Durability of flax fibre/bio-epoxy sustainable composites for structural application

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Kurzfassung

Umweltverträglichkeit und Ökoeffizienz sind wichtige Anforderungen an die neue Materialgeneration. Mit synthetischen Glas-/Kohlenstofffasern verstärkte Polymerverbundwerkstoffe werden in Hochleistungsbauteilen umfassend eingesetzt, sind aber nicht umweltfreundlich. Naturfasern (insbesondere Flachsfasern), die mit biobasierten Polymeren verstärkt sind, gewinnen daher aufgrund ihrer ökologischen Vorteile und guten spezifischen mechanischen Eigenschaften zunehmend an Bedeutung. In jüngster Zeit ist der Einsatz von nachhaltigen Naturfaserverbundwerkstoffen (NFCs) in Strukturbauteilen für die Industrie von großem Interesse, deren Langlebigkeit jedoch bisher nur unzureichend bekannt ist. Die Arbeit untersucht die Alterungseffekte von Feuchtigkeit und Wasser sowie die mechanische Belastbarkeit von Flachsfaserverbundwerkstoffen (FFCs) auf lange Sicht.

Verbundlaminate werden aus Flachsfasern und einem biobasierten Epoxidharz im Harzinjektionsverfahren hergestellt. Es wird festgestellt, dass FFCs gute statisch-mechanische Eigenschaften aufweisen. Die mechanischen Eigenschaften zeigen jedoch eine Empfindlichkeit gegenüber der Wasseraufnahme. Der Verbundmodul und die Faser-Matrix-Grenzflächenbindung nehmen mit der Wasseraufnahme ab, während die Verbundfestigkeit je nach Faseranordnung unterschiedliche Trends bei der Wasseraufnahme aufweist. In einigen Fällen hat die Wasseraufnahme einen positiven Einfluss auf die Verbundfestigkeit. Die Zugfestigkeit von [0°] FFCs in Faserrichtung zeigt eine Abnahme zu Beginn der Wasseraufnahme und einen nachfolgenden Anstieg von bis zu 15% gegenüber der Festigkeit im trockenen Zustand. Die Wasserabsorptionsempfindlichkeit von FFCs wird erfolgreich durch einen in dieser Arbeit vorgeschlagenen Furfurylalkohol-(FA)-Behandlungsansatz verbessert. Durch die verbesserte Faser-Matrix Anbindung und der Bindung zwischen Fasern wird die Feuchtigkeitsaufnahme verringert. Die mechanischen Eigenschaften werden ebenfalls weniger durch Wasseraufnahme beeinträchtigt.

Die Kriechverformung von FFCs wird hervorgehoben. [0°] FFCs weisen eine nennenswerte Kriechverformung bei geringer Belastung auf, die hauptsächlich durch die zeitabhängige Scherverformung der Matrizen (Hemicellulose/Pektin-Matrix in Flachsfasern und der Epoxid-Matrix) verursacht wird. Die Kriechverformung kann durch den in dieser Studie vorgeschlagenen FA-Behandlungsansatz signifikant reduziert werden. Die Wasseraufnahme kann die Zeitstandfestigkeit von FFCs bei hoher Belastung verlängern. Die Dauerfestigkeit für eine hohe Anzahl von Zyklen (1 Million) beträgt für [0°] FFCs ca. 120 MPa (40% der Bruchzugfestigkeit) und für [±45°] FFCs ca. 40 MPa (55% der Bruchzugfestigkeit). Interessanterweise steigt die Steifigkeit von [0°] FFCs über die Ermüdungslebensdauer, was sich an der erhöhten Steigung der Hysterese Schleife mit der Anzahl der Lastzyklen zeigt. Die Versteifungswirkung wird auf die Neuausrichtung der Flachsfasern über die Lebensdauer zurückgeführt.

Abstract

Environmental sustainability and eco-efficiency are important requirements for new generation of materials. Polymer composites reinforced with synthetic glass/carbon fibres are extensively applied in high performance structural components but they are not eco-friendly. Natural fibres (especially flax fibres) reinforced bio-based polymers therefore gain growing attention owing to their inherent environmental benefits and good specific mechanical properties. Recently, the application of sustainable natural fibre composites (NFCs) in structural components is of great interest to industry, however their durability is not well understood to date. The work investigates the moisture/water ageing effects and the mechanical durability of a flax fibre reinforced composites (FFCs) in long term.

