance when impregnated by the unsaturated polyester resin. It is supposed that the vacuum infusion technique alters the surface of treated fibres by partially removing the treatment molecules. Moreover the washing step involved during the treatment processing also probably removed hydrophobic components of the surface of flax fibres such as waxes.

The effects of water ageing on polyester matrix behaviour included the resin post-crosslinking due to an incomplete curing reaction and plasticisation. The FT-IR analysis of the polyester resin highlighted the presence of bonded water molecules even after drying. Otherwise, a fibrous substance was found to be removed from flax fibre reinforced composites samples during ageing.

The composites water sorption led to a swelling phenomenon. The dimensional changing behaviour experienced by glass fibre composites was associated to the swelling of the polyester matrix, while flax

fibre composites displayed a swelling behaviour associated to the hydrophilic nature of their components. Even if GFRC swell during ageing, no cracking was observed at the interface, neither in the matrix rich areas. Otherwise, interfacial cracking was generated in FFRC samples immersed in water at 70°C, preferentially located in the interior of the fibre bundles, at the fibre-matrix interface and at the center of the fibre (the lumen).

GFRC samples were subjected to both plasticisation and resin post-crosslinking mechanisms, which were found to induce opposite effects on their viscoelastic behaviour. The analysis of the ultimate properties showed that interface degradation took place at 70°C, which was confirmed by the ILSS tests. Concerning FFRC, resin and fibres plasticisation and interfacial degradation were observed, but a frictional effect caused by fibres swelling also seemed to occur.

This section brought to light the occurrence of irreversible and reversible phenomena during ageing of composites in water. The effect of these mechanisms on the flax and glass fibre composites properties were characterised experimentally and compared to the data available in the literature. In the next section, the composites aged in water until saturation will be dried in order to dissociate irreversible from reversible phenomena.

IV-2. Reversibility of properties after hydrothermal ageing

The water saturated materials were exposed to dry atmosphere in order to verify the irreversible changes of the polyester resin and the composites properties induced by water sorption. It is of practical interest here to dissociate the impact of irreversible ageing mechanisms in composites behaviour from the reversible ones, the latter being related to the presence of water within these materials.

The water desorption was followed during drying to report the changes in physical, dimensionnal and mechanical properties of glass and flax fibre composites compared to those of the unreinforced polyester resin. The mechanisms observed at this point will support the understanding of the composites mechanical behaviour (elastic and ultimate properties) after drying. The role of the interfaces is investigated by interlaminar shear strength tests.

IV-2.1. Generalities

After water saturation was reached, samples were desiccated in a controlled atmosphere of 23°C/2%RH until weight stabilisation. The mass variation was monitored during drying and the mechanical properties of composites were analysed once samples reached weight stabilisation. The effects of reversible phenomena on composites behaviour, induced by plasticisation, are supposed to be suppressed once water is removed from samples. Hence, the changes observed on composites behaviour after drying are exclusively due to irreversible phenomena [42][33]. Some caution needs to be taken when comparing the composite properties before and after drying because this approach supposes that no changes are introduced during drying. This hypothesis is questionable because composites materials are not at the same equilibrium state before ageing (after processing) and after drying: samples are stored in a climatic room (23°C and 50% RH) before ageing and then dried at 23°C/2%RH after ageing. So the swollen fibres in storage conditions are supposed to unswell during drying which can introduce additional damage mechanisms in composites behaviour (such as fibre-matrix debonding)[97].

The drying conditions were settled at room temperature to avoid the evolution of composite properties related to temperature, and at 2% of relative humidity in order to accelerate the kinetics of desorption.

In order to determine the initial humidity into fibres when stored at 23°C/50%RH, tests were performed on flax fibres (see Appendix 1). It was confirmed that flax fibres have a moisture content of about 7% in weight before processing. It was also verified that the infusion process do not influence the fibres humidity level. Given the difference between the reference equilibrium state (23°C/50%RH) and the state after drying, unaged composites were dried after processing in order to investigate the influence of the drying conditions on the removal of the initial humidity within the flax fibre composites: three flax composite samples were exposed to 2%RH and their masses were followed during more than 5000 hours.

Finally, the viscoelastic and ultimate properties were determined for dried samples to assess the impact of reversible (physical) and irreversible (chemical) ageing on the mechanical properties of flax fibre composites. Among the ultimate tests, the interlaminar shear resistance of dried composites make possible the analysis of the irreversible damage at the interface

IV-2.2. Physical properties

IV-2.2.1 Water desorption

Composite samples were immersed in water during 3600 hours and then dried in a dry atmosphere for more than 900 hours to complete a full sorption/desorption cycle. The mass variation during the sorption/desorption cycle of flax and glass fibre composites as a function of temperature and testing time is shown in Figure IV-XXVI. It can be noted that the flax fibre composites do not return to their initial weight and samples display a lower mass compared to initial state before ageing. A weight loss of $2.0\% \pm 0.1\%$, $2.3\% \pm 0.1\%$ and $2.8\% \pm 0.1\%$ compared to the initial state before ageing was observed for samples aged at 30°C , 50°C and 70°C respectively. This weight loss reported after desiccation could be explained by two factors: (i) the fibres get drier than in the initial state and (ii) some components of the composite material are removed during the water ageing. Indeed, it was shown in the last section that a fibreous substance was removed during immersion in water (see Figure IV-XIII – page 132).

Unaged flax fibre composites were dried in order to verify the hypothesis of the fibres desiccation when exposed to 2%RH. The results show that unaged composites lost $1.3\% \pm 0.0\%$ of humidity in weight which can partly explain the weight loss undergone by water aged flax fibre composites.

By observing the water variation for glass fibre composites, it was shown a slight decrease in weight after drying of around $-0.16\% \pm 0.03\%$ for samples aged in water at 30°C . However, the samples exposed to water ageing at 50°C and 70°C displayed an opposite increasing weight behaviour of $0.30\% \pm 0.04\%$ and $0.20\% \pm 0.04\%$ respectively. This result may be related to the existence of competitive and opposite behaviours during ageing : the removal of polyester resin components and the attachment of water to polymer chains [42]. The analysis of the unreinforced polyester resin can provide more elements to the understanding of these mechanisms.

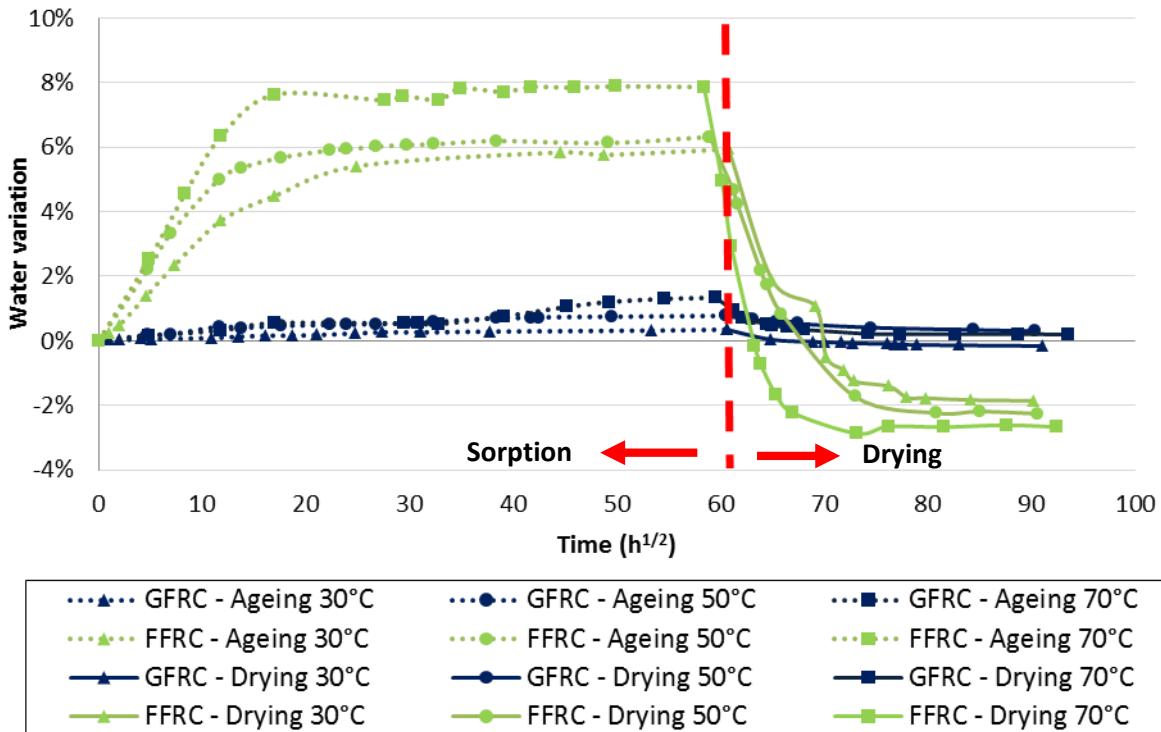


Figure IV-XXVI Flax and glass fibre composites relative mass variation during water ageing at 30°C, 50°C and 70°C, and during drying at 2% RH / 23°C.

The lixiviation of some components of the polymer matrix can also result in composite weight loss. Figure IV-XXVII shows that polyester samples lost mass after drying compared to their initial state before ageing. Polyester resin lost $0.75\% \pm 0.04\%$, $0.38\% \pm 0.02\%$ and $0.21\% \pm 0.07\%$ for samples aged at 30°C, 50°C and 70°C respectively. It is interesting to note here that, as for glass fibre composites, the polyester samples exposed to higher temperatures during immersion display a lower mass loss during drying step. It was shown in the last section that the polyester resin presented a two-stage diffusion behaviour that became more pronounced when temperature increased from 30°C to 70°C. This means that a fraction of water molecules that have diffused within the polyester resin may be linked to polymer chains through hydrogen bonds during water ageing. According to some authors, these hydrogen bonds could be sufficiently strong to endure the drying process [42] [204].

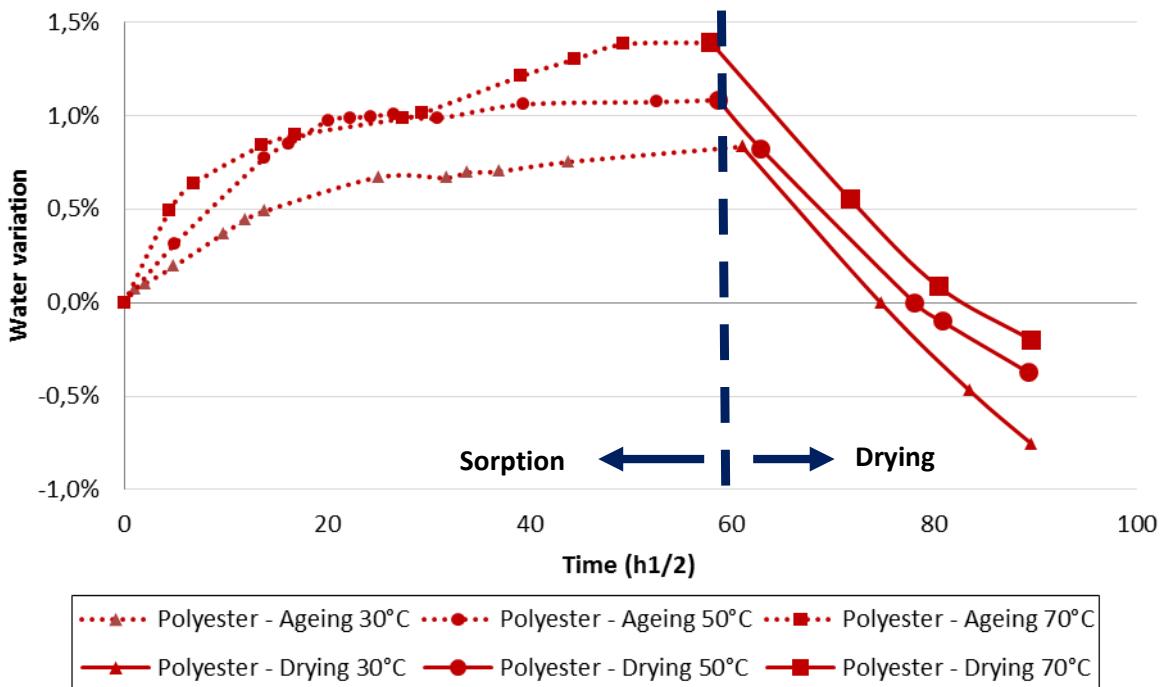


Figure IV-XXVII Polyester resin relative mass variation during water ageing at 30°C, 50°C and 70°C, and during drying at 2% RH/23%.

IV-2.2.2 Glass transition temperature of the resin

After been exposed to water ageing for 3600 h, the glass transition temperature (T_g) of the polyester samples was measured in a wet state (at saturation) and after drying (dried state). Table IV-IX shows the T_g measurements for the polyester resin aged at 30°C, 50°C and 70°.

The glass transition temperature of the polyester resin before ageing tests was reported to be $60.0 \pm 1.1^\circ\text{C}$.

T_g measurement of samples in wet state reveals the presence of either irreversible phenomena, such as resin post-cure that provokes an increase in T_g , or reversible mechanisms, such as resin plasticisation that leads to a decrease in T_g . It is then difficult to evaluate the influence of each factor separately when these are acting at the same time. For that reason, the analysis of the T_g in a dry state is supposed to reveal only irreversible phenomena.

Besides post-cure, other mechanisms may lead to an irreversible increase in T_g . Some authors report an increase in T_g with the leaching of low molecular weight species (LMWS) as the mobility of the polymers decreases when the LMWS are removed [198]. The lack of more accurate analyses here, such as the measurement of samples molecular weight, does not allow us to conclude on this point.

Table IV-IX Glass transition temperature of polyester resin in a wet and dried state according to the ageing temperature (samples aged in water for 3600h).

Testing conditions	Glass transition temperature (°C)						
	Wet state			Dried state			
Water immersion	30°C	55.9	±	0.7	73.6	±	0.9
	50°C	55.5	±	1.1	74.2	±	0.6
	70°C	52.2	±	1.1	76.4	±	1.4
Unaged and dried samples				60.0 ± 1.1 °C			

IV-2.3. Dimensional aspects

Thickness and width of composites were measured at saturation and after drying for samples aged in water at 30°C, 50°C, and 70°C. As it can be seen in *Figure IV-XXVIII*, the swelling in thickness and width direction are completely reversible for glass fibre composites but only partially reversible for flax fibre composites. In addition, FFRC present an irreversible thickness swelling that increases with the ageing temperature.

The composites morphology at saturation is different to that of dried composites in terms of swelling sorption at the microcracks and debonding around the fibre [205]. Indeed, it was shown in the last section that microcracks appear in the region next to the fibre bundles due to the fibres swelling (for composites aged at 70°C) (see Figure IV-XVIII – page 138).

The partial recovery observed for flax fibre composite thickness highlights the predominant effect of irreversible swelling over the reversible plasticising. This predominance of irreversible swelling becomes more important with the increasing temperature. It is interesting to note here that, even if swelling is often characterised as a reversible phenomenon, its effect on composites behaviour can be irreversible.

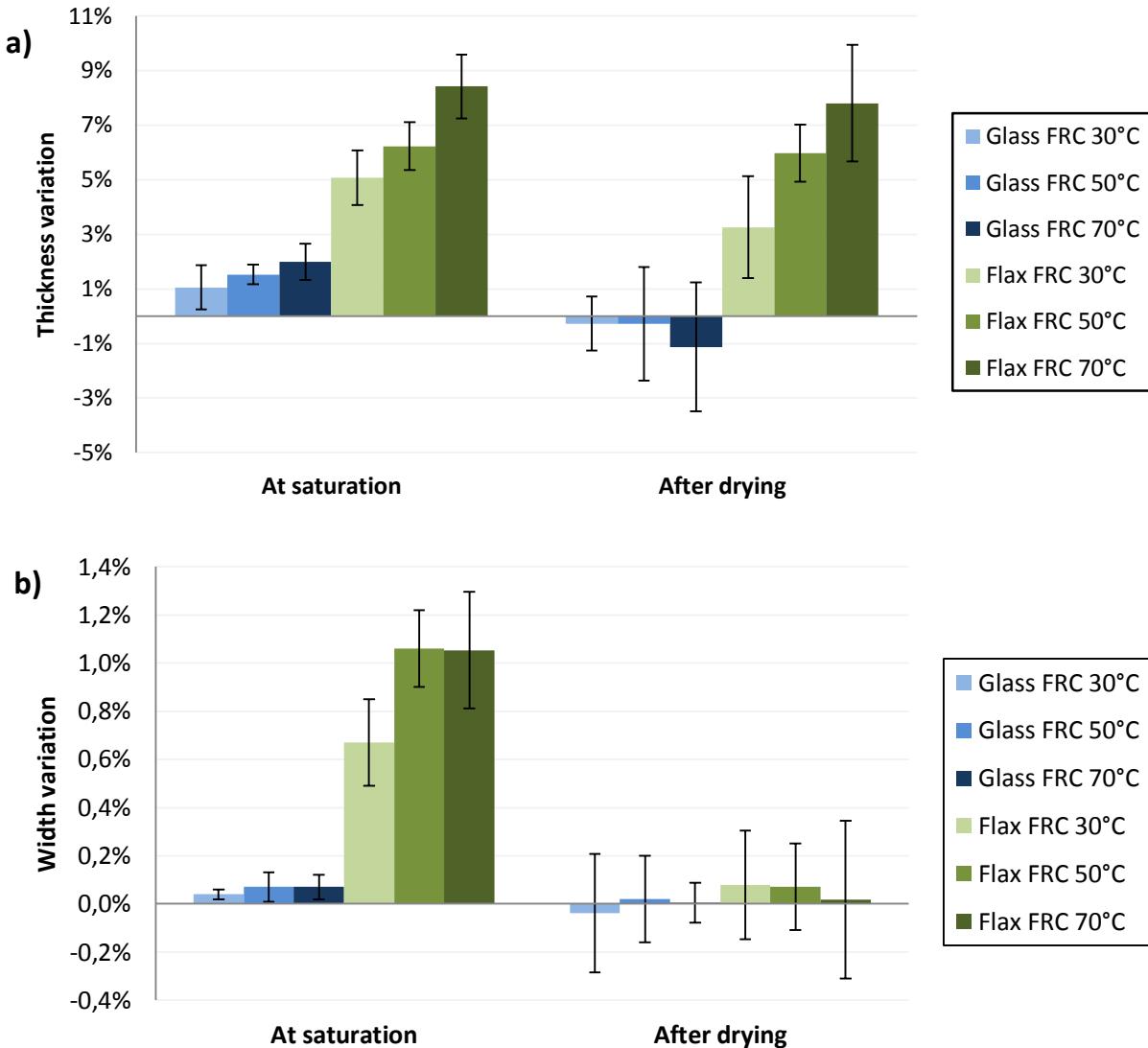


Figure IV-XXVIII Thickness (a) and width (b) changes of flax and glass fibre composites saturated at 30°C, 50°C and 70°C, and after drying.

IV-2.4. Mechanical properties after drying

The analysis of the water sorption and the swelling reversible behaviour of composite points up the occurrence of irreversible damage in these materials but does not provide the elements necessary to evaluate their effects on the materials properties during service conditions. The characterisation of the elastic behaviour and the fracture properties (elongation at break and strength) aim to correlate the ageing mechanisms described before to the irreversible degradation of composite properties.

IV-2.4.1 Viscoelastic behaviour

Figure IV-XXIX shows the absolute and relative elastic modulus after drying for FFRC, GFRC and the polyester resin aged at different temperatures. The plasticising effect of water on materials rigidity is no more active when samples are dried. The evolution of the materials rigidity after drying highlights the irreversible mechanisms that take place during ageing [206]. These irreversible mechanisms may lead to materials degradation, such as fibre/matrix interfacial debonding, or to the strengthening of

their properties, such as resin post-crosslinking and the frictional effect caused by irreversible part of the fibres swelling.

The polyester resin shows an elastic modulus that increases by about 21% when exposed to water ageing at 30°C probably linked to the stiffening effect of the post-crosslinking in water. Then a degradation is observed for samples aged at 50°C and 70°C which can be associated to the presence of remaining water in samples even after drying [207].

The glass fibre composites completely recovered their initial elastic modulus for samples aged at 30°C and 50°C but a slight decrease in elastic modulus is observed at 70°C. No difference was observed between the elastic modulus of saturated and dried samples. We shall come back to this mechanism of damage by studying the ultimate properties and the interlaminar shear of glass fibre composites that is the subject of the next part.

Flax fibres composites showed an elastic modulus that decreases with increasing temperature. The effect of plasticisation and fibres swelling on biocomposites behaviour are, at least partially, no longer active. A degradation of biocomposites elastic modulus was only observed at 70°C, related to the fibre/matrix interface debonding observed by SEM analysis (see Figure IV-XVIII – page 138).

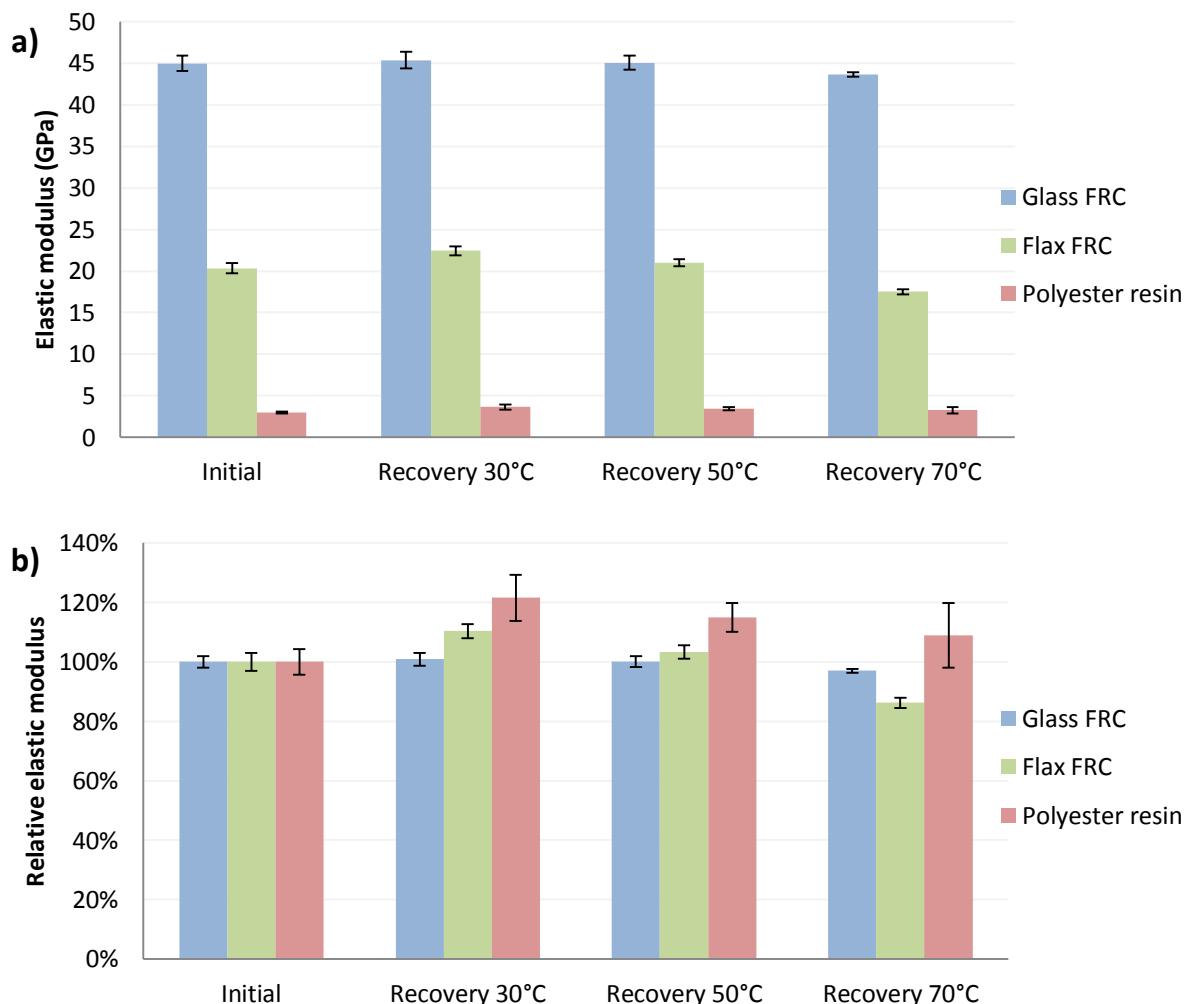


Figure IV-XXIX Absolute (a) and relative(reference to unaged samples) (b) elastic modulus after drying of glass FRC, flax FRC and the polyester resin aged in water at 30°C, 50°C and 70°C.