Composite laminates are made of flax fibres and a bio-based epoxy via resin transfer moulding process. It is found that FFCs do exhibit good static mechanical properties. However, the mechanical properties show a sensitivity to water absorption. Composites modulus and fibres-matrix interfacial bonding decrease with water absorption, while composite strength shows distinct trends upon water absorption depending on the layout of fibres. In some cases water absorption has a positive effect on the composite strength. Tensile strength of [0°] FFCs in fibre direction demonstrates a decrease in the beginning of the water absorption and a followed increase of up to 15% higher than the strength at dry state. The water absorption sensitivity of FFCs is successfully improved by a furfuryl alcohol (FA) treatment approach proposed in this work. Both moisture absorption rate and retention properties are improved as a consequence of improved fibre-matrix and inter-fibre bonding.

Attention on the creep deformation of FFCs is highlighted. [0°] FFCs display appreciable creep deformation at low stress mainly caused by the time-dependent shear deformation of the matrices (hemicellulose/pectin matrix in flax fibres and the epoxy matrix). The creep deformation can be significant reduced by FA treatment approach proposed in this study. Water absorption

can extend the creep rupture life of FFCs at high stress. The fatigue strength for a high number of cycles (1 million) is approximatively 120 MPa (40% of the ultimate tensile strength) for [0°] FFCs, and is approximately 40 MPa (55% of the ultimate tensile strength) for [±45°] FFCs. Interestingly, the fatigue dynamic modulus of [0°] FFCs increases over the fatigue life, evidenced by the increased slope of the hysteresis loop with the number of load cycles. The stiffening effect is attributed to the realignment of flax fibres over fatigue life.

Contents

List of Abbreviations

Symbol	Description
ATR	Attenuated Total Reflection
AE	Acoustic emission
DA	Diels–Alder
DMTA	Dynamic mechanical thermal analysis
DSC	Differential scanning calorimetry
FA	Furfuryl alcohol
FFCs	Flax fibre reinforced composites
FRPs	Fibre reinforced plastics
FTIR	Fourier transform infrared spectroscopy
GFRPs	Glass fibre reinforced plastics
NFCs	Natural fibre composites
PFA	Polymerized furfuryl alcohol
PFCs	Plant fibre composites
PTSA	p-Toluenesulfonic acid
RH	Relative humidity
SEM	Scanning electron microscope
T_g	Glass transition temperature
TTSP	Time-temperature superposition principle
UD	Unidirectional
UTS	Ultimate tensile strength
VARTM	Vacuum assisted resin transfer moulding

1 Introduction

Fibre reinforced polymer composites (FRPs) are one of the most competitive and important engineering materials in lightweight design because of their excellent specific properties, i.e. high strength-to-weight ratio and stiffness-to-weight ratio. They have been widely used in many industries, e.g. aircrafts, automobiles, wind energy, transportation, sports, etc. However, their extensive usage arises discussions on environmental concerns [1,2]. Conventionally used reinforcing fibres in FRPs are carbon fibres, glass fibres and other synthetic polymeric fibres [3]. These fibres are normally produced from non-renewable resources and the production process consumes extensive amount of energy [4], emitting large quantity of CO_2. Furthermore, disposal of composites made by them is also a concern due to the poor degradability. To reduce the dependence of FRPs industry on the non-renewable resources and to alleviate the environmental impact, applications of environmental-friendly bio-composites have been the subject of intensive research in recent years [5,6].

Bio-composites refer to FRPs that are made of natural fibres and bio-based polymers. Among the available natural fibres for bio-composites, plant fibres are found very promising due to their good specific mechanical properties. E.g. flax fibres have comparable specific strength and even better specific modulus compared to E-glass fibres [7,8]. In addition, plant fibres have other advantages, e.g. low cost, low density, easy handling, non-abrasive nature, etc. compared to glass and carbon fibres [5,7]. Recently, plant fibre composites (PFCs) have already seen applications in automotive, sports, transport vehicles and construction industries [2,9,10]. Several researches also prove the promising static mechanical properties of PFCs [11,12]. However, the expansion of applications of PFCs in structural components are still hindered to date due to several reasons [5,13].

Firstly, a concern lies in the hydrophilia of plant fibres, which brings two problems related to durability of PFCs: The moisture sensitivity of PFCs and

the poor compatibility between hydrophilic plant fibres and hydrophobic polymer materials.

Indeed, plant fibres are cellulosic fibres and have many polar functional groups such as hydroxyl groups. When PFCs are exposed to humid atmosphere or rain, absorbed water molecules in the composites are susceptible to form hydrogen bonds with these polar functional groups and then remain in the composites [13]. The hollow structure of plant fibres further facilitates the absorption of water molecules of bio-composites. Several studies demonstrate that PFCs can achieve a high weight increase of over 10% within few months immersed into water [14,15]. Mechanical properties of PFCs are found sensitive to water absorption. Fibre–matrix interface weakening and plasticization phenomena are reported to be the main damage mechanisms induced by water ageing [16]. Composites modulus is pointed out to decrease significantly [17]. Whereas, positive and negative effects of water absorption on the strength of PFCs are both reported [15,17–19]. Therefore, the mechanical durability of PFCs upon water absorption still of great necessity to be further understood.

The compatibility between plant fibre and matrix can be improved by fibre treatments. Several researchers report that mechanical properties of PFCs are enhanced due to the improved fibre-matrix bonding via fibre treatments [5,20]. Whereas, very few have proved the durability of the claimed improvement under different conditions (e.g. humid, elevated temperature, chemical abundant) that a composite material might encounter in practice. In fact, the suitable fibre treatments that can assure a good improvement of fibre-matrix bonding for long term service has to be tailored specially for given environmental conditions and matrix type. It is therefore beneficial that the researchers can provide sufficient effective fibre treatments in preparation for the possible upcoming expansion of applications of PFCs in structural components. However, it should also be noted that the treatment should not undermine too much the environmental advantage and cost effectiveness of plant fibres.

Secondly, the knowledge on the mechanical behaviour of PFCs under long term loads is insufficient. In structural applications, components are often subjected to various load situations, including cyclic loads (fatigue), long term constant loads (creep), progressive loads and combinations of them. Material properties obtained from standard quasi-static tests like monotonic tensile tests, compression tests, bending tests etc. are not sufficient for engineering design. Properties like stiffness and strength would evolve with time in a unique way compared to conventional FRPs due to the distinct plant fibre structure and fibre architecture. Very recently, mechanical properties of PFCs at long term cyclic loads have just gained attention [21]. Recent few studies focusing on the creep behaviour of PFCs under flexural loads have been performed but couldn't provide a deep understanding on creep behaviour of PFCs. A clear understanding of material response of PFCs under long-term load conditions is therefore of great necessity.

1.1 Objectives

This work therefore studies the durability of a flax fibre reinforced bio-based epoxy composite, aiming to grow the confidence in extended applications of PFCs in structural components.

The specific objectives of this study are to:

- investigate the sensitivity of mechanical properties of FFCs upon water absorption in the short term and in the long term.
- provide an alternative fibre pre-treatment approach to improve the fibre-matrix bonding properties and maintain the improvement with water absorption at long term, a treatment without undermining the benefits of plant fibres too much at the same time.
- gain a better understanding of the mechanical properties of PFCs under long term constant loads and fatigue loads.

1.2 Structure of this work

This work is structured in 7 chapters.

The following chapter 2 provides detailed information on flax fibres properties and the current research progress in investigating the durability of flax fibre composites (FFCs). Chapter 3 introduces the study methods and provides the material properties of the used materials in this study.

The results and discussions on the durability of are mainly introduced in chapter 4 to chapter 6. Chapter 4 reports and analyses the evolution of mechanical properties of FFCs upon water absorption at two severe wet conditions. Chapter 5 presents the development of an alternative fibre pre-treatment and its influence on the mechanical durability of FFCs. Chapter 6 shows the mechanical performance of FFCs under long term constant loads and fatigue cyclic loads. Their unique mechanical response is also analysed.

Chapter 7 summarises the main conclusions and findings of this study and gives suggestions on possible further researches on the durability of FFCs. Partial results of the present work have been published in journal articles [22,23].

2 Theoretical and scientific background

2.1 Flax fibres

2.1.1 General introduction

Flax fibres are a renewable resource. They are cost effective, lightweight, nonabrasive, and mechanically efficient [7,24]. The cultivation of flax was very popular throughout Europe, Asia and North Africa in history. Usage of flax fibres can date back to 5000 BC, when ancient people in Egypt used flax fibres to make clothes and sails [25]. Flax fibres remained the major textile fibres used by mankind until the popularity of cotton fibres and other synthetic fibres increased [26]. In the past few decades, flax fibres have gained new growing interests from both academic and industrial sectors in composites manufacturing due to the increasing concern about environment. Many efforts have been devoted to replacing synthetic glass fibres with flax fibres in order to reduce the environmental impact. Products made of flax fibre composites have occupied certain places in some engineering applications, e.g. automotive parts and construction building materials [7,9].