Concerning the damping behaviour of glass and flax FRC (see Figure IV-XXI), it can be observed that values after drying are lower than in the initial state before ageing for composites aged in water for all analyzed temperatures, excepted for flax fibre composites aged in water at 70°C, for which an increase of 40% is observed. This general behaviour can be partly explained by the stiffening effect of the resin post-crosslinking. However, for the case where an increase is observed, Regazzi [208] highlighted that the evolution of biocomposites damping behaviour is exclusively linked to the presence of water within their structure. This statement supports the hypothesis that a portion of the diffused water molecules remains hooked up to the polymer chains even under drying conditions [42] [204]. Other hypothesis relate a micro-friction mechanism between the polymer matrix and the detached fibres that might induce an increase in biocomposites damping behaviour [170].

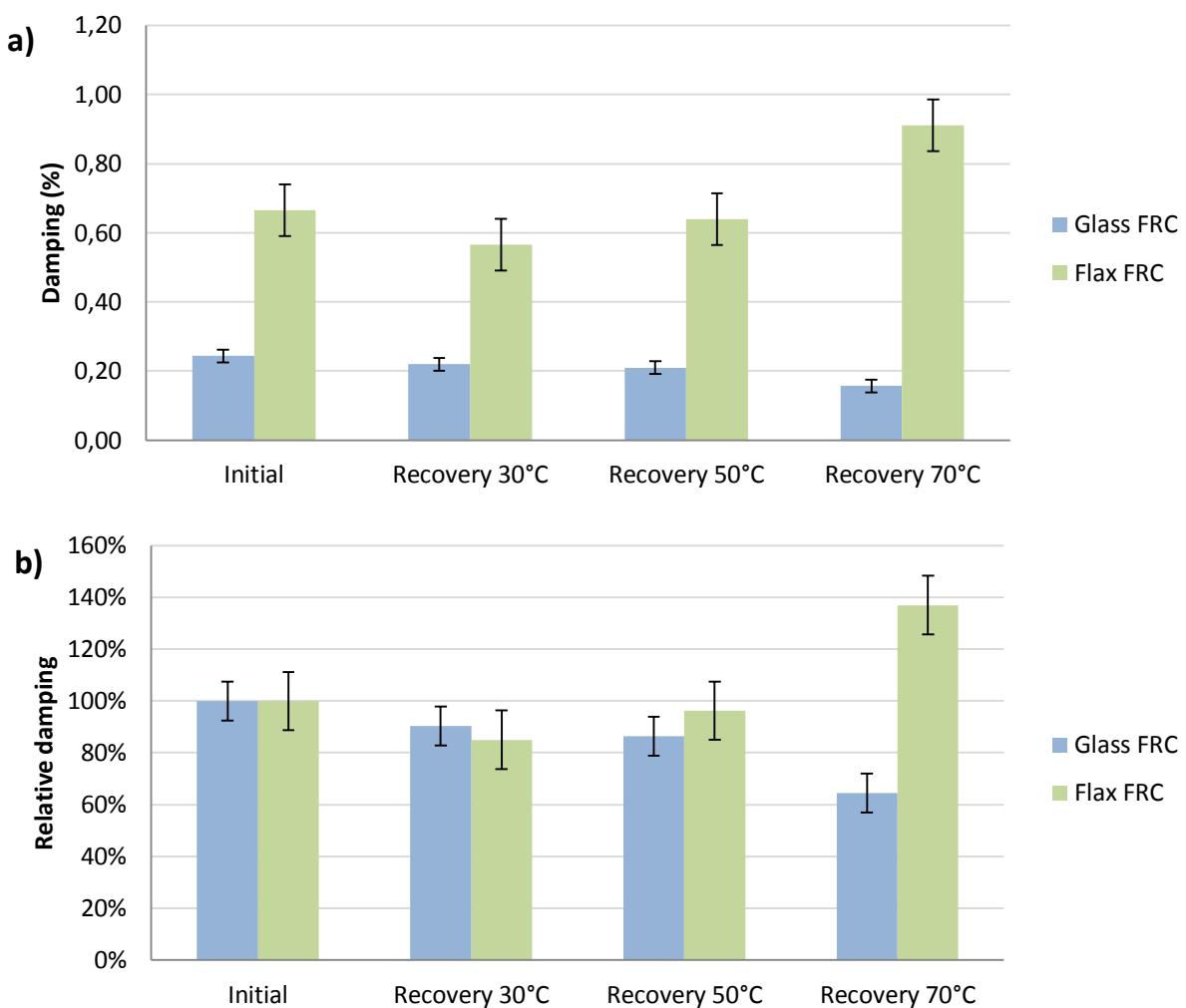


Figure IV-XXX Absolute (a) and relative (reference to unaged samples) (b) damping properties of dried glass and flax FRC aged in water at 30°C, 50°C and 70°C.

IV-2.4.2 Ultimate properties at break

The ultimate tensile stress and strain of composite materials and the polyester resin were measured after drying for samples aged at 30°C, 50°C and 70°C, and then compared to their initial state before ageing. The absolute and relative values (reference to unaged samples) of tensile strength and strain are shown in Figure IV-XXXI and Figure IV-XXXII.

No changes can be observed on GFRC ultimate stress for samples exposed to water ageing at 30°C and 50°C. However the tensile strength of dried samples aged at 70°C dropped by 20%. By comparing the decrease of 20% for dried composites to 36% for water saturated composites, it can be concluded that around 16% of the observed decrease in GFRC tensile strength is due to reversible mechanisms, such as plasticisation and swelling. This result highlights the competition between reversible and irreversible mechanisms in glass fibre composites behaviour during ageing.

Concerning the flax fibre composites, samples display an increase in tensile strength when exposed to water ageing at 30°C compared to the unaged composites. This behaviour was also reported for saturated composites (see Figure IV-XXII – page 141) and related to a frictional effect caused by fibres swelling [203]. Dried flax composites aged at 30°C present an increase of 9% compared to the unaged composites. By comparing the increase of 9% for dried composites to 47% for water saturated composites, it can be concluded that around 38% of the observed increase in FFRC tensile strength is due to reversible mechanisms, mainly linked to the fibres swelling. It is interesting to note here that the ageing mechanisms of flax fibre composites immersed at 30°C are mainly reversible. A similar recovery rate of 40% is related for flax fibre composites aged in water at 50°C, but this rate decreases to 8% when composites are exposed to water ageing at 70°C.

The polyester resin presents a slight increase in the ultimate strength and strain for samples exposed to ageing at 30°C and 50°C probably linked to the post-crosslinking in water. The resin samples exposed to ageing at 70°C showed a decrease of 3% in tensile strength and strain that can be due to the resin hydrolysis. The effects of post-crosslinking and the hydrolysis of the resin cannot be decoupled by drying samples because of their irreversible nature.

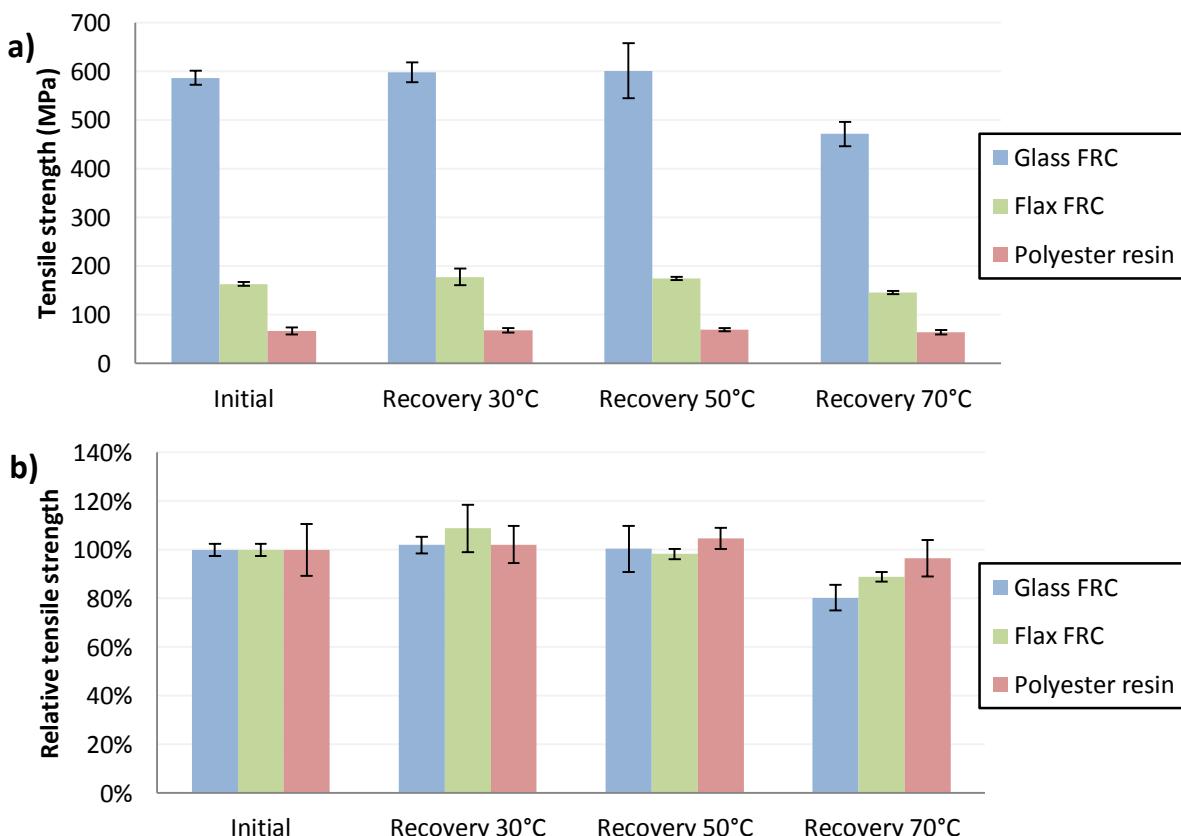


Figure IV-XXXI Absolute (a) and relative (reference to unaged samples) (b) tensile strength after drying of glass FRC, flax FRC and the polyester resin aged in water at 30°C, 50°C and 70°C.

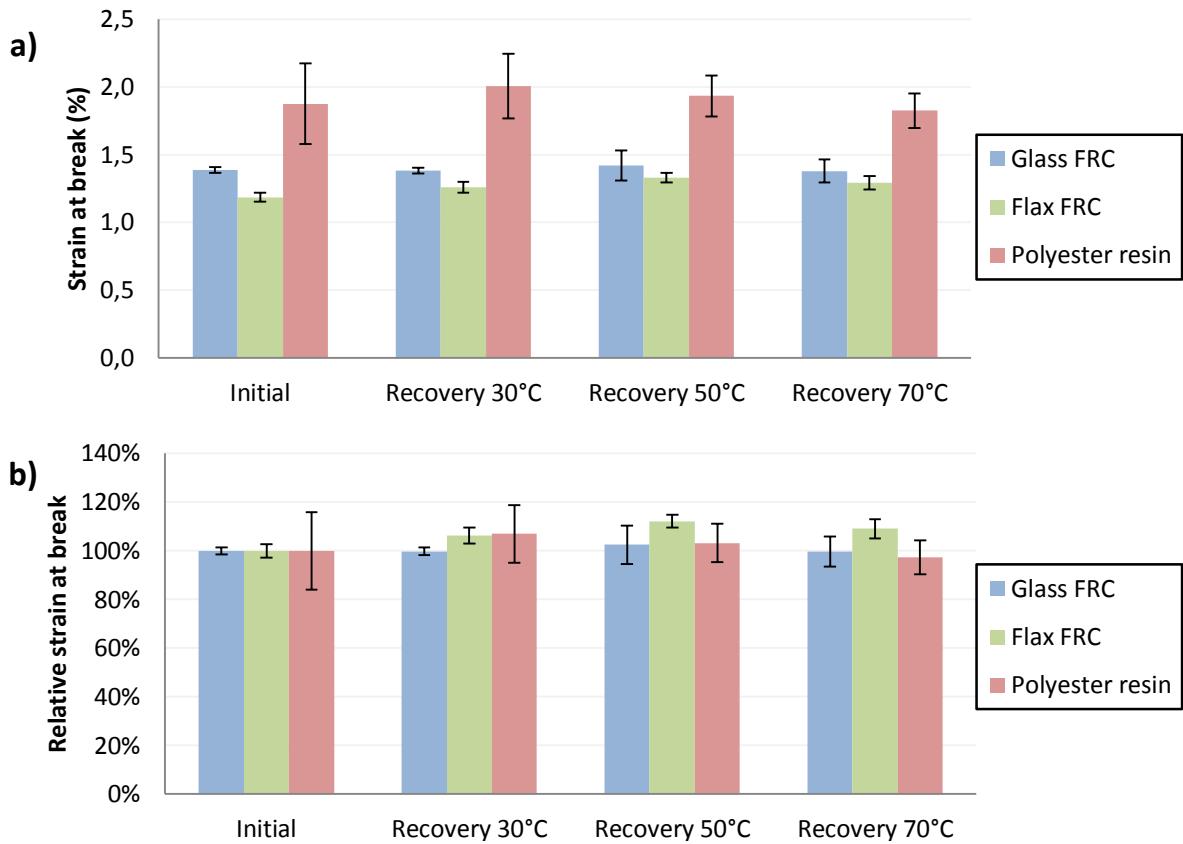


Figure IV-XXXII Absolute (a) and relative (reference to unaged samples) (b) tensile strain at break after drying of glass FRC, flax FRC and the polyester resin aged in water at 30°C, 50°C and 70°C.

IV-2.4.3 Interlaminar shear strength

The results for the relative interlaminar strength of flax and glass fibre composites at saturation and after drying are shown in Figure IV-XXIV. The glass fibre composites show an ILSS seemingly unaffected by the water ageing at 30°C and 50°C. However, an irreversible degradation at the fibre-matrix interface is observed for samples aged at 70°C and is probably linked to a physical-mechanical mechanism. Indeed, the differential swelling displayed by GFRC during ageing at 70°C may be related to the interfacial shear damage presented in this part.

An opposite behaviour is reported by Pawson and Jones [209] for glass-vinylester composites aged in water at 50°C in which the authors demonstrate that the fibre-resin bonding is reversible on redrying wet specimens. In the literature, several works report the degradation of the fibre-matrix interface that leads to a decrease in composites mechanical properties when exposed for long time (or high temperature) to water ageing [197][202] [210]. It is important to remember here that the degradation of GFRC interface is often related to long time exposure and/or high temperature imposed to samples, and not as described here to the chemical and/or thermo-mechanical phenomena induced by the water uptake.

The ILSS of flax fibre composites was found to be impacted by water ageing for all the temperatures investigated in this study. The observed shear strength decrease during ageing seems to be completely irreversible for all samples exposed to water ageing.

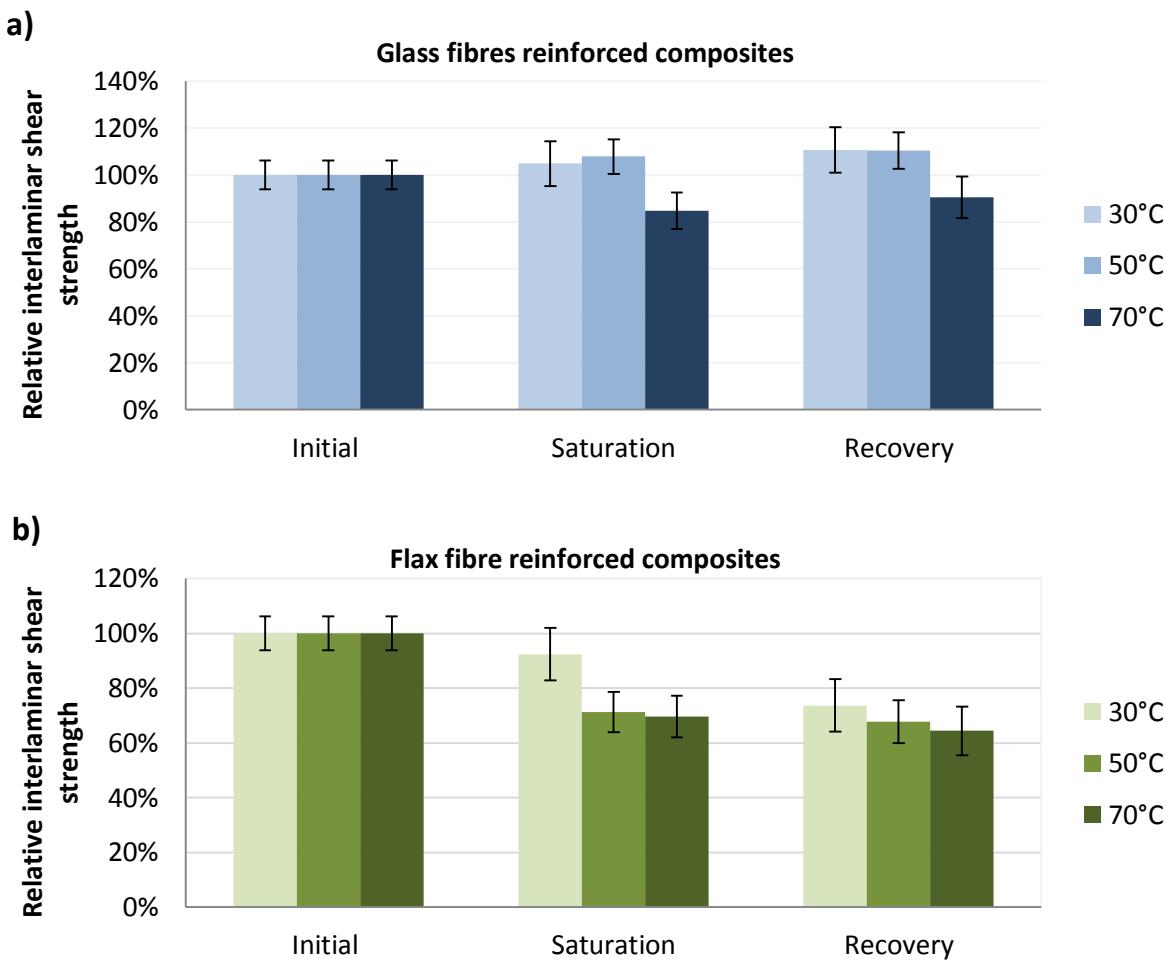


Figure IV-XXXIII Relative shear strength (reference to unaged samples) of glass (a) and flax (b) fibre composites saturated at 30°C, 50°C and 70°C, and after drying.

IV-2.5. Conclusions

This section addressed observations of the reversible and irreversible ageing mechanisms that took place during hydrothermal ageing of flax and glass fibre composites. Swelling and plasticisation of both polyester resin and flax fibres were found to increase with ageing temperature, mainly at 70°C when the ageing temperature was higher than the polymer's Tg. On the other hand, irreversible ageing was identified by residual swelling, removal of polyester resin and flax fibre components, microcracking and interfacial degradation.

Dried flax fibre composites displayed a lower mass compared to initial state before ageing related to the removal of fibre components during ageing. Concerning the polyester resin, it was noted the occurrence of concomitant phenomena related to the leaching of some components and to the formation of hydrogen bonds between water and polyester resin that was found to be strong enough to endure the drying process [42][204].

A weight decrease was then observed, but not only related to the leaching of fibre and resin components. It was also observed that the drying conditions had modified the composites morphology by drying the initial humidity present into fibres before ageing.

The swelling behaviour induced by water uptake was found to be completely reversible for glass fibre composites but only partially reversible for flax fibre composites, in which the irreversibility had increased with an increasing temperature. It was interesting to note that, even if swelling is often characterised as a reversible phenomenon, its effect on composites behaviour can be irreversible.

The initial properties at break of GFRC remain constant when exposed to water ageing at 30°C and 50°C, but exposure to 70°C induced irreversible degradation associated to the interfacial damage. This result highlighted the competition between irreversible and reversible mechanisms in glass fibre composites behaviour during ageing.

Concerning FFRC, the degradation of the interfacial shear strength was observed for all the temperatures investigated in this study. Indeed, the interfacial damage seems to be the most important factor responsible for the loss of properties observed during ageing. However, the increase in ultimate properties observed at 30°C and 50°C can be explained by a frictional effect caused by fibres swelling. Furthermore, the ageing mechanisms of flax fibre composites immersed at 30°C was reported to be mainly reversible, while irreversible damage was observed at 50°C and 70°C linked to the interfacial degradation.

The mechanisms of degradation observed here were correlated to the effect of water and temperature on the composites properties during ageing. However, composites are also exposed to mechanical loading in real-life conditions that can accelerate these phenomena or create others. The next section will address the hydrothermal ageing behaviour of biocomposites subjected to mechanical loading.