Flax fibres are extracted from the stem of flax plant (Figure 2-1). A flax stem (1-3 mm in diameter) contains 20–50 flax fibre bundles (technical fibres) having length in the range of 60- 140 cm [27]. Each fibre bundle consists of 10-40 elementary flax fibres (average 33 mm in length and 19 μm in width) that are bonded together by pectin [28].

Extracting flax fibres involves a series of steps [25]. Retting process is normally the first process after harvesting flax plants. It utilizes natural enzymes to soften and separate the fibrous core from the outer layer of the plant. Retted flax straws are then processed through breaking and scutching to separate the fibres from the rest of the plants. A sequence of mechanical operations is involved in these processes. After scutching flax tows are obtained. Tows are processed further through hackles to separate long fibres

from shorter tows and align the fibres at the same time (hackling process). High-quality hackled flax tows can be spun into flax yarns which are long continuous fibre bundles consisting of twisted flax fibres. In composites manufacturing, flax fibres and other plant fibres are normally in the form of yarns due to their short fibre length [29].

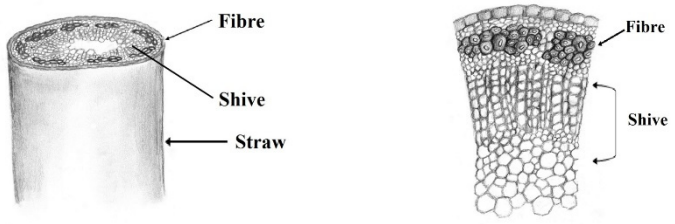


Figure 2-1: Cross section of a flax stem (left) and the relative position of flax fibres (right) (Figures from https://flaxcouncil.ca/growing-flax/chapters/flax-straw-and-fibre/)

The fact that flax fibres are produced by nature and processed by mankind brings unique properties to flax fibres. These properties are of great importance to properties of composites made by them. The following sub-chapters introduce the flax fibre properties in detail.

2.1.2 Structure and chemical composition

Single flax fibres (or elementary flax fibres) are essentially single cells of flax plant. They have irregular shaped (polygonal [30] or spindle-shaped [31]) cross sections ranging 15-30 μm in diameter. Flax fibre has a rather complex hierarchical structure that is characterized with multiple concentric layers of cell walls. Each layer differs in the thickness and constitutive components (Figure 2-2).

The first layer is a thin primary wall (0.1 -0.5 μm) that connects middle lamella and the thicker secondary cell wall (Figure 2-2). It contains 3 – 4 layers of cellulose micro-fibrils dispersedly embedded in a polymer compound that is mainly composed of pectins, hemicellulose and some proteins [32]. The primary wall serves in two contradictory functions: it is rigid enough to withstand the internal and external stress, whereas it has to

be flexible enough to allow cell expansion during plant growth at the same time [33].

The secondary cell wall is a sandwich-like structure constructed by three sub-layers (S1, S2, S3 in Figure 2-2) and accounts for around 80% of the fibre cross section [28]. All sub-layers are in essence micrometre scale composites that cellulose micro-fibrils embed in amorphous matrix mainly composed of hemicellulose and pectins [7]. A cellulose micro-fibril is highly crystallized (degree: 70% [28]) cellulose chains that interact with each other by hydrogen bonds. The diameter of cellulose fibrils is in nanometre scale and varies depending on the number of cellulose chains [33]. In S2 layer (5-10 μm thick), cellulose micro-fibrils are well aligned with a low micro-fibril angle of around 10° (the angle between fibrils and fibre axis) [30]. This makes S2 layer mainly responsible for the fibre strength and fibre axial stiffness. S1 layer (0.5-2 μm thick) and S3 layer (0.5 -1 μm thick) also contain cellulose micro-fibrils but they are more transversely oriented. The function of S1 and S3 is to reduce the deformation of S2 under tension and compression [32].