IV-3. Mechanical-hydrothermal coupling of flax fibre composites

This part addresses the study of the biocomposites evolution when exposed to mechanical-hydrothermal ageing. A constant creep stress was applied to composite samples and their elastic modulus and creep strain followed until fracture (if fracture was not observed the test was interrupted at an ageing time of 900 hours). The influence of mechanical loadings on the ageing mechanisms of biocomposites was analysed in thermo-mechanical and mechanical-hydrothermal configurations. The results were also compared to the hydrothermal ageing in order to assess the role of each source of damage in the biocomposites behaviour.

IV-3.1. Generalities

In real conditions, different factors of damage act simultaneously, and their effects on composites are frequently coupled. It was previously observed in this chapter that flax fibre composites swelled and lost stiffness when exposed to hydrothermal conditions. The role of water on composites mechanical properties was found to generate irreversible and reversible damages within biocomposite samples. It is expected that the application of mechanical loadings to flax composites accelerates their degradation (identified by a loss of stiffness) compared to unloaded samples.

The objective of this chapter is to analyse the coupled degradation phenomena that take place in biocomposites when mechanical loadings are applied. The present methodology consists firstly to study the influence of mechanical loadings on composites behaviour without taking into account any water ageing, and then to couple both solicitations a loaded immersed set-up. The concept of synergy of degradation will be employed in this chapter to define the difference of degradation between the coupled and uncoupled ageing conditions. Which means that the evolution of biocomposites properties when exposed to mechanical-hydrothermal coupled conditions is supposed not to be equal to the sum of the hydrothermal and the mechanical ageing factors taken separately [97].

The analysis of the coupling effect of mechanical loadings on the hydrothermal ageing behaviour of biocomposites takes into account that the role of each source of damage is previously understood. The role of water and temperature on the mechanical properties of biocomposites was studied in the last parts of this chapter for a hydrothermal (HT) ageing set-up. In the present part, creep mechanical tests were performed in a dry atmosphere in order to avoid the effect of water and analyse only the effect of creep mechanical loadings on biocomposites behaviour. It is the thermo-mechanical (TM) analysis. Then the mechanically loaded samples were immersed into water in a coupled mechanical-hydrothermal (MHT) configuration.

IV-3.2. Creep behaviour

The influence of temperature on the evolution of the creep strain of flax fibre composites during thermo-mechanical tests is presented in Figure IV-XXV. All samples presented a creep strain amplitude of around 0.2% during thermo-mechanical ageing (TM) (total strain minus the instantaneous elastic strain), but fracture was only observed for composites exposed to 50°C and 70°C. Samples exposed to

creep stress at 30°C presented a slightly less sudden strain increase during the first hours of testing that became stabilised without fracture being observed.

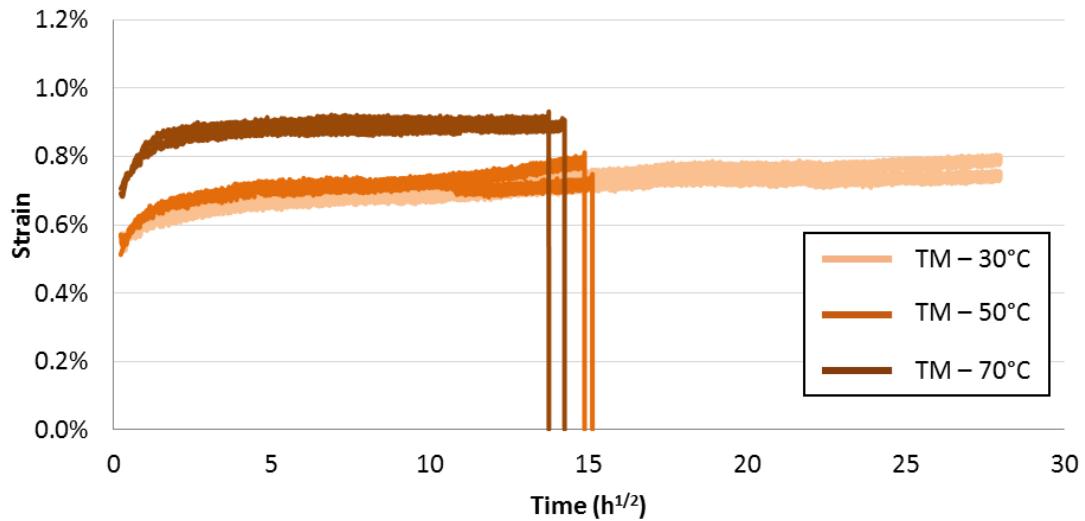


Figure IV-XXXIV Creep strain of flax fibre composites (two samples per temperature) subjected to creep stress (60 MPa) in dry atmosphere for different temperatures.

The evolution of the relative elastic modulus (modulus of the aged sample divided by the modulus of the unaged one) during the thermo-mechanical ageing of flax fibre composites is presented in Figure IV-XXVI. Acceleration is observed for the relative modulus loss with increasing temperature. This effect of temperature on relative modulus decrease is more clearly seen here for thermo-mechanical ageing than that previously observed during hydrothermal ageing (see Figure IV-XIX – page 139). It was previously confirmed that the temperature accelerated the water sorption, which led to an increase in biocomposites degradation during hydrothermal ageing. However, in the absence of water, the thermal effect on biocomposites degradation can be confirmed separately from the water effect. Fractures of flax fibre composites were observed when their modulus decreased by about 55% of the initial value before ageing.

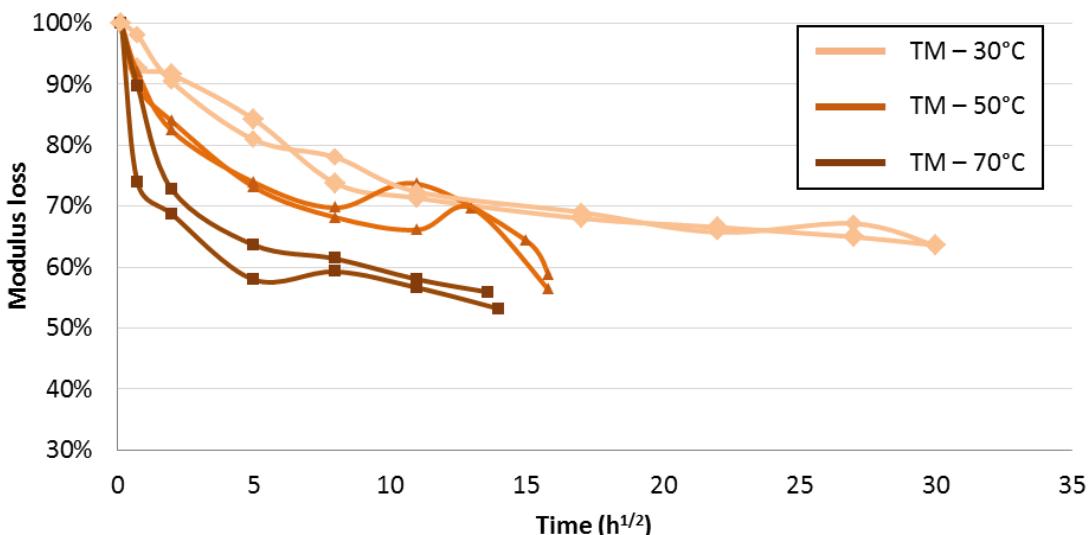


Figure IV-XXXV Relative modulus of flax fibre composites (two samples per temperature subjected to creep stress (60 MPa) in dry atmosphere for different temperatures (TM).

IV-3.3. Mechanical-hydrothermal ageing

The role of each source of damage was studied up to now separately by exposing biocomposites to water plus temperature (hydrothermal) and temperature plus mechanical loads (thermo-mechanical) configurations. The last part of this chapter addresses the study of the ageing mechanisms of flax fibre composites exposed to water plus temperature plus mechanical loads. The same set-up used before for thermo-mechanical tests was used in this part to evaluate the mechanical-hydrothermal behaviour of biocomposites.

IV-3.3.1 Water uptake and swelling

Before evaluating the evolution of mechanical properties, it is of interest to verify the water sorption and swelling of biocomposite samples during mechanical-hydrothermal ageing and to compare to the unloaded situation (hydrothermal). The effect of mechanical loads on the water sorption kinetics can be analysed by comparing these two ageing configurations.

Figure IV-XXXVI shows the water sorption behaviour of loaded (MHT) and unloaded (HT) flax FRC samples immersed in water at 30°C and 70°C. The few points collected during ageing do not allow a precise interpretation about the equilibrium water concentration at saturation, neither about the diffusion coefficients. However, some trends were observed. No interpretation was addressed for the water concentration behaviour at saturation of composites exposed to mechanical-hydrothermal ageing at 70°C, because the samples fractured at about 50 hours of ageing, long before the expected equilibrium plateau at about 290 hours of ageing for unloaded samples (exposed to hydrothermal ageing). The tests performed at 30°C showed that the applied stress appeared to have no significant influence on the water concentration at saturation. Furthermore, it seems that flax FRC presented a little increase in water diffusion kinetics when mechanical loads were applied to samples.

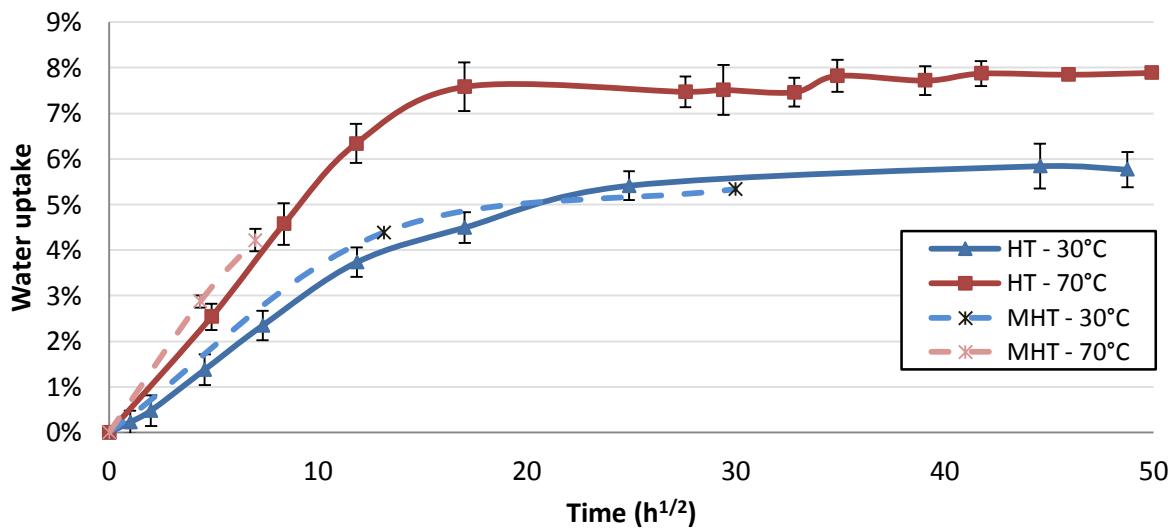


Figure IV-XXXVI Water uptake behaviour of flax fibre composites exposed to hydrothermal (HT) and mechanical-hydrothermal (MHT) ageing at 30°C and 70°C.

The increase observed in water sorption kinetics for loaded samples can also be observed in the swelling behaviour of flax FRC (see *Figure IV-XXXVII*). No modification was found in the width and thickness variation of loaded biocomposite samples immersed at 30°C compared to unloaded ones.

On the contrary, loaded samples exposed to water ageing at 70°C showed a higher variation in width and thickness compared to the unloaded composites, which confirms the acceleration of the composites ageing with the application of mechanical loading. It also indicates that other mechanisms than water diffusion influence the swelling of biocomposites at 70°C.

The increase in water absorption as an effect of the additional mechanical loading was also observed by Youssef et al. [211]. The authors employed a multi-scale model based on the free volume theory to investigate the coupled behaviour of mechanically loaded carbon nanotube/epoxy composite. The results highlighted that the application of a radial pressure on unidirectional reinforced composites accelerated the water diffusion, but it also affected the maximum moisture absorption. Only the case of radial loads was analysed and the modelling parameters considered the fibre reinforcement as impermeable to water sorption. These conditions differ substantially from the present study, which consists in applying a creep tensile stress to (permeable) flax fibre composites. But, from the perspective of the stress state, the tensile creep stress induces a positive volumic-stress comparable to the radial tensile stress applied on the cylinder which justifies the observed phenomenology.

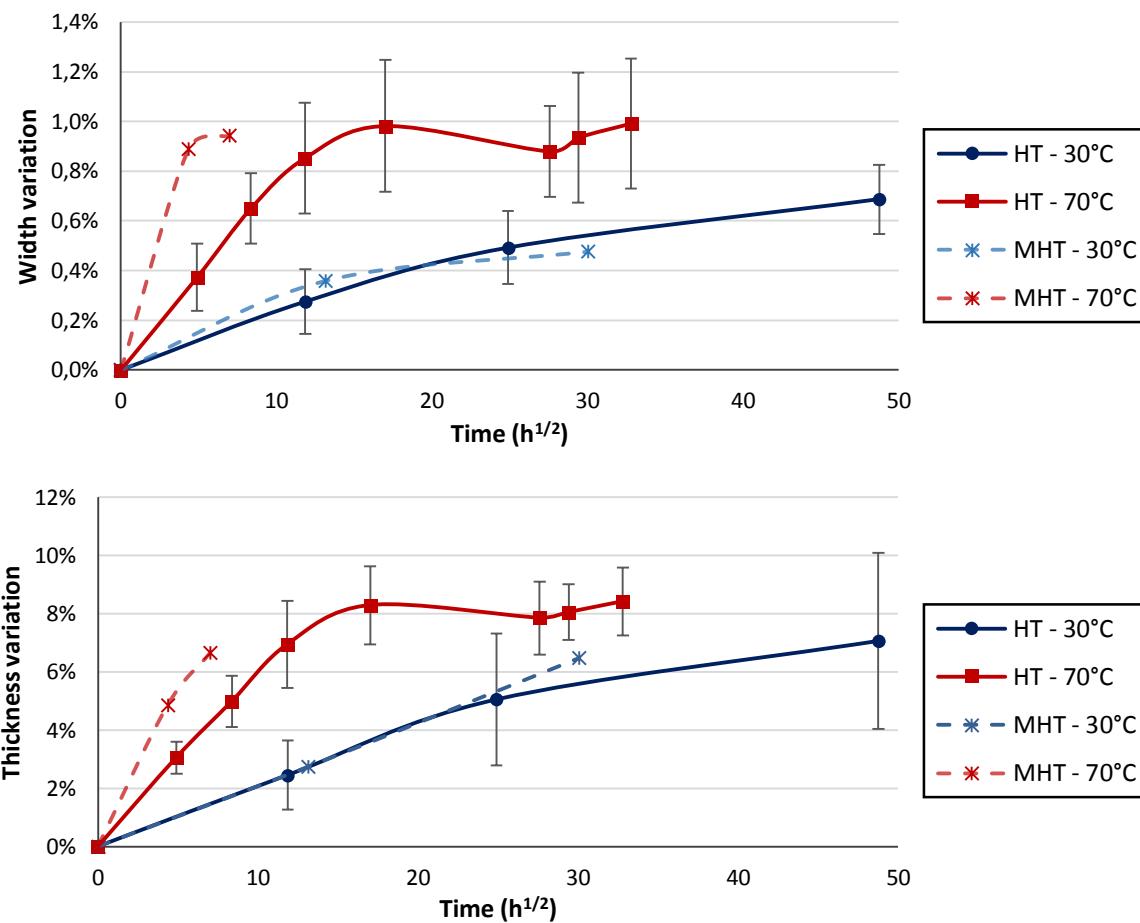


Figure IV-XXXVII Swelling behaviour of flax fibre composites exposed to hydrothermal (HT) and mechanical-hydrothermal (MHT) ageing at 30°C and 70°C.

It was previously observed in this work that the swelling of polymer and polymer composites depends on the water concentration and temperature (see Figure IV-XV – page 136). The referred graph showed that the composite samples increasing volume was found to be different from that

attributed to the absorbed water initially, but that the ratio get closer (approximately) for long time immersion. This phenomenon was related to the fill of the free volume with the absorbed water.

The analysis of the relationship between the swelling and the water uptake behaviour for MHT and HT tests is addressed in *Figure IV-XXXVIII*. It seemed that biocomposites presented an additional swelling due to the application of mechanical loads to samples, but no supplementary water uptake was observed. The initial water uptake is related to the effect of filling the free volume with water without swelling samples, but further swelling is observed for long periods. This mechanism can indicate that the initial swelling is governed by water uptake but long-term swelling is supposed to be thermo-mechanically activated.

Furthermore, the biocomposite samples exposed to MHT ageing at 70°C showed an anomalous behaviour in which the composites volume swelling was found to be higher than the relative water uptake. Here, the effect of mechanical loading on composites swelling is supposed to be accelerated by temperature, leading to a thermo-mechanical-swelling activated much faster than the hydric-swelling. It is interesting to note that the free-volume theory is not sufficient to explain the swelling behaviour of biocomposites exposed to coupled ageing, and there is probably a coupled effect of mechanical damage with the growing of cavities or cracks as suggested by the module decreasing during the previous thermo-mechanical tests.

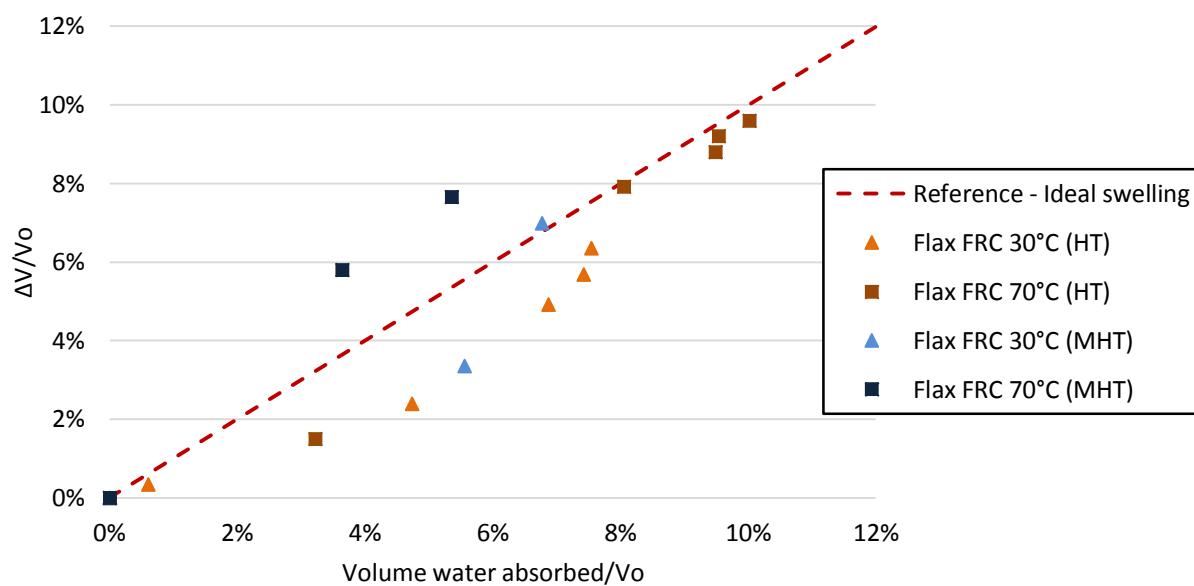


Figure IV-XXXVIII Swelling behaviour of flax fibre composites exposed to mechanical-hydrothermal ageing (MHT) compared to hydrothermal ageing (HT) for composites aged at 30°C and 70°C.

IV-3.3.2 Creep behaviour

In this part, the modification of the biocomposites mechanical properties (creep strain and elastic modulus) caused by the application of different level of load in immersion was investigated.

Figure IV-XXXIX shows results for creep tests carried out with flax FRC immersed in water at 30°C for different mechanical loads (two tests were realised for each load). No fracture was observed for composite samples subjected to 60 MPa of applied stress and the tests were stopped at an ageing time of 900 hours. However, samples subjected to 90 MPa and 120 MPa fractured at after an ageing time

of about 33 hours and 5 hours, respectively. The applied stress does not seem to affect the creep strain at break, found to be around 1.4% whatever the load applied. However, the increasing applied stress was shown to reduce the time to fracture.

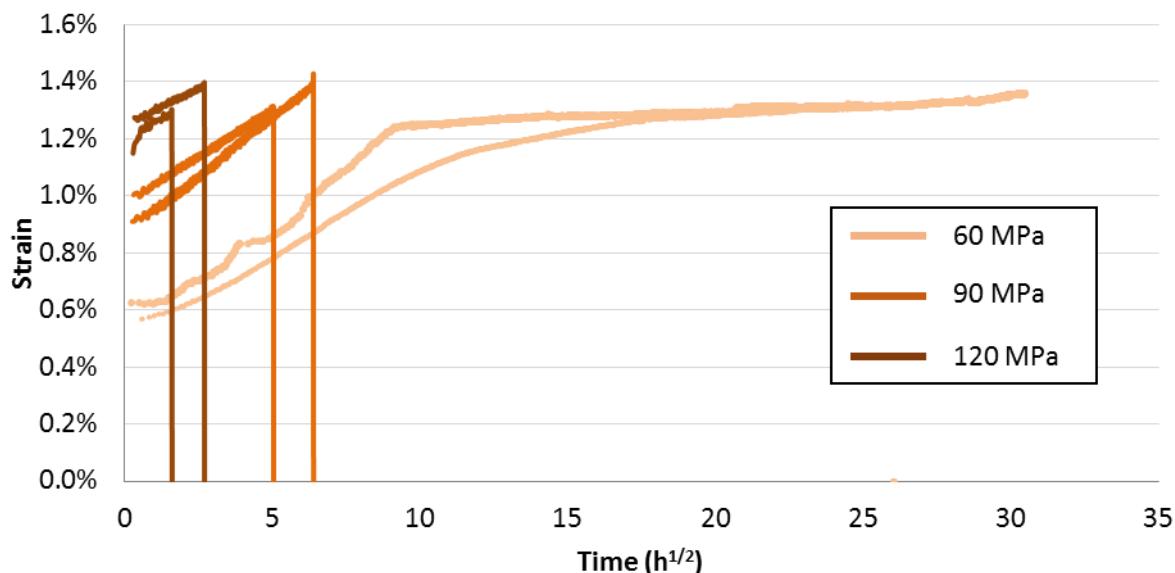


Figure IV-XXXIX Creep strain of flax fibre composites (two samples per temperature) immersed in water at 30°C for different mechanical loadings.

The influence of temperature on the creep behaviour of flax fibres composites immersed in water (HTM curves in blue) is presented in Figure IV-XL. It can be noted that the strain at break was not influenced by the water ageing temperature while the ageing time before breaking varies according to temperature. Flax fibre composites remain loaded during about 23h and 115h (for water temperature of 50°C and 70°C, respectively) before break. No fracture was observed for flax fibre composites immersed in water at 30°C until 900 hours of ageing testing.

Furthermore, the influence of water ageing on creep behaviour was highlighted by an increase in strain at break by comparing thermo-mechanical (TM) and mechanical-hydrothermal (MHT) ageing. Indeed, flax fibre composites exposed to hydro-thermo mechanical ageing presented a total strain at break similar (even higher) to values obtained for a uniaxial tensile stress test ($\varepsilon_{\text{total}}$ at break : $1.2 \pm 0.1\%$) while the flax composites exposed to thermo mechanical ageing fractured between 0.7% and 0.9% of total deformation (depending on the ageing temperature) of which 0.2% of creep deformation. The plasticising effect of water can be the cause here for the higher strain observed for immersed composites. The water sorption was also found to decrease the time-to-fracture of biocomposites. Flax composites exposed to mechanical-hydrothermal conditions at 70°C fractured before the first 40 hours of ageing time while those exposed to thermo-mechanical conditions cracked at around 200 hours of ageing time at the same temperature. This effect seemed to be thermo-activated.

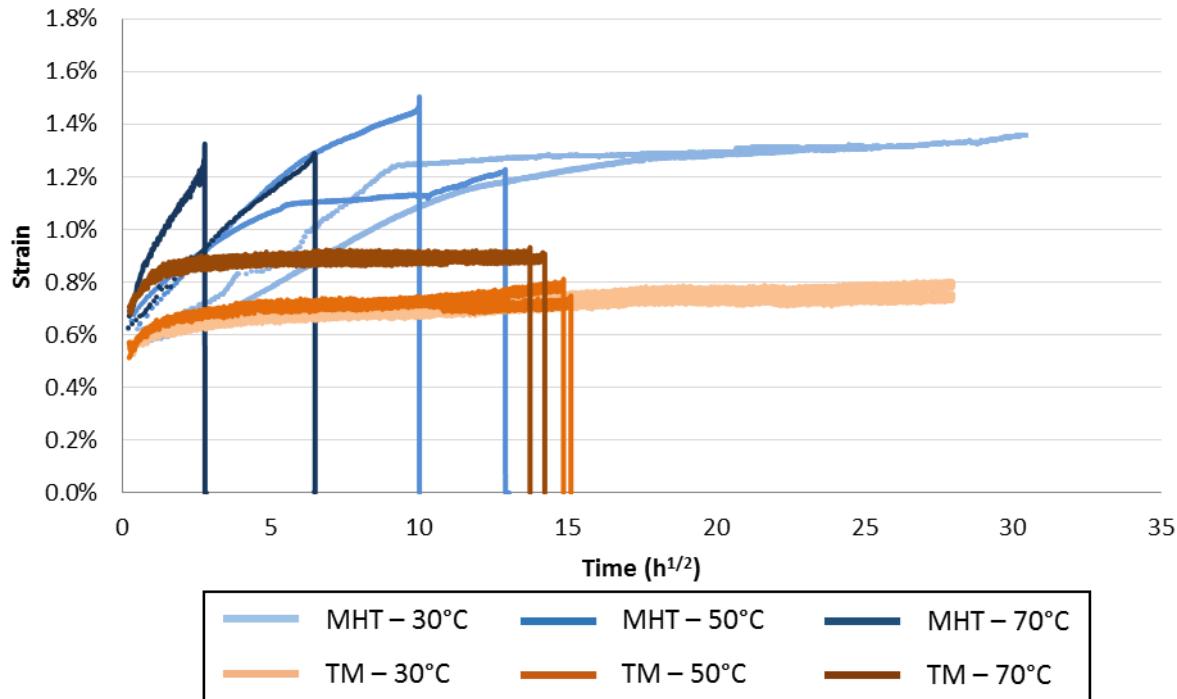


Figure IV-XL Creep strain of flax fibre composites (two samples per temperature) subjected to creep stress (60 MPa) immersed in water (MHT) and in dry atmosphere (TM) for different temperatures.

IV-3.3.3 Mechanical-hydrothermal coupling

The analysis of the relative elastic modulus evolution as a function of ageing time completes the study of the coupled ageing effects on the mechanical properties of biocomposites (see Figure IV-XLI). The relative modulus loss was analysed for composites aged at 30°C, 50°C and 70°C in HT, TM and HTM configurations. It is important to remember here that different experimental set-ups were employed to calculate the evolution of the relative elastic modulus during ageing. The TM and MHT tests were performed using a tensile creep set-up while HT modulus measurements employed the vibration analysis. Some differences between these two configurations can be cited here, that were also discussed by Regazzi [97] in his work:

Test temperature: In-situ creep tests were carried out at the ageing temperature but HT mechanical tests were done at room temperature, which does not correspond to the real ageing conditions. Indeed, the thermo-activated reversible phenomena, such as swelling, are not taken into account in ex-situ tests;

Swelling: The elastic modulus was calculated in ex-situ (HT) tests by taking into account the volume variation during ageing. On the other side, the elastic modulus calculation of in-situ aged composites was based on their initial dimensional values and no volume update was done during ageing;

Testing speed: the determination of the elastic modulus by static creep and dynamic vibration tests present some differences linked to the fact that viscoelasticity is involved and influence the elastic modulus measured by dynamic tests.

In both cases (creep and vibration analysis), the elastic modulus was calculated by operating tensile tests.

Otherwise, the analysis of modulus loss during ageing shows that the effect of TH ageing cannot be distinguished from MHT ageing for biocomposites exposed to ageing at 30°C. The elastic modulus was found to decrease by about 35% at an ageing time of 900 hours for all the ageing configurations. This confirmed the absence of coupling effect when a mechanical stress is superimposed to an environmental stress at this temperature. The results obtained at 50 °C show an ambiguity in the analysis. It can be verified that composites exposed to TM and MHT ageing presented a similar modulus loss while the unloaded hydrothermal aged composites presented a lower modulus loss during ageing. At this temperature, and in the absence of coupling between the mechanical and environmental stresses, we would have to obtain the decrease of module for MHT ageing such as the adding of the decreases modules of the two both ageing (HT and TM). The damage generated by the thermo-mechanical ageing predominating, It seems that superimposing a water ageing does not affect more the material mechanically. Liang et al. [212] observed a modulus increase of 2% when flax composites are exposed to fatigue solicitations at 0.8 UTS. According to the authors, this stiffening phenomenon is explained by the self-strengthening of the flax fibre related to the realignment of the flax microfibrils.

The additivity of the three effects (mechanical, thermal and water) appeared more effective at 70°C and became more visible on the graph. The elastic modulus was found to drop by 40% after 4 hours of test for MHT ageing. Thus, composites subjected to mechanical loadings at 50°C and 70°C presented a modulus loss of about 55% before breaking.

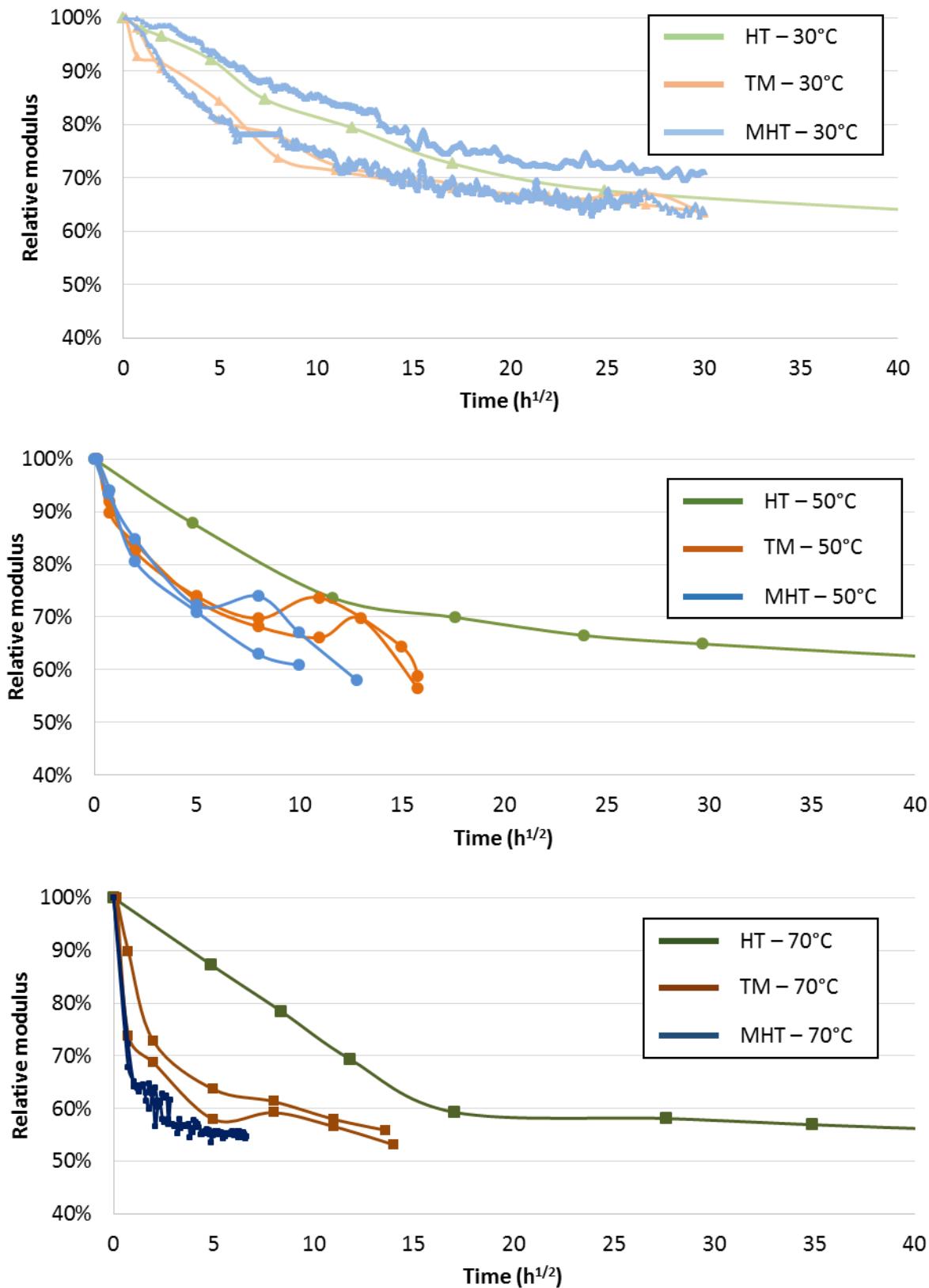


Figure IV-XLI Relative modulus as a function of ageing time for flax fibre composites ((two samples per temperature) exposed to hydrothermal (HT), thermo-mechanical (TM) and mechanical-hydrothermcal ageing at different temperatures.

The flax fibre composites exposed to ageing at 70°C presented a modulus evolution affected by coupling in all test configurations. It can be observed from *Figure IV-XLI* that the effect of mechanical loads in biocomposites modulus loss was found to be more important than that of water. Regazzi [97] showed an opposite behaviour for PLA/flax composites immersed in water. The effect of water was found to be more important than mechanical loads on the decrease of the biocomposites elastic modulus during ageing. The author also observed that the decrease of PLA/flax composite elastic modulus was more pronounced in the polymer matrix than in the composite. Otherwise, the synergy of degradation for coupling aged composites was observed to decrease with increasing composite fibre content.

In this work, a modulus loss of around 27% was observed with application of mechanical loads to composite samples, while only 6% of modulus loss was observed when loaded composites were immersed in water (for an ageing time of 25 hours).

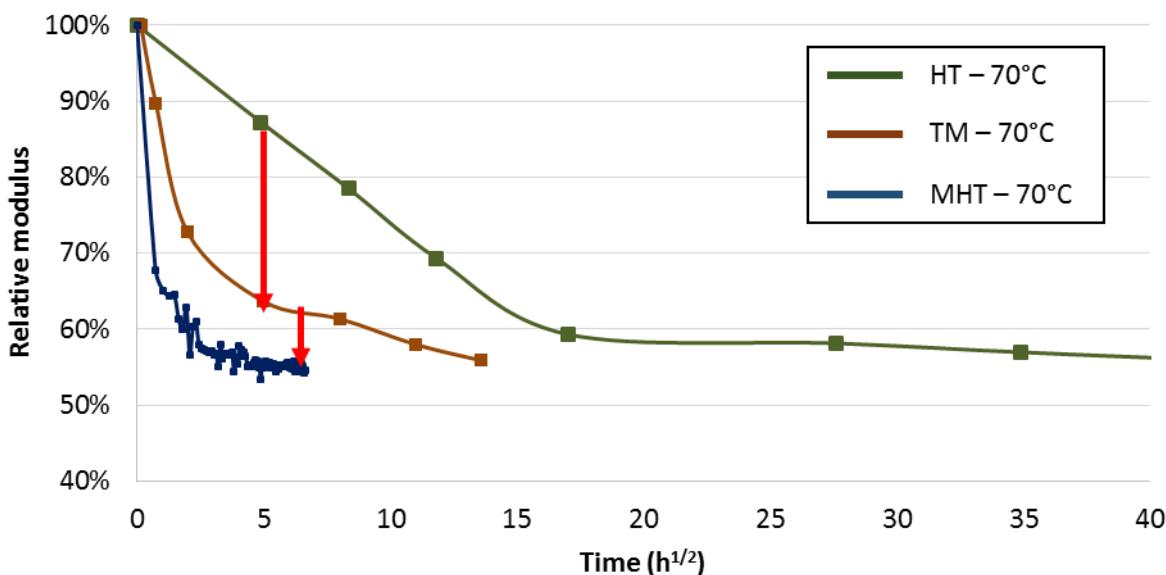


Figure IV-XLI Relative modulus as a function of ageing time for flax fibre composites exposed to hydrothermal (HT), thermo-mechanical (TM) and mechanical-hydrothermal ageing at different temperatures.

It seems that not only the effect of water on biocomposites ageing behaviour needs to be taken into account when studying their degradation behaviour but the mechanical loads were also found to highly influence the evolving mechanical behaviour of flax fibre composites during ageing.

IV-3.4. Conclusions

The study of the biocomposites coupled ageing highlighted the presence of some phenomena linked to the degradation of these materials, such as additional water uptake and swelling, stiffness loss and the reduction in the time-to-fracture when samples were exposed to hydric and mechanical coupled solicitations.

Flax fibre composite samples presented a coupled ageing behaviour that increases with the temperature. The swelling of composites was observed to be a hydrically but also mechanically activated mechanism. Here, the theory of the free volume is not sufficient to explain the additional

swelling displayed by coupling aged samples. The temperature and the mechanical loadings were found to reduce the time-to-fracture of biocomposites while the exposure to water caused the increase of the creep strain related to the plasticising effect of water.

Finally, it was noted that the effect of mechanical loads on biocomposites modulus loss was found to be more important than that of the immersion in water. A coupling synergy was not observed but the loss of modulus for MHT tests was found to be lower than the sum of TM plus HT, which means that a stiffening phenomenon took place during coupled ageing. Liang et al [212] observed a similar behaviour for flax fibre composites tested under tension-tension fatigue loading and related this stiffening phenomena to the realignment of the microfibrils contained in the flax fibres.

Chapter V. Modeling the hydrothermal behaviour of flax fibre composites

In the perspective of predicting the evolving mechanical behavior of biocomposites subjected to hydrothermal ageing, it is necessary to develop a model accounting of the composites microstructure. The purpose of this chapter is to model the water diffusion behaviour of flax fibre composites by taking into account their real morphology. A description of the flax fibres morphology and distribution in the polyester matrix was previously realised in this work and is taken into account in this chapter to create a sorption model at two scales: a composite macro scale model and a yarn micro scale model.

The macro scale describes the arrangement of the yarns inside the composite and intends to determine its diffusional properties. Once the yarn diffusion properties were identified, these results served as a basis to support the micro scale model that aims to determine the in-situ diffusion properties of flax fibres and the polymer matrix. Both models were developed in a direct and a parametric configuration. The direct model uses real macroscopic images to identify the in-situ diffusion parameters of the biocomposites components, while the parametric model employs a statistical study to analyse the influence of the microstructural parameters on the diffusional properties of the composites.

Chapitre V – Modélisation du comportement hydrothermique des composites renforcés par des fibres de lin

Dans la perspective de prédire l'évolution des propriétés mécaniques des biocomposites soumis à l'action de l'eau et de la température, il est nécessaire de développer un modèle qui intègre la microstructure de ces matériaux. Ce chapitre propose une modélisation de la diffusion hydrique pour des composites renforcés par des fibres de lin qui tient compte de leur morphologie réelle. Une description de la morphologie des fibres de lin et de leur distribution dans la matrice polyester précédemment réalisée est utilisée dans ce chapitre pour créer un modèle de sorption à deux échelles : un modèle macro à l'échelle du composite et un modèle micro à l'échelle interne à la mèche.

*L'échelle macro décrit l'arrangement des mèches dans le composite et vise à déterminer les propriétés diffusionnelles de la mèche. Une fois ces propriétés identifiées, elles servent de référence au modèle à l'échelle micro qui vise à déterminer les propriétés diffusionnelles *in-situ* des fibres de lin et de la matrice polyester insaturé. Ces deux modèles sont développés dans deux configurations : directe et paramétrique. Le modèle direct utilise les images microscopiques réelles du composite pour identifier les propriétés diffusionnelles de leurs composants, alors que modèle paramétrique utilise une étude statistique pour analyser l'influence des paramètres microstructuraux dans le comportement diffusionnel du biocomposite.*

V-1. Methodology

The microstructure of a natural fibre reinforced composite can be very complex as exposed in section III-2.3 (page 106) and is expected to impact the diffusion properties of the composite in comparison with a periodically reinforced composite [173]. It was observed in this work that flax fibres presented a more complex dispersion in the polymer matrix than glass fibres. The latter were found to be mono-diameter objects quasi homogeneously dispersed inside the matrix, while flax fibres presented a complex organisation in the polyester matrix that depends on the observation scale. At the micro scale, called intra-yarn in this work, flax fibres were organized into unitary fibres and bundles of fibres quasi-homogeneously dispersed in the matrix. At the macro scale, named composite scale in this work, yarns are found to be surrounded by rich polymer matrix zones and more or less arranged in staggered rows. This multi-scale organisation is supposed to influence how the biocomposites absorb water during ageing.

There are two objectives in this last part. The first one concerns the creation of a two-scale numerical model that describes the water diffusion behaviour of flax fibres composites by taking into account their real morphology. The second one consists in applying this model to predict the in-situ diffusion behaviour of the flax fibres and the polyester resin inside the composite. As a matter of fact, this second objective could allow predicting the composite properties knowing the properties of its components.

Joliff et al. [213] compared the experimental data to analytical and numerical models to show the influence of the fibre distribution and interface properties on the water sorption behaviour of glass fibre reinforced composites (GFRC). It was shown that the polymer matrix (an epoxy resin) presented a diffusional behaviour inside the composite different from the experimental measurements on the unreinforced resin samples. The author revealed the presence of an interphase of 10 µm width around glass fibres that presented a glass transition temperature much lower than the bulk resin. This result suggested the presence of an undercrosslinked or plasticised matrix zone around the fibre that exhibits higher diffusivity than in the bulk zone. In this work, the experimental characterisation of the composites, and the polyester resin, diffusion behaviour presented in the previous chapter will be employed here to assess the composites diffusion properties by a 2D finite element model based on Fick's law. In this chapter, reference experimental values are those corresponding to the flax fibre composites sorption behaviour when exposed to water immersion at 30°C.

The methodology employed to create the multi-scale diffusion model is summarized in Figure V-1.

Initially, the microstructural configuration of flax fibre composites at the macro and micro scale was determined from cross-sectional images obtained by electronic microscopy. These images were employed to create two models: a direct and a parametric model.

The direct model was based on the use of real microscopic images to create the model's geometry and simulate the water diffusion behaviour of flax fibre composites. It is a quite simple and straightforward method which mainly requires the digitisation of the morphology to build the composite geometry in Comsol Multiphysics® finite elements software (details are given further in section V-3.2.1181). But it presents some drawbacks such as a very fine-meshed model (more than 1

million elements) due to the presence of many complex objects, and thus time consuming FE computation.

The parametric model was built on the basis of a statistical analysis of the dimensions and the dispersion of flax fibres (unitary fibres and bundles of fibres) into the flax yarns. The geometry of the resulting model is much simpler than the direct model, so as the mesh, thus reducing the computation complexity. As it is a parametric model, it is possible to analyse the influence of all parameters on the global behaviour of flax fibre composites. The price for such model is an exhaustive statistical analysis to describe the composites real microstructure.

The statistical study of flax fibre composites cross-section was realised by analysing the microscopic images with the *Aphelion®* software. Parametric microstructures were created by using a Microsoft Excel® macro-command for the inter-yarn macro scale (see section V-3.2.3 – page 183), and *Digimat®* software for the intra-yarn micro scale (see section XV-3.1.3 page 179). All types of microstructure cited on this part, macro and micro, direct and parametric, were subsequently integrated in Comsol® software as a FE model to simulate the water diffusion at the corresponding scales. The steps for elaborating these models will be further described in this chapter.

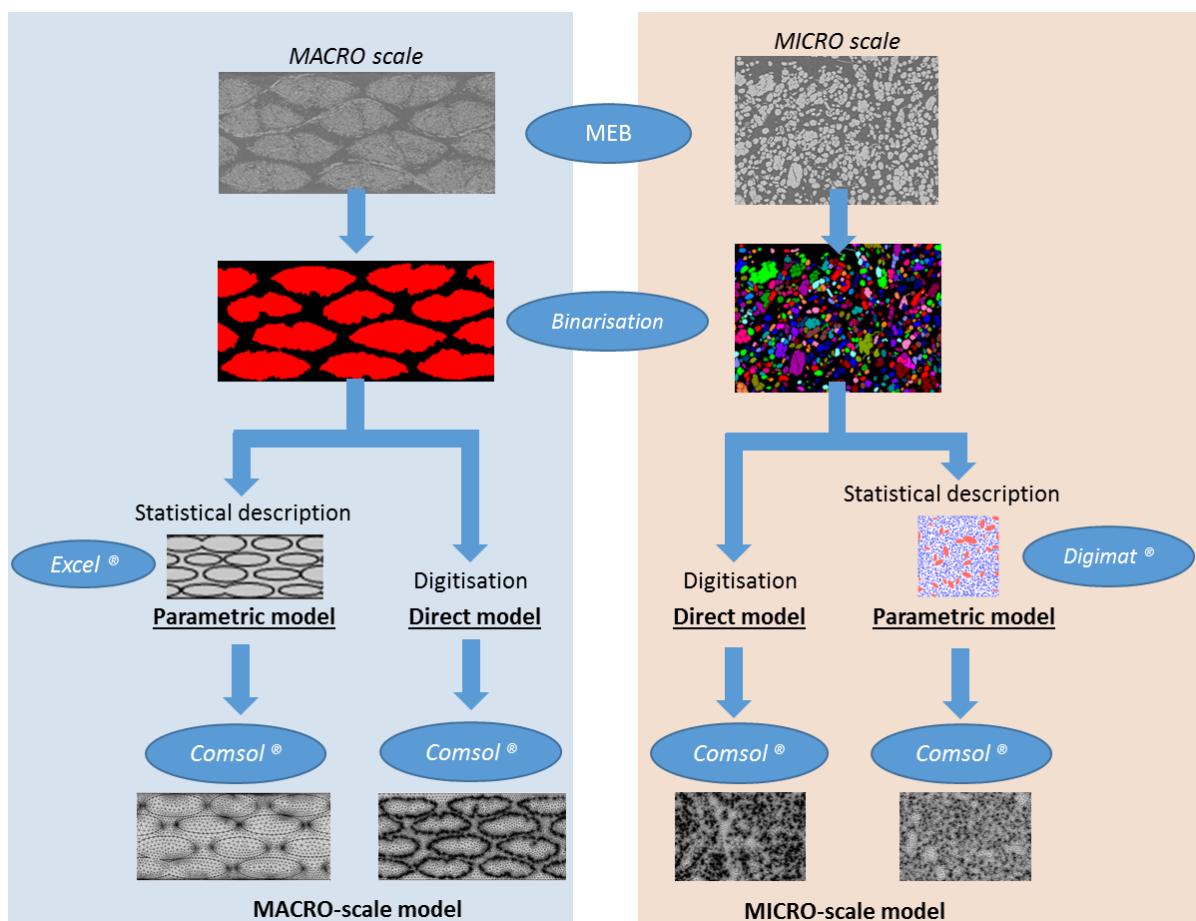


Figure V-I Methodology employed for the creation of two-scales numerical model that identifies the diffusion properties of flax fibre composites by taking into account their real morphology.