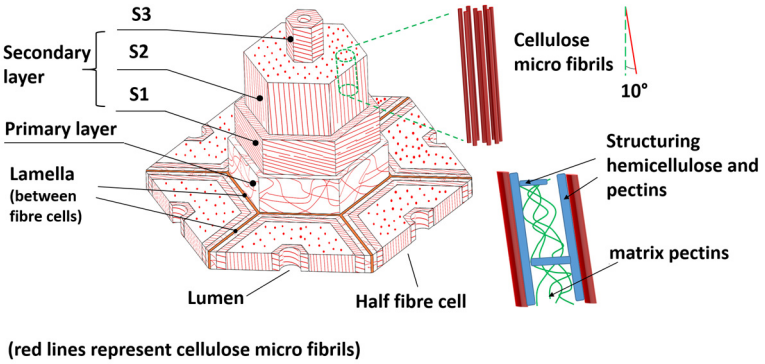


Figure 2-2: Illustration of a flax fibre cell in a bundle and the structure of the flax fibre cell (drawn according to the descriptions of references [28,30,32,34])

Figure 2-3 illustrates the proportions of constituents of flax fibres. It should be noted that the proportions of each constituents can vary with fibre species, growing condition, plant maturity level, locations of fibres in plant,

test methods, etc [30,35]. Cellulose accounts for over 60% of the total weight of flax fibres, followed by other basic constituents i.e. hemicellulose, lignin and pectin. Constructed water and other impurities e.g. wax are also found [13,36]. Cellulose is the stiffest and the strongest organic constituent in the fibre. However, it is a semi-crystalline polysaccharide with a large amount of polar hydroxyl groups, making amorphous regions of cellulose susceptible to absorb water molecules [7,13]. Hemicellulose is branched, fully amorphous and has a significantly lower molecular weight than cellulose. Because of its open structure containing many hydroxyl and acetyl groups, hemicellulose is partly soluble in water and hygroscopic [37]. Pectins are complex polysaccharides. Two types of pectins are present in flax fibres: those that existing in the middle lamella (Figure 2-2) and the primary wall, which form large macromolecules and ensure cohesion between cells, and those in the secondary layers which are part of the matrix holding the cellulose micro-fibrils together [38]. Lignin is a complex three-dimensional aromatic molecule composed of phenyl groups. It is in nature hydrophobic and protects the hydrophilic cellulose and hemicellulose [32].

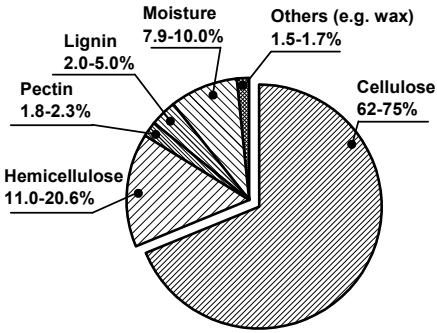


Figure 2-3: Chemical composition of flax fibres (data from Yan et. al [7])

The fact that flax fibres are nanoscale composites reinforced with off-fibre axis aligned micro-fibrils brings flax fibres a unique nonlinear mechanical response, which is reviewed in subchapter 2.1.5. Nature occurring constituents of flax fibres determine the thermal stability and the unique

hydrophilicity of flax fibres, which are introduced in subchapter 2.1.3 and 2.1.4, respectively.

2.1.3 Thermal stability

The thermal stability of fibres is an important parameter determining the maximum processing temperature of fibre plant composites. It is generally admitted that flax fibres, like the majority of plant fibres, have a low thermal stability arising from the low thermal stability of flax fibres constituents [28,39,40]. Degradation of wax on the surfaces of flax fibres occurs at 120 °C. Exposure to a higher temperature of 180 °C would result in the degradation of pectin. At 230 °C, an additional degradation of hemicellulose and part of cellulose takes place [39]. Degradation of flax fibre constituents alters the fibre cell structure change, resulting in degradation in fibre properties. It is therefore suggested that production temperatures higher than 180°C should be avoided for flax fibre composites [39].

2.1.4 Hydrophilic properties

Like other plant fibres, flax fibres are prone to absorb substantial amount of water from the environment via the extensive polar hydroxyl groups of polysaccharides in flax fibres. According to the literature, equilibrium water contents of flax fibres are in the range of 6-15%, depending on the fibre types and the environmental relative humidity (RH) [27,40]. Zhang et al. [41] investigated the water absorption behaviour of flax fibres exposed to different humid environments. They found the equilibrium water content increases approximately linearly with the surrounding RH until it reaches 70% RH, and increases drastically thereafter (Figure 2-4). Stamboulis et al. [42,43] even reported a 24% equilibrium water content and a maximum 42.58% water content for untreated green flax fibres conditioned in 93% RH and 100% RH environment, respectively. Dried flax fibres absorbed water at a relatively fast rate. It is found that flax fibres reach equilibrium water content at ambient temperature within 60 minutes regardless of RH value [44].