The macro-scale model employs the geometry of the real composite samples (25mm x 3.2 mm – width x thickness) and constitutes a representative elementary volume (REV) by default, whereas the elementary volume at the micro-scale (inside a yarn) is not defined by default and is one subject of the

study. For this purpose, a criterion is proposed to define the REV size, which is based on the analysis of the statistical dispersion of each diffusion parameter (diffusion coefficient and water concentration at equilibrium). The objective here is to find the REV size at the micro-scale that minimizes the dispersion on the sorption curve's slope and saturation. Three EV's sizes were studied: $200 \times 200 \mu\text{m}^2$, $400 \times 400 \mu\text{m}^2$, $700 \times 700 \mu\text{m}^2$. A schematic representation of the methodology employed here is shown in Figure V-II.

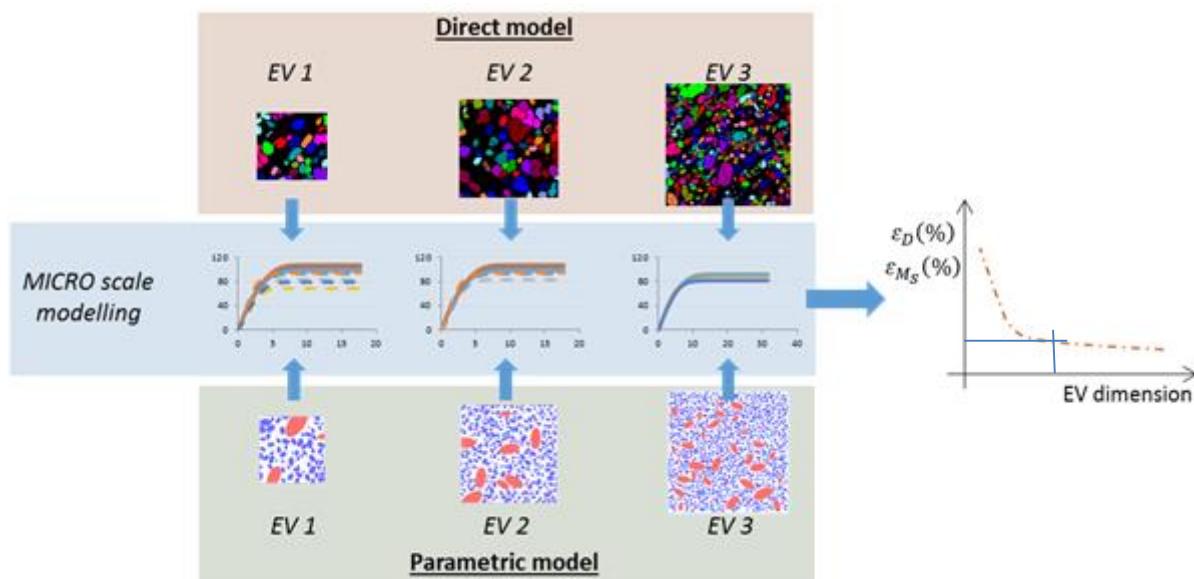


Figure V-II Methodology employed to define the micro-scale REV's size.

The methodology employed until now allows the creation of a multi scale model that will use the diffusion properties of the flax fibres and the polyester resin to describe the diffusion behaviour of the composite. However, the diffusion behaviour of the flax fibre and the polyester resin taken separately may be different from their behaviour in-situ (i.e. inside the composite). It is of interest in this part to determine their in-situ behaviour by a finite element model updating (FEMU) method. The methodology employed in this part is shown in Figure V-III (D is the diffusion coefficient and M_s is the saturation at the equilibrium).

The model calculates the water uptake at the equilibrium of flax yarns in composites, which proves to satisfy the rule of mixtures, and the diffusion coefficient is determined by a FEMU (finite element model updating).

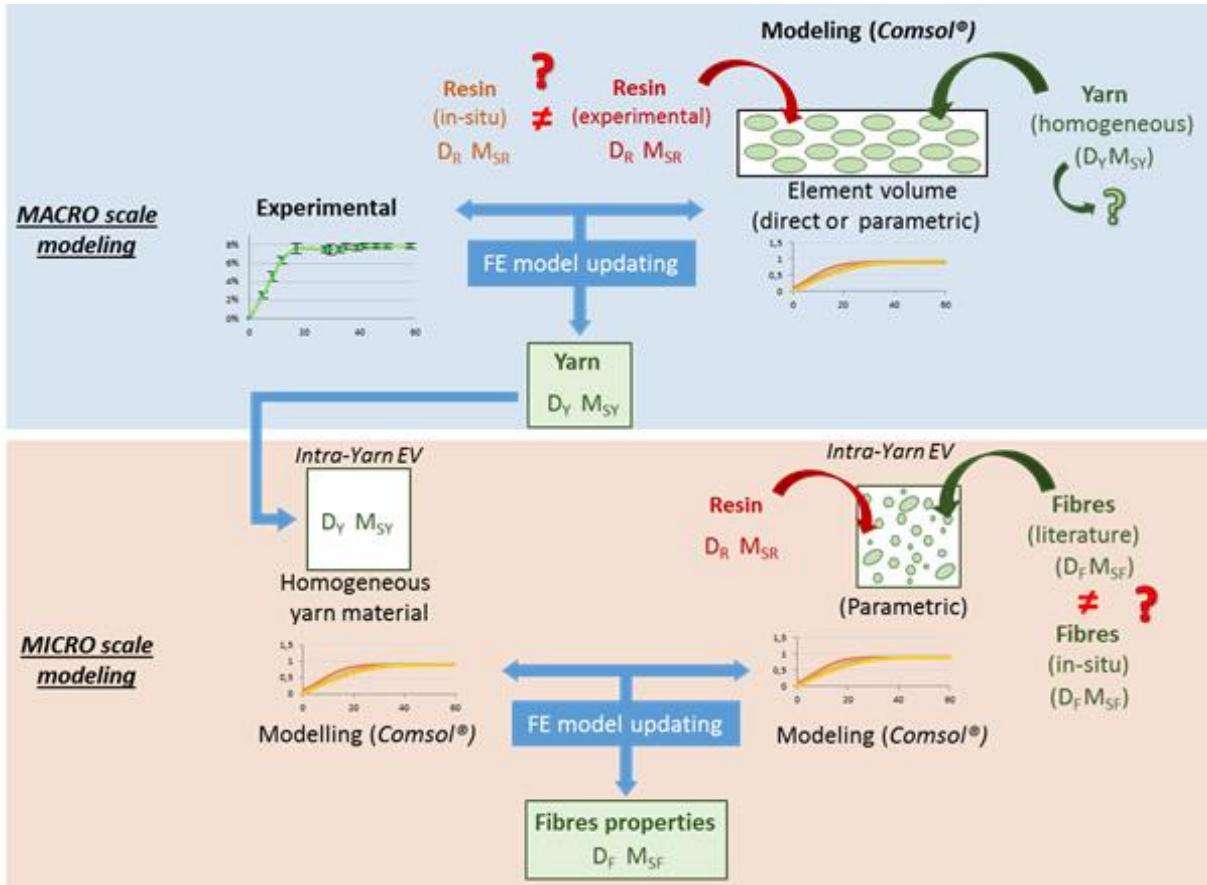


Figure V-III Methodology employed to the identification of the in-situ diffusion properties of the flax fibres and the polymer matrix inside composites.

V-2. Diffusion model implementation

The diffusion model chosen for the FE computations is based on the local Fick's law, whose partial differential equation is expressed as follows in Equation V-I:

$$\frac{\partial C}{\partial t} = D \Delta C \quad \text{Equation V-I}$$

where D : Diffusion coefficient (m^2/s);
 C : Water concentration (%).

Equation V-I is analogous to the heat conduction equation (Fourier equation), and can be easily implemented in most FE softwares, including Comsol®.

Usually, the water concentration in a material sample can be calculated by using a 1D Fick analytical model. It is indeed the most commonly employed method to estimate the water diffusion in natural fibre composites [4] [206] [1]. However, this approach assumes a semi-infinite domain, which could be fulfilled for parallelepiped samples that exhibit a thickness much lower than their width and length. Because the samples used in that study exhibit a width to thickness ratio that doesn't fully satisfy this assumption, the use of a 1D diffusion model could lead to errors [135].

So, a numerical 2D diffusion model of the water diffusion through the transverse cross-section has been implemented (see Figure V-IV).

The implemented diffusion model employs a factor W relative to the normalised water concentration (C/C_{sat}). The coefficient k described in the scheme below is defined as the slope of the water uptake response, which is almost linear at early times on a $W\%-\sqrt{t}$ graph.

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial^2 x} + \frac{\partial^2 C}{\partial^2 y} \right) \quad \text{Equation V-II}$$

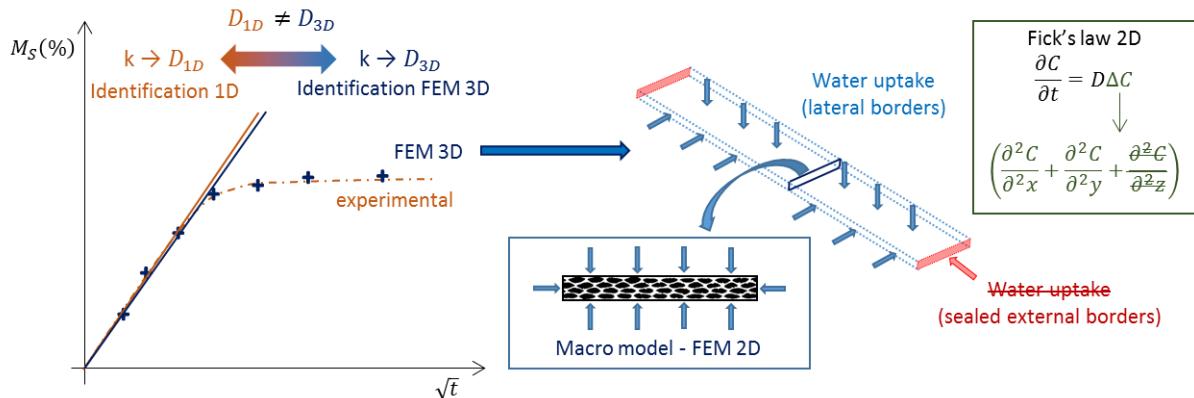


Figure V-IV Schematic representation of the elaboration of a 2D Fick's law diffusion model.

V-3. Creation of the two-scales diffusion model

V-3.1. Micro scale modeling

V-3.1.1 Images treatment

The SEM technique was used to analyse the morphology of flax fibres when impregnated by the polyester resin. Nine images were then acquired at a magnification of 200X, which allowed to observe the distribution and the geometry of flax fibres (unitary fibres and bundles) inside the yarn. The images were then analysed using the image analysis software *Aphelion®* that allows the determination of statistical parameters of the composites morphology, such as fibres and bundles surface area, Feret width and Feret ratio. The complete description of the images treatment and analysis step were already addressed in section II-4.2.1b (page 80), and the results are described in the Table V-I.

The shape factor corresponds to the Feret max. divided by Feret min.

Table V-I Statistical parameters of the composite morphology (unitary fibres and bundles).

Particles	Number analysed	Feret diameter (max.) (μm)	Shape factor	Surface reinforcement (%)
Unitary fibres	4.140	19.0 ± 5.4	1.43 ± 0.23	34 ± 2
Bundles	288	68.7 ± 19.6	1.70 ± 0.43	12 ± 2

V-3.1.2 Direct model

The microscopic images, already binarised and vectored, were integrated in the micro model by using the Comsol® software, and the diffusion of water as a function of the ageing time in the interior of the yarn is represented in Figure V-V: Contour maps of the normalised concentration (C/C_{sat}) computed for the micro scale direct model are presented for different times. It can be observed that water diffusion behaviour at the micro scale is influenced by the dispersion of the fibres inside the yarn. The water progresses faster when fibres touch each other, which was found to create a preferential path of diffusion and led to an inhomogeneous spatial distribution of the water sorption. However, when fibres are not connected to each other, the diffusion kinetics of water inside the yarn seems to be globally governed by the polymer matrix.

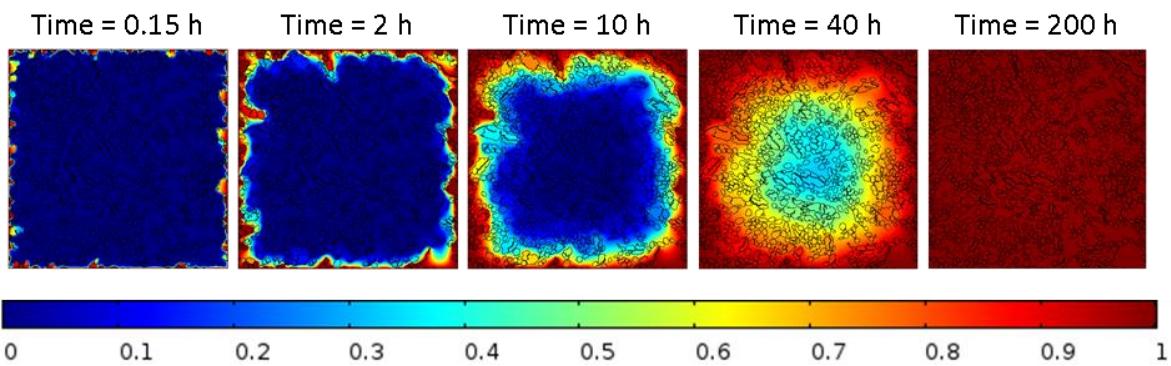


Figure V-V Contour maps of concentration computed for the micro scale direct model employed for modelling the water sorption behaviour inside a flax yarn.

The water sorption behaviour inside the yarn was verified for different elementary volume sizes. The Figure V-VI shows the sorption curves of the flax/polyester yarn accessed by the direct micro scale model for the elementary volumes: $200 \times 200 \mu\text{m}^2$, $400 \times 400 \mu\text{m}^2$ and $700 \times 700 \mu\text{m}^2$. It can be noted that the slope of the first part drops drastically with the increasing size of the elementary volume. The water concentration at saturation was also found to decrease with the increasing size of the elementary volume, even if it was expected that this value remains the same for all EV's size. This result can be explained by the fact that the smaller volume exhibited fibre content slightly superior to that determined experimentally by microscopic image analysis. This discrepancy variation was estimated to be of +8%, +3% and -4% for $200 \mu\text{m}$, $400 \mu\text{m}$ and $700 \mu\text{m}$, respectively. Otherwise, the smaller elementary volumes presented a higher surface of fibre directly exposed to water, i. e. located at the border of the elementary volume instead of being surrounded by the polyester resin. This can explain the presence of a faster water sorption observed at the entrance of the curve, which decelerates during the ageing time (this is particularly visible for the $200 \mu\text{m}$ EV).

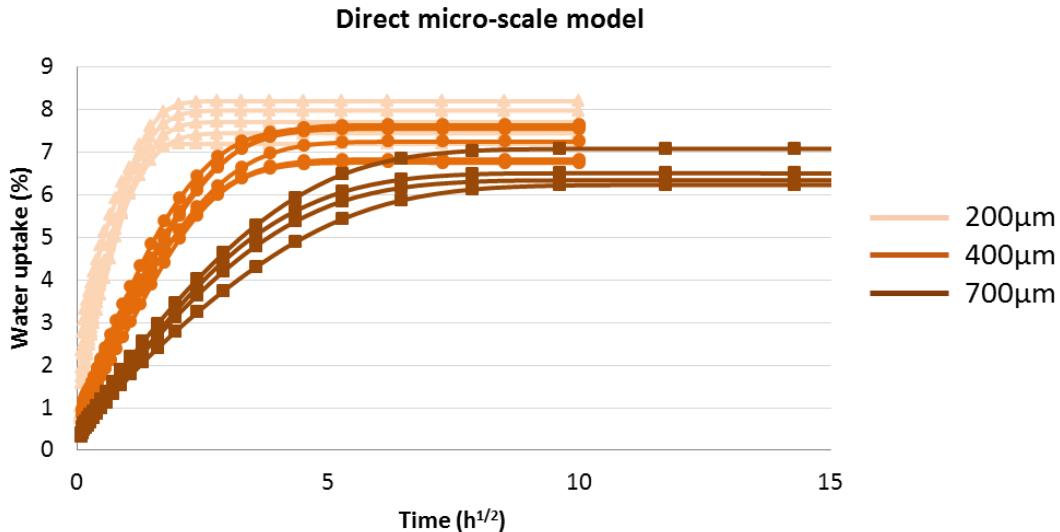


Figure V-VI Yarn diffusion behaviour as a function of ageing time calculated by the direct micro-scale mode for different elementary volumes (200 μm , 400 μm and 700 μm).

V-3.1.3 Parametric model

The Figure V-VII show the microstructure generated by the parametric model (Figure V-VII-a), the meshing in the fibre and bundles (in grey) and in the matrix (in pink) (Figure V-VII - b), and the modelling of the water uptake inside the yarn (Figure V-VII-c).

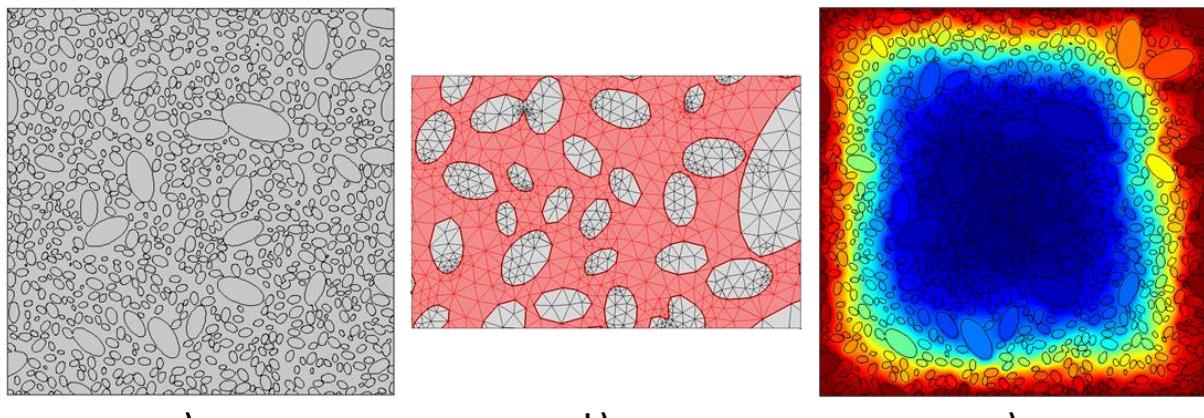


Figure V-VII Creation of the parametric micro-scale model: a) Parametric microscopy; b) Meshing c) water diffusion modelling.

The Figure V-VIII shows the sorption properties of the flax/polyester yarn accessed by the parametric micro scale model for different elementary volumes (200 μm , 400 μm and 700 μm). It can be noted that this model produced less scattered results than the direct model, because of more controlled geometrical and fibre content input parameters in this case led to a reduction in the results dispersion. The water sorption at saturation is no more dependent on the size of the EV, however the effect of the fibres placed at the surface of the EV was always visible at the early time of diffusion.

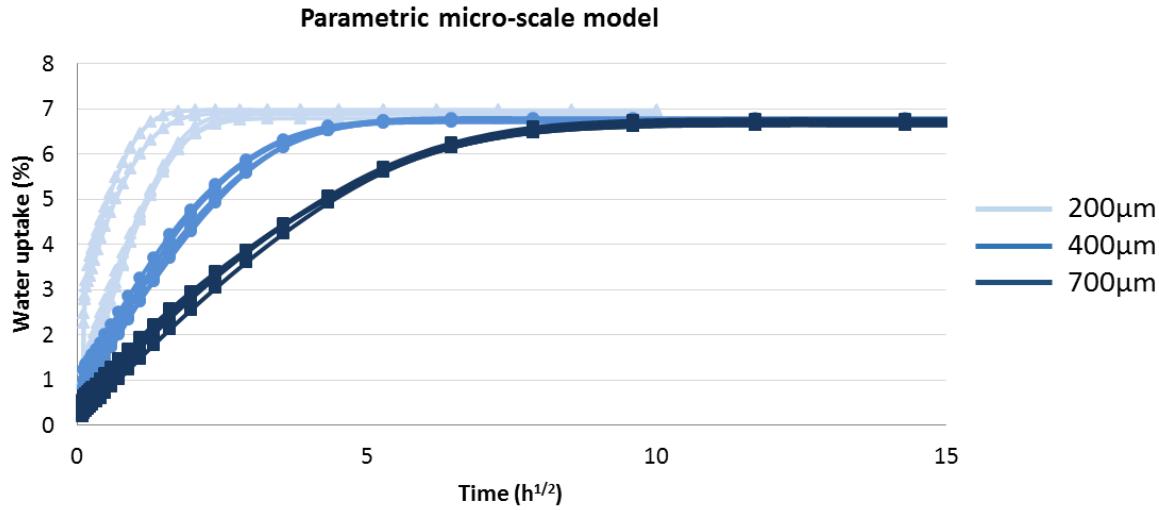


Figure V-VIII Yarn diffusion behaviour as a function of ageing time calculated by the parametric micro-scale model for different elementary volumes (200μm, 400μm and 700 μm).

V-3.1.4 Comparing the direct to the parametric model

The Figure V-IX shows the water uptake at saturation for the direct and the parametric model with their respective dispersion values (dispersion here is equal to the standard deviation divided by the mean). As observed previously in this chapter, the water concentration at saturation (C_{sat}) determined by the direct model decreases with the increasing EV size, while this parameter was found to be independent of the EV size for the parametric model, and the direct model presents a more important variation in water uptake value than the direct model. The values of the yarn water uptake converged for both modelling approach to the same value of around 6.5%.

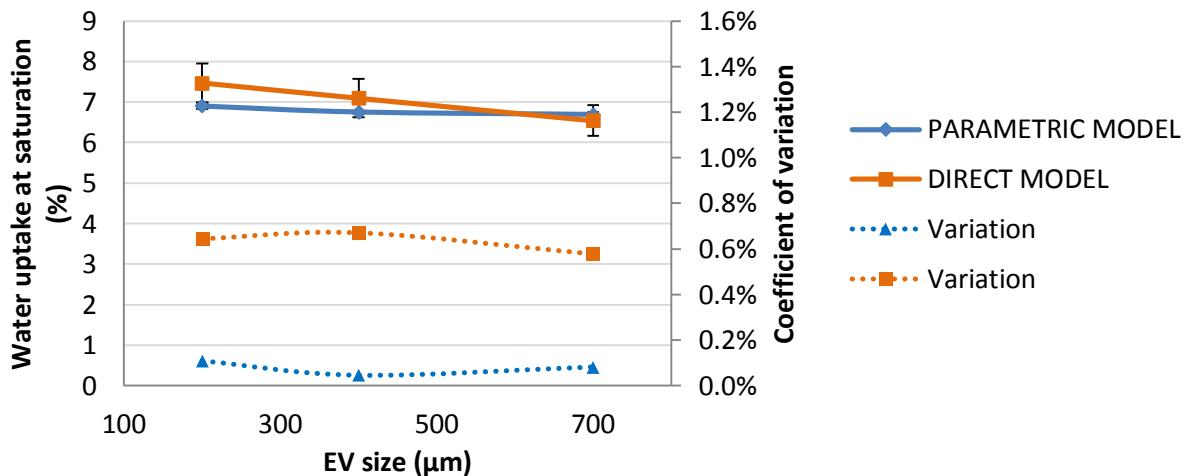


Figure V-IX Comparison between the parametric and the direct model results for the water uptake at saturation at the yarn scale for different elementary volumes (200μm, 400μm and 700 μm).

The Figure V-X shows the influence of the EV's size on the diffusion rate k , defined as the slope of the water uptake response which is almost linear at early times on a $W\%- \sqrt{t}$ graph, for the direct and the parametric model with their respective statistical dispersion values. The diffusion rate k was found

to be strongly dependent on the VE's size for both models (direct and parametric). Moreover, its dispersion decreased with the increasing EV size, showing lower values for the parametric model compared to the direct model. The average value of k converged toward $1.3\%/\text{h}^{-1/2}$.

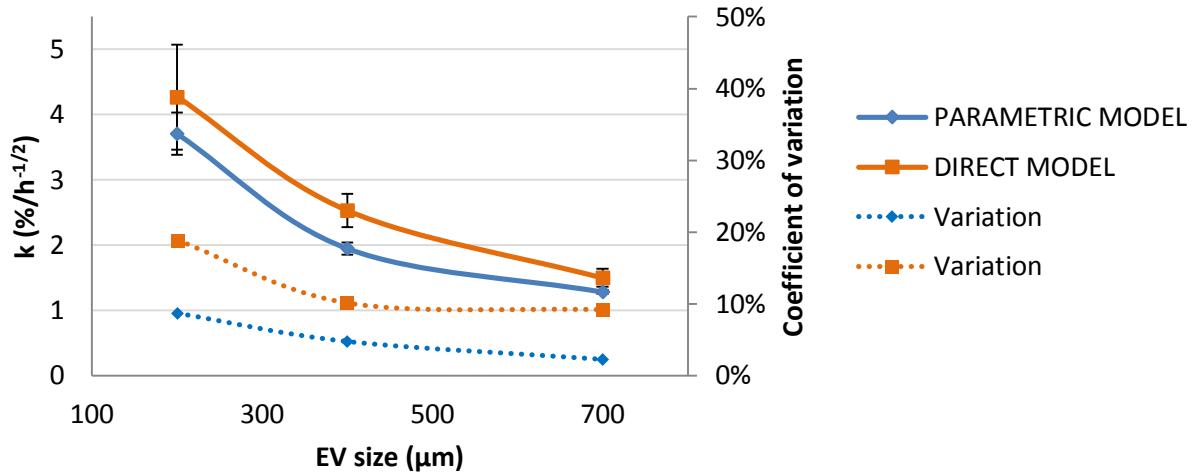


Figure V-X Comparison between the parametric and the direct model results for the coefficient k at the yarn scale for different elementary volumes (200 μm , 400 μm and 700 μm).

The comparison between the two models brings to light that the representation of the morphology with the parametric model led to a slight underestimation of the yarn diffusion and to less scattered results at the micro-scale. Improving of the parametric model by taking into account other descriptors (especially relating to the shape of fibres and bundles) should provide even more compelling results.

The elementary volume of $700 \times 700 \mu\text{m}^2$ was found to be representative of the water diffusion in the flax yarn, resulting in a variation of 0.1% and 2% for the water uptake at saturation and the diffusion rate, respectively.

The next step intends to integrate the results obtained at the micro-scale into a model of the yarn behaviour at a macro-scale (composite scale).

V-3.2. Macro scale modeling

V-3.2.1 Images treatment

The microscopic images of the flax fibre composites samples cross-section were stitched together using *PTGui®* (image stitching software that creates panoramas by superposing multiple images). The SEM images presented a 20% of superposition rate from one image to another, which allowed to reassemble the whole cross section of composites samples (25 mm width by around 3.2 mm thickness) from microscopic images at a magnification of 200x. A total of 80 images were realised for each sample. The images scale was verified before and after stitching in order to ensure that this step preserves the dimensions of the cross-section. Then, the reconstructed panoramic images were cleaned by using the open source software *Gimp 2.8*. This step was described in section II-4.2.1b (page 80). After processing, the images were binarised using the software *Aphelion®* before being vectored using the software *Inkscape®*.

Following this part, the steps for the creation of the macro scale diffusion model are then described separately for the direct and the parametric model.

V-3.2.2 Direct model

The panoramic stitched images, already binarised and vectored, were integrated to the direct macro model by using the Comsol® software and the progress of water during diffusion along the time in the composite is represented in Figure V-XI.

It is interesting to note that water diffuses faster in the flax yarns located at the lateral borders than in those placed at the horizontal borders. This effect is due to the presence of a resin layer in the outside horizontal border that slows down the water diffusion in this region. The yarns placed at the lateral borders present no external resin layer because this region was cut during the machining step. This observation brings to light an experimental configuration that creates a heterogeneous state of water diffusion during the first hours of water exposure. Therefore, the variation of the resin thickness at the surface of the samples can lead to a significant change in the diffusion coefficient. . In addition, sealing the border surface of the sample should lead to more conclusive identification of the diffusive behaviour because more homogeneous on the width of the sample. This phenomenon will be discussed later in this chapter.

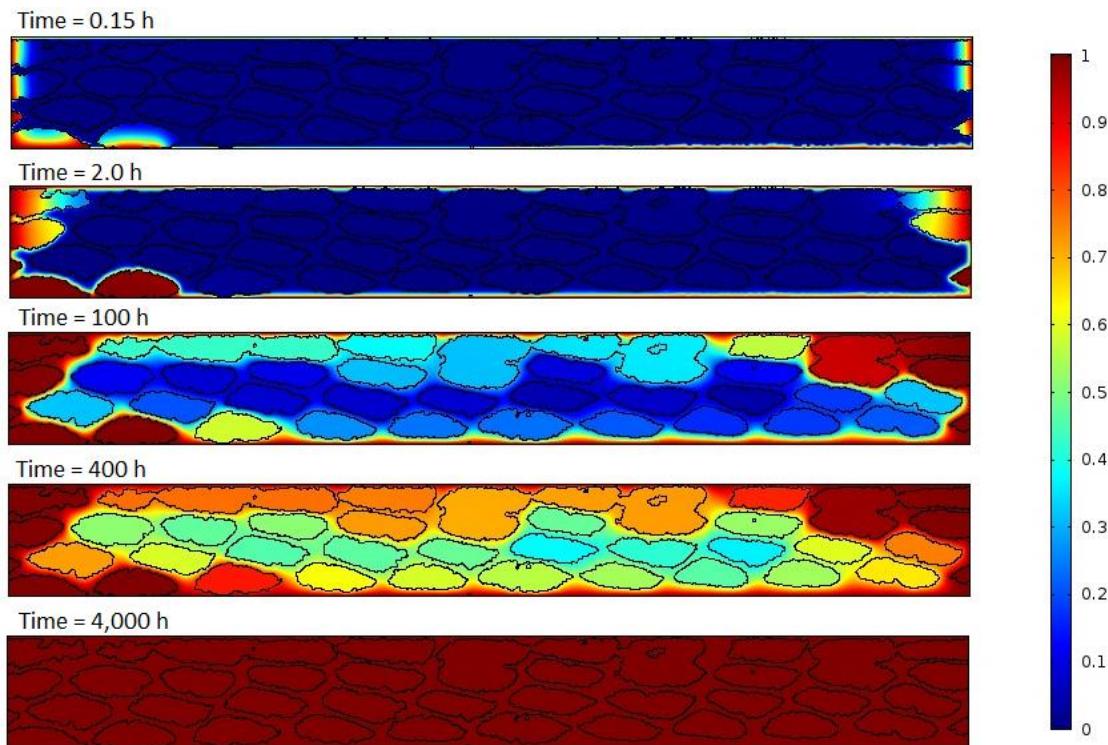


Figure V-XI Macro scale direct model employed for modelling the water sorption behaviour of flax fibre reinforced composites.

At this scale, two components can be identified: the polyester matrix and the flax yarns. The diffusion properties of the polyester resin were determined experimentally while the properties of the flax yarn were defined by the micro scale model and from the FEMU method (D_{matrix} : 8E-13 m²/s and $M_{\infty matrix}$: 0.9% ; D_{yarn} : 1e-11 m²/s and $M_{\infty yarn}$: 8.7%). Three realistic models corresponding to different samples analyzed morphologically were studied here. The results of the water sorption behaviour of

FFRC as a function of the ageing time are reported in Figure V-XII and compared to the experimental results. For these three cases, two different diffusion kinetics can be distinguished: the faster diffusion rate observed during the first hours of ageing is related to the presence of yarns at the surface of the sample. This behaviour was also observed previously at the intra-yarn micro-scale. The Fick's law applied to the multi-scale model does not completely describe the water diffusion behaviour of flax fibre composites. In all cases, the underestimation by the numerical model can be explained by wrong values of material parameters. If those of the flax fibres are identified on the basis of the Femu approach, those of the resin were obtained experimentally from neat polyester samples and were not subject to additional identification. As explained previously, the diffusion rates of the flax fibre and the polyester resin taken separately may be different from their behaviour inside the composite and could explain their misestimation.

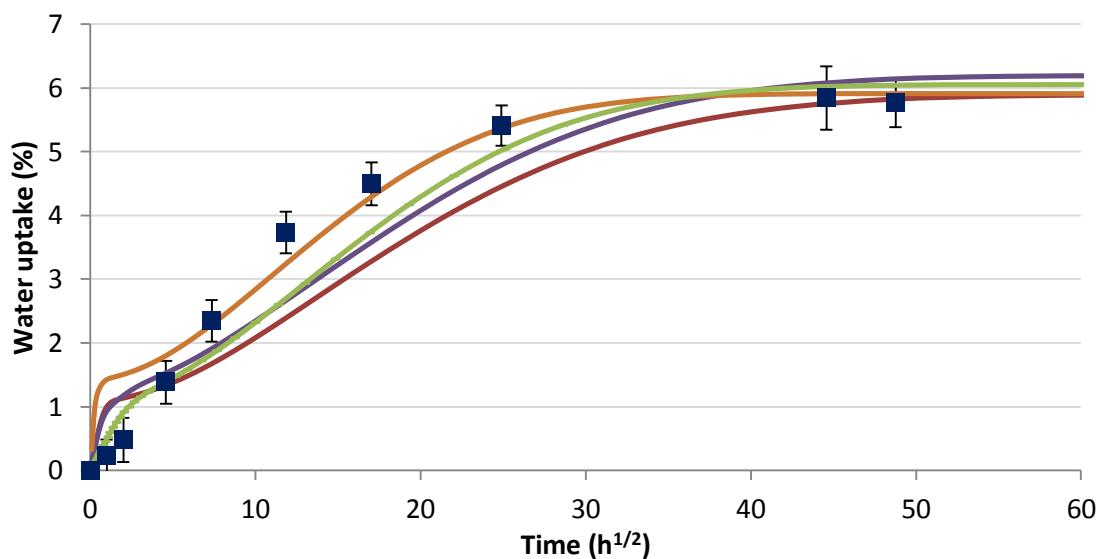


Figure V-XII FFRC's diffusion behaviour modelled by the direct macro-scale model (compared to the experimental results).

V-3.2.3 Parametric model

A Microsoft Excel® program was developed to automatically generate data required for the parametric macro-scale geometry by taking into account the statistical study of the geometrical parameters. The parameters: yarn height and length, inter yarn distance, inter ply distance, yarn content and sample thickness are schematically shown in Figure V-XIII, and the results of the statistical analysis are presented in Table V-II.

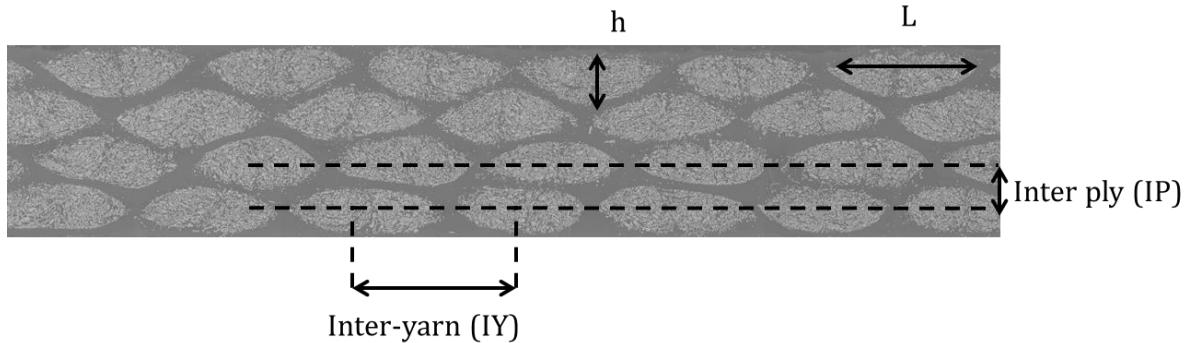


Figure V-XIII Yarn height (h) and length (L), inter yarn distance (IY), inter ply distance (IP) of vacuum infused flax fibre composites.

Table V-II Statistical analysis of the yarn height (h) and length (L), inter yarn distance (IY), inter ply distance (IP) of vacuum infused flax fibre composites.

Yarn parameter	Mean value (mm)	Standard deviation (mm)	Dispersion
IP	0.81	0.12	15%
IY	2.37	0.21	9%
h	0.72	0.12	17%
L	2.18	0.17	8%

The distribution of the flax yarns in the polyester matrix (Figure V-XIV-a). These data were then integrated to Comsol® to generate the model geometry which was meshed (Figure V-XIV-b). The water sorption was then simulated (Figure V-XIV-c).

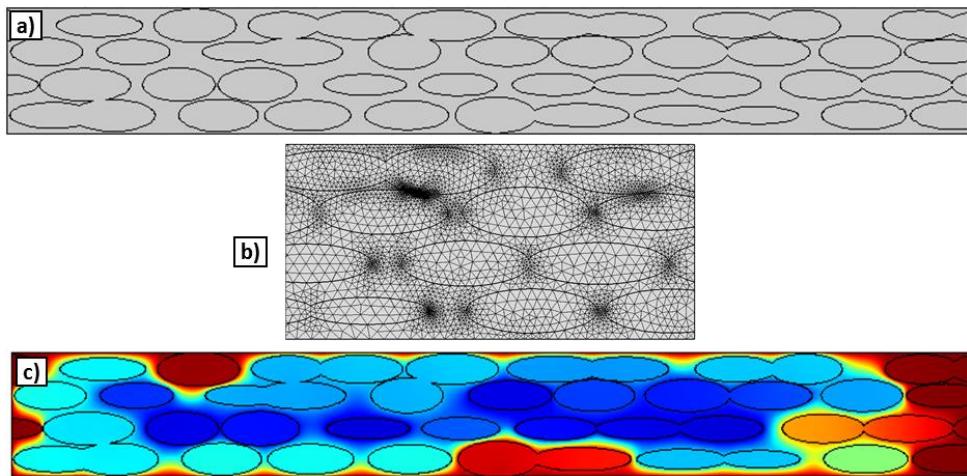


Figure V-XIV Creation of the parametric macro-scale model: a) Parametric microscopy; b) Meshing c) water diffusion modelling.

The results of composites diffusion simulation is shown in Figure V-XV. All results employed the same diffusion parameters ($D_{\text{matrix}}: 8E-13 \text{ m}^2/\text{s}$ and $M_{\infty, \text{matrix}}: 0.9\%$; $D_{\text{yarn}}: 1e-11 \text{ m}^2/\text{s}$ and $M_{\infty, \text{yarn}}: 8.7\%$), and the difference observed between the curves is due to the statistical distribution (geometry and dispersion of the yarns) introduced in the model. While it was observed the same underestimation as for the realistic model, the variation on the water uptake at saturation is related to the composite's

fibre volume content, while the variation of the diffusion kinetics is due to the dispersion of the yarns inside the matrix. It was already discussed in this chapter that an increase in diffusion kinetics was observed when the yarns were interconnected, which creates a preferential path for water to diffuse faster in these regions than in the rich polymer matrix zones (Figure V-XVI).

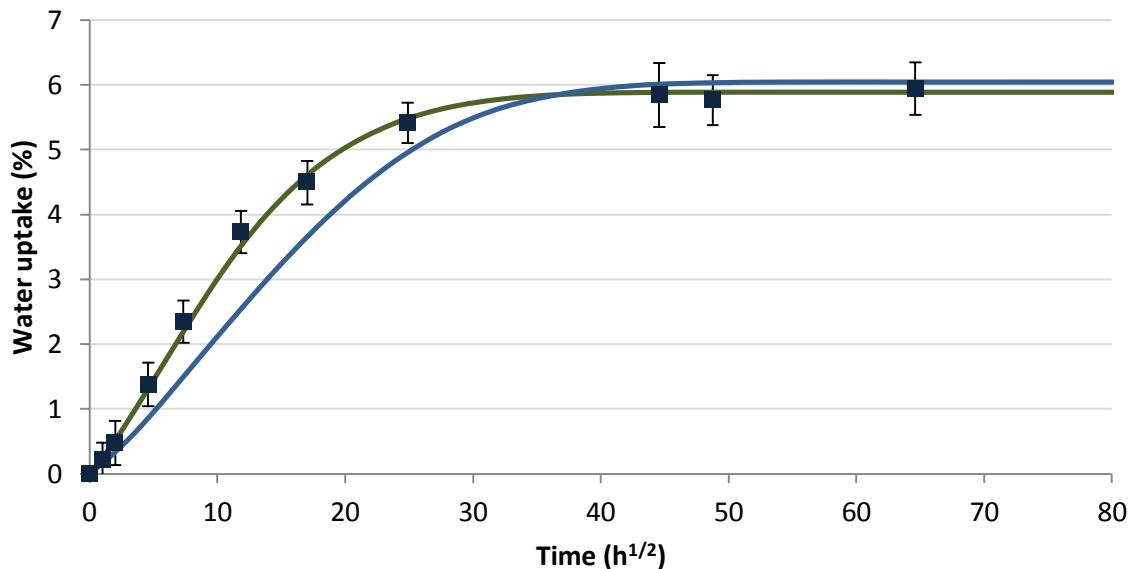


Figure V-XV FFRC's diffusion behaviour calculated by the parametric macro-scale model.

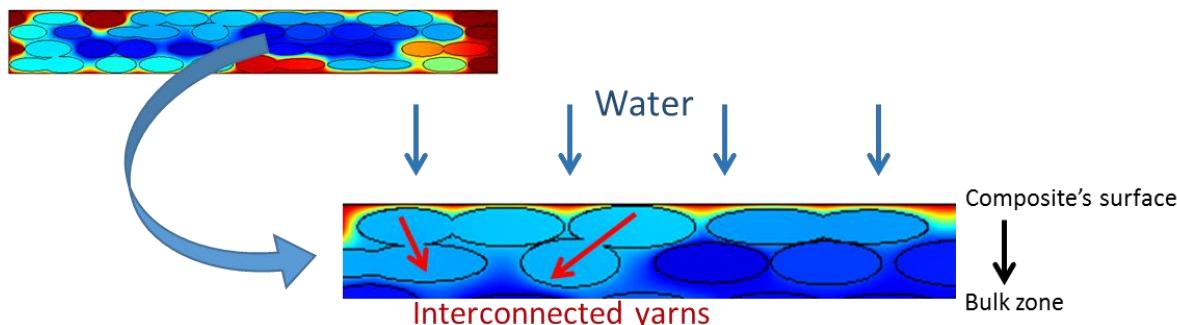


Figure V-XVI Diffusion behaviour of composites showing the acceleration on water sorption due to the presence of interconnected yarns.

V-3.3. Discussion

The creation of the direct and the parametric multi-scale model was described and briefly discussed in this part. The introduction of a statistical analysis based on the real morphology of flax fibre composites allowed creating a parametric model and describe its diffusion behaviour. The analysis of the results for this model established the reliability of the statistical study in representing the real morphology of the composite. The diffusivity of the water in composites determined by modelling was found to be slower than that determined experimentally. This result is confirmed by simulation conducted using the direct model. Some questions are put forward aiming to explain the difference

observed between modelling and experimental results, with the key point consisting of the representativity of introducing ex-situ measurements to identify the material parameters and especially those of flax fibres from FEMU approach at a micro-scale.

The next part will address an analysis on the sensitivity of the composites diffusion behaviour to the diffusion parameters of the flax fibres and the polyester matrix. The direct computation of the composite diffusive behaviour on the basis of given material parameters will be compared to the experimental results presented in this work. The given materials parameters are also discussed and compared to the values found in literature (for the polyester resin and flax fibres).

Finally, a discussion about the parameters taken into account to create the model and the validity of a 2D Fick's model to represent the diffusion behaviour of vegetal fibre reinforced composites is addressed at the end of this chapter.

V-4. Sensitivity of the composites diffusion behaviour to the in-situ diffusion parameters of the flax fibres and the polymer matrix

The methodology employed here aims to analyse the sensitivity of the water diffusion in composites on the in-situ properties of the flax fibres and the polymer matrix diffusion properties. A homogeneous model was used to determine the equivalent diffusion properties of the yarn (see Figure V-III – page 176). These values (diffusion coefficient and the water uptake at saturation) were determined by a model updating and then introduced in the macro-scale model to predict the composites behaviour based on the properties of their constituents (fibre and matrix). The methodology applied to this study was previously described in Figure V-XVII.

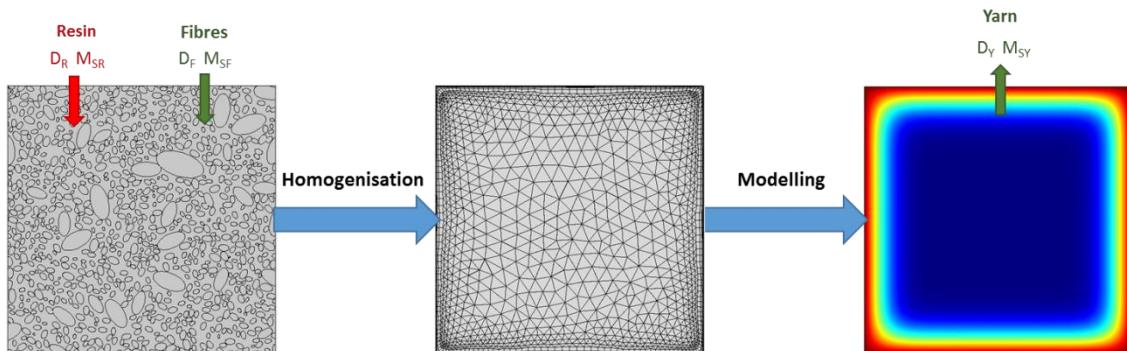


Figure V-XVII Methodology employed to access the homogenised yarn diffusion properties from the properties of the fibre and the matrix at the micro-scale model.

V-4.1. Flax fibres diffusion behaviour

The results of the water sorption behaviour of FFRC as a function of the ageing time are reported in Figure V-XVIII. The influence of the fibres diffusion coefficient on the composites diffusion behaviour is presented here. It can be observed that increasing the fibres diffusion coefficient lead to an increase on the global kinetics of diffusion of the composite. But a limit is reached when the global behaviour is no longer dependent on the diffusivity of the flax fibre. This occurrence of a capped diffusion rate was previously observed at the intra-yarn micro-scale and was related to the fact that it is the polyester

matrix that governs the modelled diffusive behaviour of the composites. This hypothesis is valid if there is no or few interconnection between flax yarns. This is observed experimentally in the cross section of samples, but the interconnection between fibres along their length could result in a tridimensional effect that was not considered in this model.

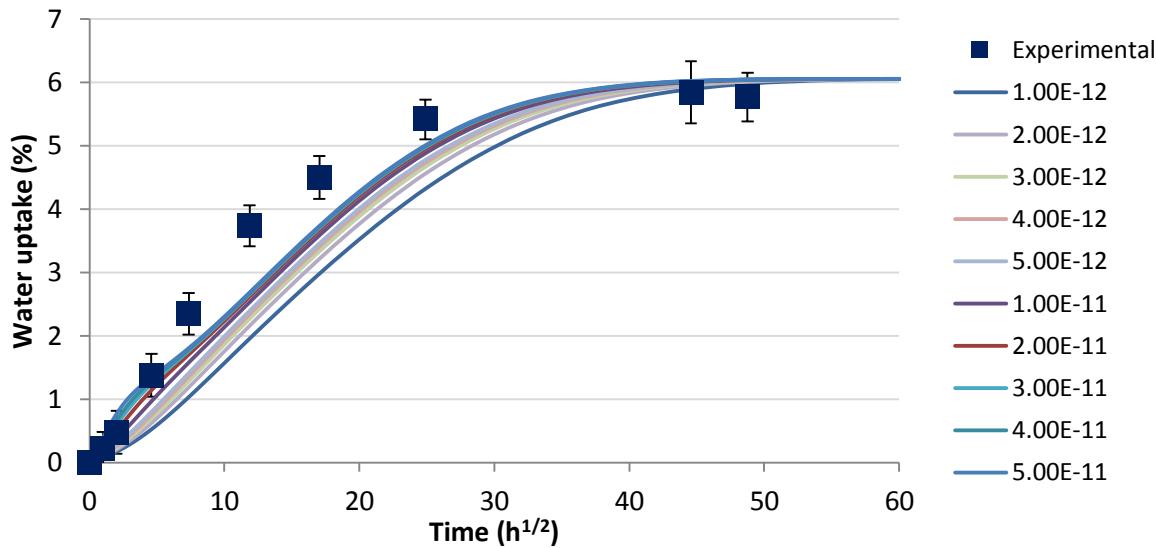


Figure V-XVIII Influence of the fibre diffusion coefficient on the FFRC's diffusion behaviour determined by the direct macro-scale model.

The Figure V-XIX presents the influence of the water uptake at saturation of the flax fibres on the diffusion behaviour of flax fibre composites. In order to fit the composites water uptake at saturation, which was experimentally determined to be at $5.8 \pm 0.5\%$, the fibres sorption at saturation was estimated by modelling to be at $18.9 \pm 1.8\%$. These results are superior than those determined by ex-situ measurements for flax fibres exposed to hygrothermal conditions : 12% [132] and 14% [137].

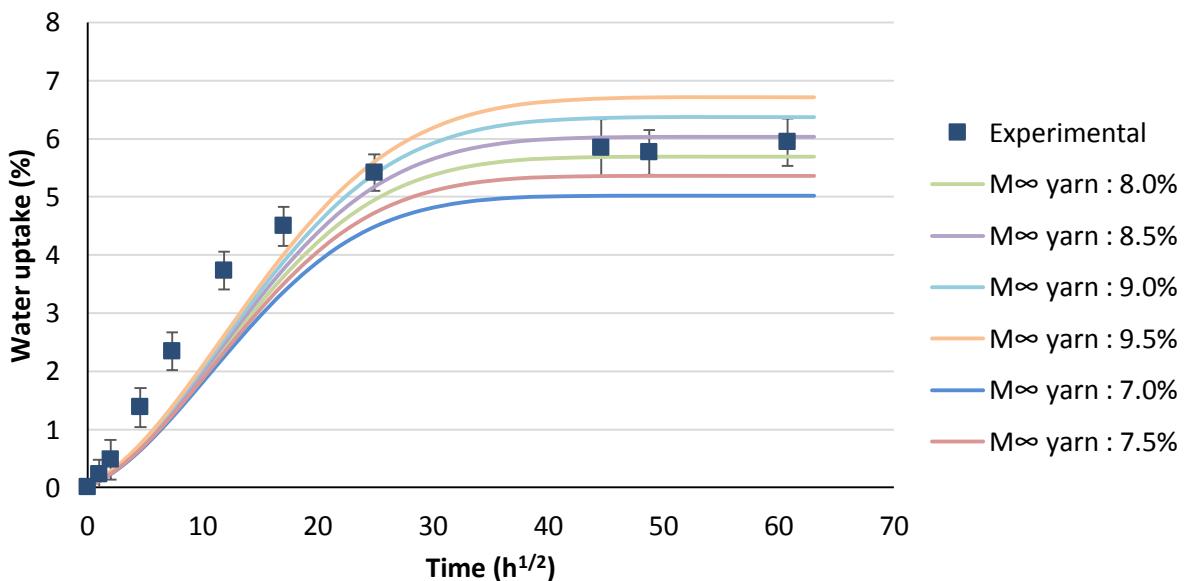


Figure V-XIX Influence of the yarn diffusion coefficient on the FFRC's diffusion behaviour determined by the direct macro-scale model.

V-4.2. Polymer matrix diffusion behaviour

The Figure V-XX shows the influence of the matrix diffusion properties on the FFRC's diffusion behaviour, and compares these results to the experimental tests realised in water at 30°C. It can be observed that the composites diffusion behaviour is strongly dependent on the matrix diffusion properties. It is recalled that the experimental diffusion coefficient of the polyester matrix (D_{matrix} : 8E-13 m²/s) was introduced in the previous simulation and the result at the composite scale was compared to the experimental tests. The diffusion kinetics of the FFRC defined by the macro model were found to be underestimated compared to the experimental results. Indeed, the diffusion coefficient for the polyester matrix that best fitted the experimental diffusion curve of the composite was 3E-12 m²/s, which may suggest that the polyester matrix does not present the same diffusion kinetics inside the composite compared to the unreinforced polyester samples. This difference can be related to the fact that the polymer matrix presents an evolving crosslinking state from the polymer sample compared to its state in the composite. Another hypothesis is related to the presence of porosities in the polymer matrix (inside the composite) that results in an acceleration of the water sorption [125]. Indeed, it was shown in the last chapter that the porosity was principally confined in the polymer rich areas between the flax yarns, i.e. a matrix porosity type, but this parameter was not taken into account for modelling.

Joliff et al [214] reported a similar behaviour for the diffusion coefficient of an epoxy resin that was found to be at 1.5E10-12 m²/s for the unreinforced polymer matrix compared to 1.0E-11 m²/s for the polymer matrix in a glass fibre composite. The authors observed a decrease in the polymer glass transition temperature around the fibre, and a water diffusion coefficient about five times higher in the interphase than in the matrix.

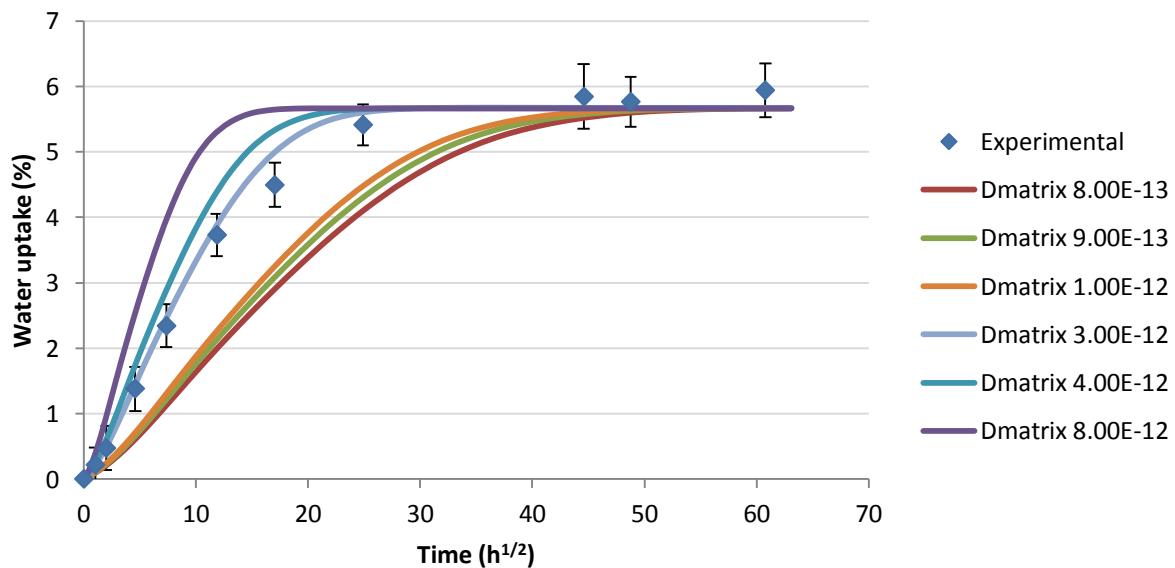


Figure V-XX Influence of the polymer diffusion coefficient on the FFRC's diffusion behaviour calculated by the direct macro-scale model (compared to the experimental results in water at 30°C).

V-5. Critical analysis and perspectives of the model

Initially, it seemed logical to create a multi-scale model based on the analysis of the microstructural configuration of the flax fibres inside the polyester matrix. The microscopic images revealed that a region rich in fibres (yarns) was surrounded by a region rich in matrix, which led to the creation of a model at two scales. The micro-scale (called *intra-yarn*) was created based on the analysis of the dispersion of unitary fibres and bundles in the interior of the yarns, and a macro-scale (called yarn) highlighted the dispersion of yarns in the polyester matrix. Furthermore, it was observed the presence of fibres in the weft and warp directions from the microscopic images. As the fibres in the warp direction do not participate in the determination of the fibre volume content, these were subtracted from the model by masking them. Then here, a first critical analysis of the model consists in the representativity of this model if the warp fibres are not taken into account. The flax fabrics used in this work was determined to be constituted by 9% of fibres in the warp direction (mass fraction of warp fibres compared to the fabric total weight), which can act as a component that links the yarns and create a “track” of diffusion where water can diffuse faster than in the polymer matrix.

It is suggested here that the two dimensional microstructural configuration of flax fibres inside the polyester matrix revealed by the SEM images is maybe not sufficient to fully describe the diffusion phenomena that takes place when biocomposites are exposed to water immersion. It was found that the flax yarns are isolated by a matrix rich region that probably possesses a diffusion kinetics much lower than those at the interior of the yarns. It should be possible to differentiate the diffusive behavior of the resin within the warp from that in the outer.

In order to take into account the entire role of the yarns in the warp direction, it would be necessary to create a diffusion model in three dimensions (3-D model). This model would allow to introduce some parameters, such as the bulk dispersion of yarns (in weft and warp direction), but also of the porosity that was experimentally revealed to be located in the matrix (by X-ray tomography technique). The fact that the diffusion behaviour of biocomposites was shown to be dependent on the fibres maximum sorption, but limitedly dependent on the fibres diffusivity, may come from the fact that the 2D model does not completely describe the entire water diffusion behaviour of biocomposites. A bulk diffusion effect is neglected by the 2D model, which can be linked to the fact that the fibres are interconnected between them in the longitudinal orientation, or by the fact that the fibres oriented in the transverse direction accelerate the diffusivity of water in the composite.

Another critical analysis consists in the concept of a yarn scale in the model. In the reality, a yarn consists of a long continuous length of interlocked fibres, suitable for the production of textiles, knitting, weaving, etc. This means that the yarns exist in reality but their modelling is controversial. The step of treating images before modelling, mainly vectoring, consists of recognising the contour of objects before meshing and modelling them. When the micro-scale is concerned, the representativity of the vectoring can be verified by comparing to the real contours at the initial image, but at a macro-scale what is the contour of a yarn? The analysis of the microscopic images showed that the yarns do not present an obvious contour, which means that the vectoring step leads to a simplification of the yarns' contours, without taking into account its heterogeneous dispersion. The simplification of the model at this step can introduce additional errors.

The creation of the parametric model at a macro scale based on the arrangement of flax yarns in the polyester resin allowed studying the influence of the processing conditions on the diffusional

behaviour of FFRC. It was observed in the Chapter III of this work that the processing conditions (mainly pressure) was found to influence the geometry and the dispersion of flax yarns in the polyester matrix, which led to different morphological and mechanical properties of the composites depending on the processing technique. Then, it would be interesting here to study numerically the difference between the diffusion behaviour of vacuum infused compared to compression moulded composites by modelling their behaviour taking into account the real morphology. Moreover, it can also be interesting to perform hydrothermal aging tests on compression moulded composites, which present interconnected flax yarns, and compare obtained results to numerical ones.

Conclusion and future work

Context reminder

This work is a contribution to the understanding of the impact of in-service aging on the mechanical and physical properties of flax fibre reinforced polyester dedicated to marine industry. There is a demand in this industrial sector for new “green” materials to substitute traditional glass/polyester composites which are energy-consuming and non-recyclable materials. Literature shows that natural fibre reinforced composites exhibit very interesting mechanical properties, but poor durability when exposed to hot and humid environment. Nevertheless, interesting studies succeeded in developing simple processes to improve the durability of such materials by chemically modifying natural fibres making them hydrophobic. When it comes to structural applications, it is of first importance to consider the impact of mechanical loadings coupled to hydrothermal conditions. The scientific and industrial knowledge on this specific point still requires advanced and precise investigations in order to make natural fibre reinforced composites competitive for structural applications.

Objectives

The objective of this thesis was to precisely investigate the evolution of physicochemical and mechanical properties of flax fibre reinforced polyester when immersed in water as a function of temperature. Drying samples and evaluating the reversibility of observed phenomena was an important step of this work before studying the impact of coupled loadings on the evolution of composite properties. The final part consisted in developing a numerical approach to predict the composites behaviour during aging.

Scientific considerations

The substitution of glass fibres by flax fibres in marine polymer composites requires a thorough understanding of the influence of processing on their initial properties and the mechanisms of degradation that takes place during ageing. In addition to the LCA that is not consider in this work.

In Chapitre III, a characterisation of basic components (flax fabrics and polyester resin) has been carried out in a first part. Before ageing, the results show that selecting materials is an important step to take into account when designing biocomposites. Three different flax fabrics supplied by Biorenforts, Chomarat and FRD, were impregnated through vacuum infusion using an unsaturated polyester resin to produce unidirectional composites. Results show a better fibre dispersion in the polyester matrix for FRD fabrics that permitted to reinforce composites at 31% of fibre volume content.

Nevertheless the higher mechanical properties were obtained for Chomarat composites due to the presence of a hybrid flax-glass fibres configuration.

The polyester resin was post-cured in the laboratory following a thermal cycle that corresponded to a post-curing treatment realised at ambient temperature during five months, which is the period during which boat components remains exposed to outdoor conditions before being launched in water (for boat hulls in the Outremer company). The crosslinking rate of 100% was never reached, which meant that the polymer remained under-crosslinked after the thermal treatment.

Once materials and thermal treatment characterised, flax and glass fibre composites were produced by the vacuum infusion technique. A fibre volume content of 31% was reached for flax fibre reinforced composites while a content of 61% was obtained for glass fibre reinforced composites, for the same processing conditions. The fibre content and composite density of vacuum infused composites remained constant whatever the number of flax layers used, while composites weight increased because of an increment in thickness.

Then, in a second part, biocomposites were manufactured by compression moulding technique and their mechanical and morphological properties were compared to vacuum infused composites. The fibre content in compression moulded samples was found to be twice the content in vacuum infused composites, which led to an increase in their mechanical properties. Porosities were observed in the polymer matrix that decreased with the increasing fibre content. The porosity content was found to be dependent on the processing technique and the fibre content.

Despite an increase in mechanical properties with the enhanced processing pressure, flax fibres composites were degraded during processing because of the considerable pressure applied to flax fabrics. The difference observed between experimental and theoretical (using the rule-of-mixtures) results was explained by the flax fibres degradation, and/or by a decohesion at the fibre/matrix interface. The work in the design of flax fabrics is an interesting way to improve the fibres dispersion into matrix and therefore to increase fibre content of flax fibre composites without degrading them. Finally, even if FFRC presented higher interfacial adhesion compared to GFRC, biocomposites exhibited much lower elastic and ultimate mechanical properties for a similar weight.

Once composite properties were characterised before ageing, these materials were immersed in water in order to analyse the loss of properties in service, and to understand the complex mechanisms that take place during ageing. The Chapter IV is dedicated to the study of the biocomposites ageing.

The swelling behaviour induced by water uptake was found to be completely reversible for glass fibre composites and polyester resin but only partially reversible for flax fibre composites. This residual swelling was found to increase with aging temperature. Another reversible phenomenon observed during hydrothermal ageing was the plasticisation of polyester resin and flax fibres. The irreversible phenomena observed during ageing of biocomposites were residual swelling, removal of polyester resin and flax fibre components, interfacial degradation and microcracking (mainly observed at 70°C). It was noted the occurrence of concomitant phenomena in the polyester resin during ageing related to the leaching of some components and to the formation of hydrogen bonds between water and polymer chains. It was hypothesised that these bonds were found to be strong enough to endure the drying process. Moreover, it was observed that the drying conditions changed the composites properties by partially removing the initial humidity present in fibres before ageing.

GFRC ultimate properties remained constant during water ageing at 30°C and 50°C, but the exposure at 70°C induced irreversible degradation associated to the interfacial damage. Concerning FFRC, interfacial degradation was observed for all the temperatures investigated in this study. Indeed, the interfacial damage seemed to be the most important factor responsible for the loss of properties observed during ageing. Finally, the ageing mechanisms displayed by flax fibre composites exposed to hydrothermal conditions at 30°C was reported to be mostly reversible, while irreversible damage was observed at 50°C and 70°C linked to the interfacial degradation.

The coupled mechanical-hydrothermal ageing of biocomposites was found to introduce additional water uptake and swelling, stiffness loss and a reduction of the time-to-fracture. The swelling of composites was observed to be a hydraulically but also mechanically activated mechanism; hence the theory of the free volume was not sufficient to explain the additional swelling displayed by coupled aged samples. The temperature and the mechanical loadings were found to reduce the time-to-fracture of biocomposites while the exposure to water provoked an increase in the creep strain related to the plasticising effect of water. It was noted that the effect of mechanical loads on biocomposites modulus loss was found to be more important than that of the immersion in water. No coupling synergy was observed and the loss of modulus for coupled mechanical-hydrothermal tests was found to be lower than the sum of thermo-mechanical plus hydrothermal modulus loss, which means that a stiffening phenomenon occurred during coupled ageing. It is hypothesised here that the realignment of the microfibrils contained in the flax fibres might explain this self-stiffening mechanism.

Future work

This study proposed a detailed analysis of the mechanical and physical properties of FFRC and GFRC before and after ageing in water. The phenomena that took place during ageing were assessed by experimental tests, but some observations need to be further investigated to better understand the ageing mechanisms involved in the case of flax fibres reinforced composites.

It could be interesting to address an experimental characterisation of the ageing behaviour of compression moulded FFRCs and to compare the results to the ageing behaviour of vacuum infused FFRC in order to evaluate the influence of the processing conditions on the ageing of composites. The multi-scale modelling developed in this work could be helpful to predict their diffusion behaviour as a function of the composites morphology.

The FFRC exhibited non-linear mechanical response at low deformation that influences the assessment of their elastic modulus (as highlighted in Appendix 2). In the literature, this behaviour was related to the progressive alignment of the cellulose microfibrils with the flax fibre axis [92], but, to our knowledge, the evolution of this non-linear behaviour during ageing was not yet related in literature. Then it could be interesting here to investigate the non-linearity of biocomposites during ageing.

Furthermore, the biocomposites were found to swell during ageing, which was related to flax fibres swelling in this work. The in-situ image analysis of flax swelling during ageing would provide important information useful to improve the proposed numerical models. Moreover, soluble components of the flax fibres and of the polyester resin were released in the water bath. Further analysis of the water

used to age composites, can give more information about the nature of the released components, especially for flax fibres in order to determine the location of these components inside the fibre's microstructure (primary or secondary wall).

The study of the FFRC's ageing behaviour included mechanical and physical characterisation that can be implemented by the analysis of the evolving behaviour of the polymer matrix in the composite, i.e. for in-situ instead of ex-situ characterisation. Here, it would be interesting to verify experimentally the effect of water ageing on the diffusion behaviour of the polyester matrix as a consequence of the evolving glass transition temperature observed during ageing. The same methodology would be applied to the flax fibres, even if the experimental set-up seems to be ambitious.

Concerning the coupled mechanical-hydrothermal analysis, DSC and FTIR experiments may allow a characterisation of the evolution of the crosslinking rate and the hydrolysis of the polymer matrix. The reversibility of the composites properties (physicochemical and mechanical) after mechanical-hydrothermal ageing could give further information about the ageing mechanisms that take place during the coupled ageing.

Finally, it is important to consider the non-Fickian diffusion behaviour to modelling the water uptake of biocomposites. The two-phase diffusion model proposed by Carter and Kibler, often referred as "Langmuir-type", might be employed to better describe the existence of mobile and bonded water molecules inside the polymer network, even if this model assumes the reversibility of the sorption. Then, it could be interesting to take into account the role of the yarns in the warp direction on the water diffusion by creating a diffusion model in three dimensions (3-D model) instead of two. This model will be obviously more complete in terms of given information, but it will allow to introduce some parameters, such as the bulk dispersion of yarns (in weft and warp direction), and also the porosity that was already revealed to be localised at the matrix (by X-ray tomography technique).

Appendix

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Appendix 1 **Humidity content measurement of flax fibres**

The humidity content of fibres was measured using an InfraRed-balance (Precisa XM66 – 50 Hz) by drying the fibres at 105°C during more than 30 minutes and monitoring their mass during this time. The humidity content of fibres was then calculated by the difference between the mass at t=0 (before drying) and the mass after drying. Tests were carried out with the FRD UD 360 g/m² flax fibres, which were stocked under constant conditions of 23°C and 50% RH before testing. The samples dimensions were 15 x 5 cm and weighted between 10 and 13g.

The results show a humidity content of 7.3 ± 0.2%.

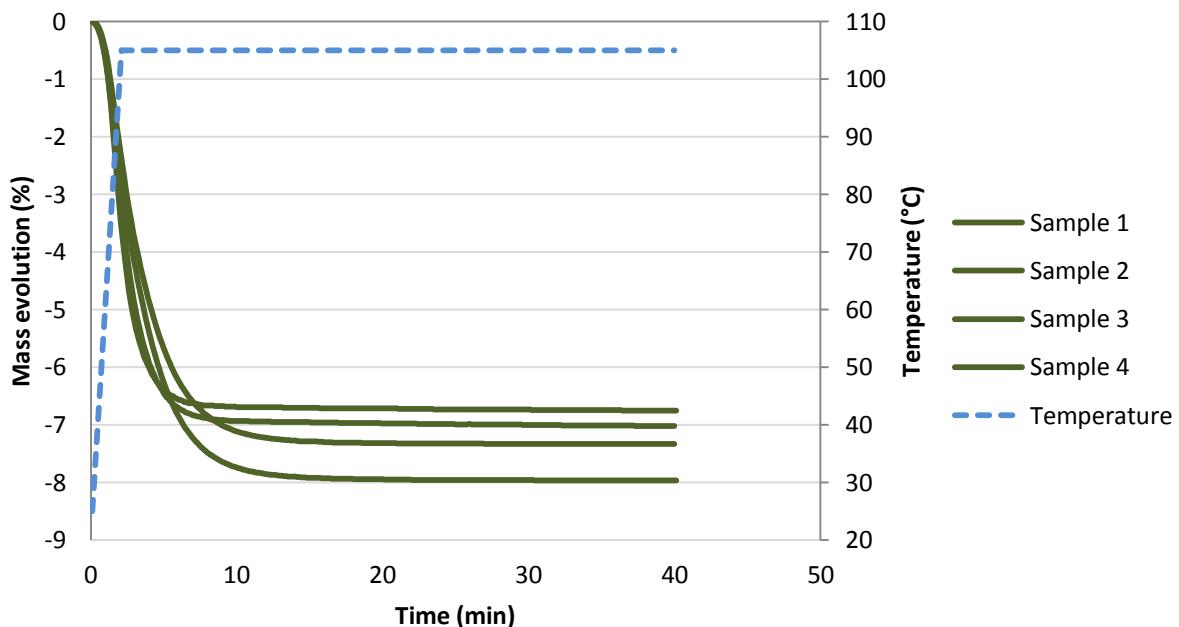


Fig A1-1 Mass evolution of flax fibres heated at 105°C as a function of time during 40 minutes.

Table A1-1 Humidity content of flax fibres (samples heated at 105°C during 40 minutes).

Sample	Initial mass	Final mass	Humidity content
1	10.095	9.413	6.76%
2	11.458	10.654	7.02%
3	12.784	11.847	7.33%
4	13.358	12.294	7.97%

It was supposed that the vacuum pressure imposed to flax fibres during processing could remove the initial humidity from fibres, but experimental tests achieved with flax fabrics revealed that the processing does not influence the fibres humidity. The methodology applied here consisted in placing four layers of flax fabrics measuring 300 x 300 mm² for a total weight of 133g inside a vacuum infusion system and impose different vacuum pressures to samples. The fibres were stocked at 23°C / 50% RH before testing and weighted before and after vacuum by using a precision balance (0.01g). The vacuum pressure was controlled by a manometer. The mass variation of fibres was under 0.1% due to the application of vacuum pressure, which highlighted that the vacuum pressure imposed to flax fibres during processing does not removed its initial humidity.

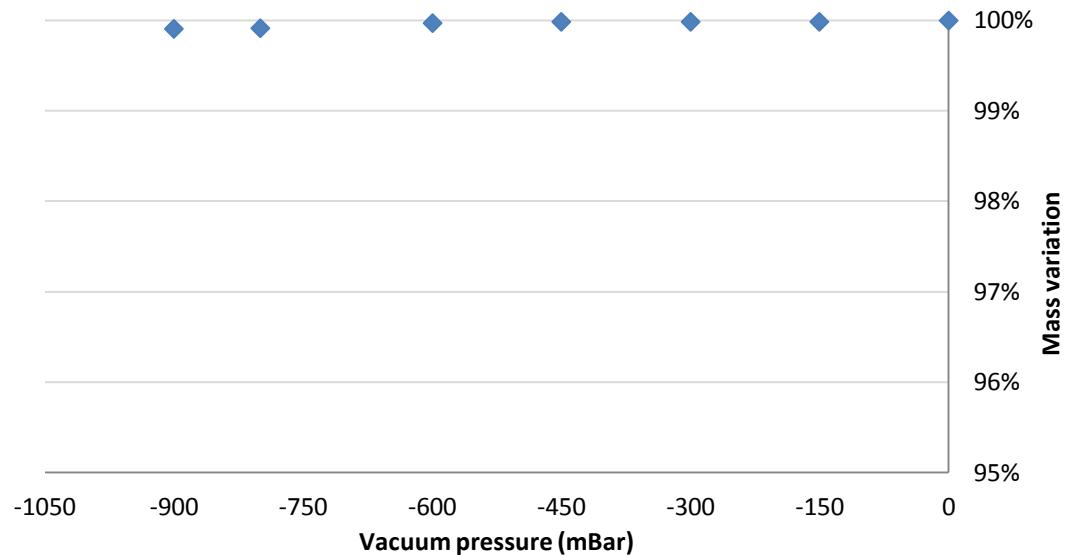


Fig A1-2 Mass variation of flax fibres as a function of the applied vacuum pressure.

Appendix 2 Viscoelastic behaviour measurement of flax fibre composites

Unidirectional flax fibre reinforced composites were tested in the axial direction in dynamic and static configurations using vibration analysis and traditional tensile test, respectively. The static modulus was determined using a MTS testing machine (model Criterion C45.105) equipped with a 10kN capacity load cell at a crosshead displacement rate of 1mm/min. The dynamic modulus was calculated from the frequency f_1 of its first “traction-compression” resonance mode of the sample measured by impulse testing (the methodology applied here to calculate the elastic modulus from the natural frequency was described in section II-4.1.2a – page 75). The results are shown in Table A2-1 for flax and glass fibre reinforced composites.

It can be noted that the elastic and dynamic modulus of GFRC were very similar and presented a good agreement with the theoretical modulus calculated by the *rule-of-mixtures*. Otherwise, a higher difference was observed between the dynamic and the elastic modulus of FFRC. The dynamic modulus is in good agreement with the rule of mixture. The difference observed between the static and dynamic modulus of flax fibre composites could be related in first approximation to the viscoelastic behaviour of both flax fibre and polyester matrix.

Table A2-1 Static and dynamic modulus of flax and glass FRC compared with the theoretical modulus determined by the *rule-of-mixtures*.

Composites	Layers	Thickness	Fibre content	Modulus (GPa)		
	Units	(mm)	%	Static	Dynamic	Theoretical
Glass FRC	6	1.7 ± 0.1	61.0 ± 0.6	45.0 ± 0.9	45.0 ± 0.9	45.8 ± 0.4
Flax FRC	4	3.1 ± 0.2	32.3 ± 1.5	15.6 ± 0.8	20.3 ± 0.6	20.8 ± 0.8

This hypothesis is schematically represented in Figure A2-1. Indeed, dynamic tests were realised using a using a *Met travib DMA 50*. Samples were cutted to size using a band saw. A tensile-compression configuration was used for testing samples presenting width and length of 5 and 50mm, respectively, at a frequency of 5 Hz. The linear domain was defined by strain sweep tests that led to displacement magnitude of 10^{-2} mm. The modulus E' , loss modulus E'' and the $\tan\delta$ were logged during testing.

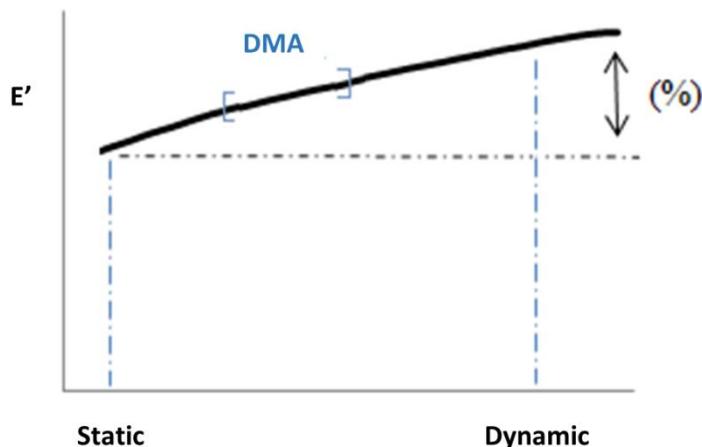


Figure A2-1 Schematic representation of the evolution of flax fibre composites modulus as a function of the loading frequency.

The evolution of the modulus and $\tan \delta$ is presented in Figure A2-2, and the data are gathered in Table A2-2. The analysis of the results highlighted that an increase in modulus of around 1.5 GPa is expected when the loading frequency increased from 10^{-2} Hz to 40 Hz. By extrapolating the evolution of modulus at 2000 Hz, the expected difference between static and dynamic modulus due to viscoelasticity could be around 2.5 GPa. Thus, the difference of 4.7 GPa as listed in Table A2-1 cannot be only explained by the viscoelasticity of flax fibre composites.

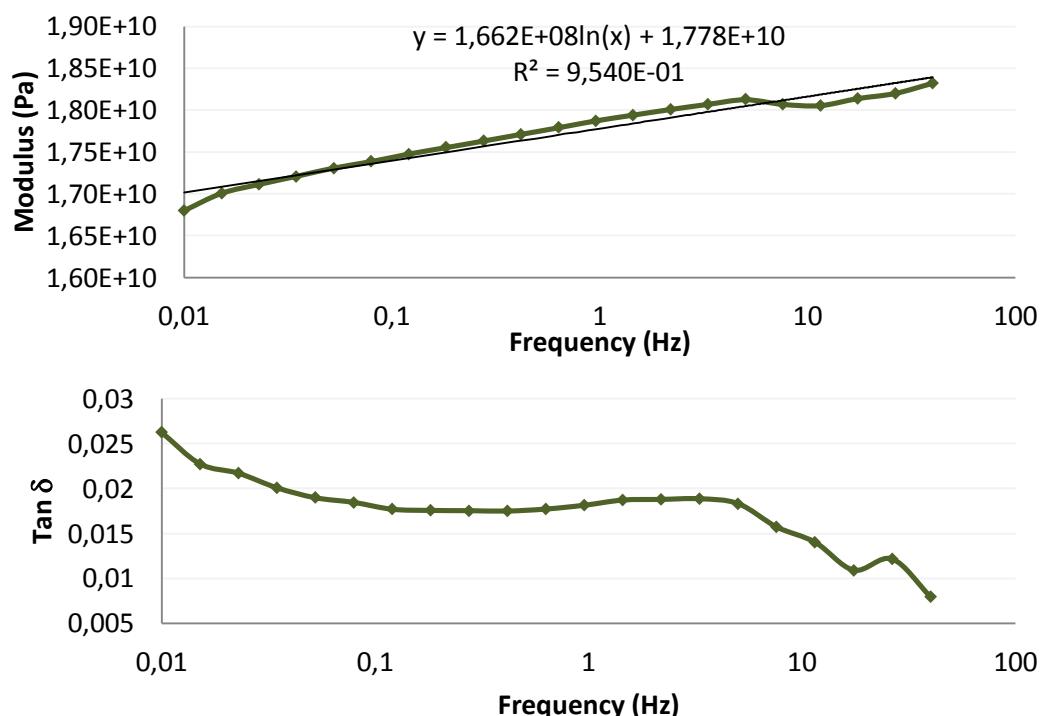


Figure A2-2 Evolution of the modulus and the $\tan \delta$ of flax fibre composites as a function of the loading frequency

Table A2-2 Flax fibre composites modulus as a function of the loading frequency

Flax FRC	Conservative modulus (GPa)		
	0,01 Hz	40 Hz	Difference
Sample 1	16.8	18.3	+ 1.5
Sample 2	16.4	17.9	+ 1.5
Sample 3	16.3	17.9	+ 1.6

The observation of the elastic behaviour of flax fibre composites during static solicitations exhibited a prominent non-linear behaviour at low strain. This phenomenon is represented in Figure A2-3. The ISO 527-4 standard dedicated to the tensile characterisation of glass fibre composites states that the elastic modulus has to be calculated in the deformation range between 0.05% and 0.25%. But for FFRC, the slope in this strain range is not constant as it can be observed in Figure A2-3. As a consequence, the modulus value strongly depends on the choice of the strain range (Table A2-3). A similar behaviour was found by Poilâne et al. [215] for a unidirectional flax fibre reinforced epoxy composite in monotonic tensile test.

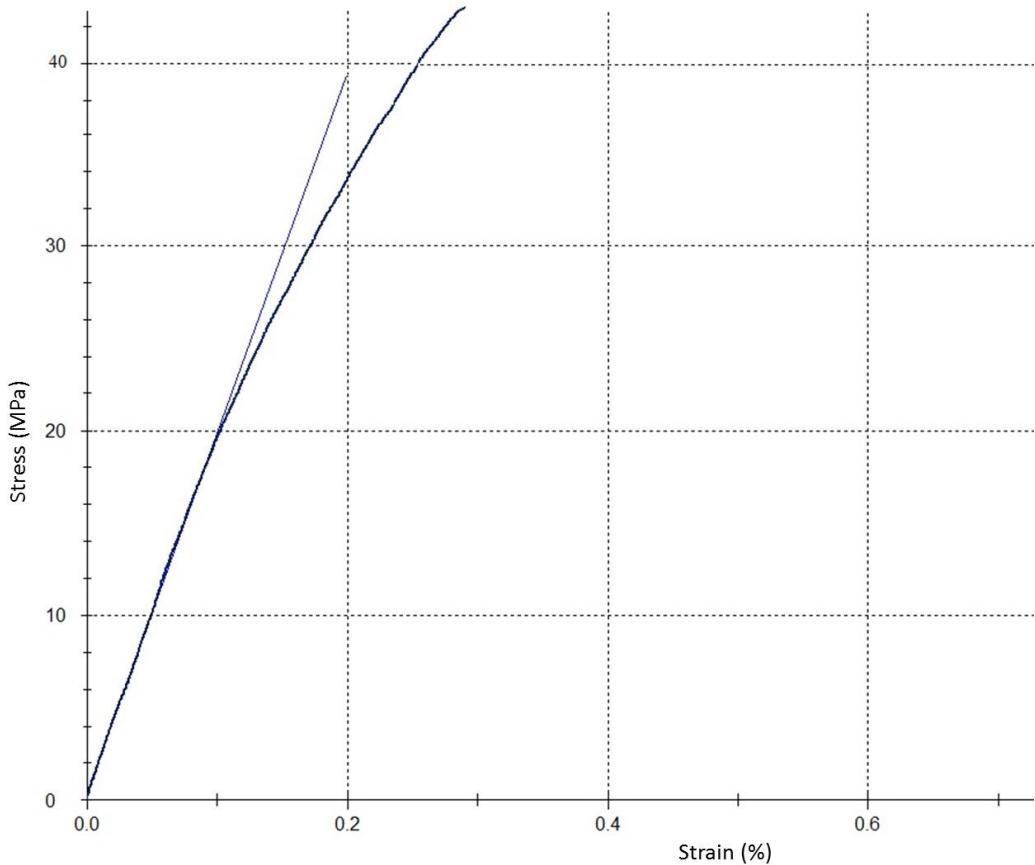


Figure A2-3 Flax fibre composites non-linear behaviour (experimental result).

Table A2-3 Influence of the deformation range on the the modulus calculation of flax FRC.

Deformation range	Modulus (GPa)
0.05% - 0.15%	19.2
0.05% - 0.20%	17.5
0.05% - 0.25%	15.6

The FFRC's static modulus measured at very low strain, i.e. between strain bounds of 0.05% and 0.15% leads to a mean value of 19.2 GPa, which is now in good agreement with that of the dynamic modulus.

Table A2-4 Corrected Static and dynamic modulus of flax and glass FRC compared to the theoretical modulus determined by the *rule-of-mixtures*.

Composites	Layers	Thickness	Fibre content	Modulus (GPa)		
	Units	(mm)	%	Static	Dynamic	Rule of mixtures
Glass FRC	6	1.7 ± 0.1	61.0 ± 0.6	45.0 ± 0.9	45.0 ± 0.9	45.8 ± 0.4
Flax FRC	4	3.1 ± 0.2	32.3 ± 1.5	19.2 ± 0.8	20.3 ± 0.6	20.8 ± 0.8

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Analyse en service de la durabilité à long terme des biocomposites en environnement marin

RESUME : Ce travail a pour objectif d'analyser l'utilisation des fibres de lin en substitution aux fibres de verre dans les composites destinés au secteur du nautisme. Cette substitution nécessite une meilleure compréhension du cycle de vie des composites depuis la sélection des matériaux, incluant le procédé de mise en œuvre et jusqu'à leur vieillissement hydrique, principalement sous conditions réelles en service (exposition à l'eau, à la température et aux sollicitations mécaniques).

Une étude préliminaire a été consacrée à la sélection des matériaux (tissus de fibre de lin et résine polyester) et à la comparaison entre deux procédés de fabrication des composites (infusion sous vide et thermocompression) sur la base de leurs propriétés morphologiques et mécaniques.

Le comportement au vieillissement de composites renforcés de fibres de lin (CRFL) et de composites renforcés de fibres de verre (CRFV) est ensuite étudié. Un ensemble de moyens originaux ont été développés afin de suivre les évolutions de la morphologie (prise en eau, gonflement) et des propriétés mécaniques (statiques et dynamiques). Tout d'abord, le vieillissement hydrothermique des composites à base de fibre de lin et de verre est caractérisé jusqu'à leur saturation en eau. Cette étape est suivie de l'étude de la dessiccation afin de contrôler la réversibilité des propriétés physiques et mécaniques. Parallèlement, une étude particulière de ce travail a été consacrée au traitement des fibres afin de réduire leur hydrophilicité dans le composite. Le couplage hydro-thermo-mécanique est alors analysé en imposant une sollicitation de fluage au biocomposite en immersion. L'application de cette méthodologie révèle l'influence significative des sollicitations couplées. Contrairement à toute attente, la superposition d'une charge au vieillissement hydrothermique ralentit la baisse des propriétés élastiques en comparaison de la somme des effets dues aux vieillissements non-couplés. Enfin un modèle de calcul par éléments finis a été mis au point afin de prédire la diffusion hydrique au sein d'un matériau. Le modèle 2D développé intègre la morphologie réelle du composite et particulièrement l'organisation des fibres de lin dans le composite à plusieurs échelles. Cette modélisation représente la première étape dans la prédiction du comportement évolutif des biocomposites pour des conditions de vieillissement en service.

Mots clés : Durabilité, biocomposites, vieillissement, propriétés mécaniques, modélisation multi-échelles

In situ long-term durability analysis of biocomposites in the marine environment

ABSTRACT : This work aims to address a complete analysis of the use of flax fibres to substitute glass fibres in composite materials designed for nautical applications. This substitution requires a better understanding of the composites life cycle: from materials selection and processing to its hydric ageing, especially under real conditions (exposure to water, temperature and mechanical loadings).

A preliminary study is devoted to the selection of materials (flax fibre fabrics and polyester resin) and to the comparison between two methods for manufacturing composites (vacuum infusion and compression moulding) through their mechanical and the morphological properties.

The ageing behaviour of flax fibre reinforced composites (FFRC) and glass fibre reinforced composites (GFRC) is then studied. A set of original methods have been implemented to monitor the evolving morphology (water uptake, swelling) and mechanical properties (statics and dynamics). First of all, hydrothermal ageing of glass and flax fibre composites is characterized until water saturation. This step is followed by the study of a drying phase in order to verify the reversibility of physical and mechanical properties. In parallel, a particular issue of this work was devoted to reducing the hydrophilicity of flax fibres into composites. The hydrothermo-mechanical coupling behaviour of biocomposites is then studied by imposing a creep solicitation to biocomposites immersed in water. The application of this methodology highlighted the significant influence of the coupled solicitations. Contrary to all expectations, superimposing a load during a hydrothermal ageing slows the loss of the elastic properties in comparison with the sum of the uncoupled ageing effects.

Finally, a finite element model was established in order to predict the hydric diffusion within the composite material. The 2D model integrates the real morphology of composites, and particularly the organisation of the flax fibres in the matrix at different scales. This modelling represents the first step in predicting the evolving behaviour of biocomposites exposed to ageing conditions.

Keywords : Durability, biocomposites, ageing, mechanical properties, multi-scale modelling