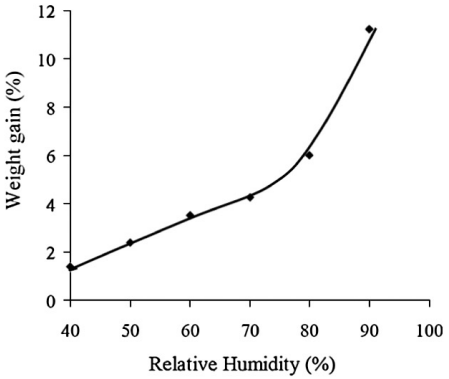


Figure 2-4: Equilibrium water absorption of flax sliver at different RH environments [41].

Hydrophilic nature of flax fibres is indeed considered as a disadvantage for the composites reinforced by them. One major concern is the restricted compatibility between hydrophilic flax fibres and hydrophobic polymer matrix which could lead to poor fibre-matrix interfacial bonding [13,20,45]. Another concern is related to the long-term durability of flax fibres composites considering that flax fibres are sensitive to water absorption. Flax fibre is reported to have a dimensional stability problem due to swelling upon moisture absorption. Pucci et al. [46] revealed that elementary flax fibres' diameter increased by 27±13% after absorbing water. This would induce hydroscopic stresses at the fibre-matrix interface [47]. In addition, water absorption of flax fibres in composites can cause changes in fibre-matrix interfacial bonding properties [41] and degrade composites properties [27]. This is of crucial importance for composites used in advanced industrial sectors e.g. automobile and aircraft industry because they could be exposed to a wide range of temperature and humidity levels. The second concern on durability of flax fibre composites upon water absorption is exactly the motivation of this study.

2.1.5 Tensile properties

Overview

The tensile properties of flax fibres are investigated by several researchers. Table 2-1 lists representative results including the reported corresponding

fibre densities and diameters. To the author's knowledge, the fibre strength and modulus values in Table 2-1 cover the range of values that can be found in literature [7]. For comparison, the properties of commonly used E- glass fibres are also listed in Table 2-1. Note that fibre diameters reported in reference [8] have a large variation and a maximum diameter of 600 μm, possibly indicating that properties of technical flax fibres (bundles composed of fibres bonded by middle lammea) are included. Specific properties of flax fibres calculated using the data in Table 2-1 are further compared with E-glass fibres. As shown in Figure 2-5, specific strength of flax fibres, although lower than that of E-glass fibres, is yet comparable. Specific modulus of flax fibre is however superior to that of E-glass. This is indeed a big advantage of flax fibre composites that boosts interests in their application in structural components.

Table 2-1: Tensile properties of flax fibres and E-glass fibres

	Strength (MPa)	Elastic modulus (GPa)	Failure Strain (%)	Density (g/cm^3)
[1]Flax[8]	345-2000	27.6-103	1.2-2.3	1.4-1.5
[2]Flax[30]	1339±486	58±15	3.27±0.4	1.53
[3]Flax[48]	1381±419	71±25	2.1±0.8	1.53
[4]E-glass[8]	2000-3500	70-76	1.8±4.8	2.5-2.59

Corresponding fibre diameters: [1] 12-600 μm, [2] 17.8±5.8 μm, [3] 15±0.6 μm, [4] <17 μm

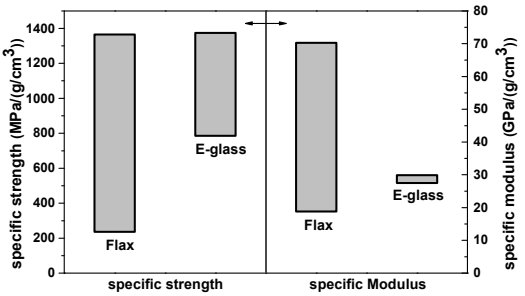


Figure 2-5: Comparison of specific properties of flax fibre and E-glass fibre
(Note: Density of flax fibre and E-glass fibre were 1.465 g/cm^3 and 2.545 g/cm^3, determined as the averaged values reported in literature)

Variation in properties

Despite the promising specific properties of flax fibres, there are large variations in both fibre strength and stiffness. Indeed, the variability in flax fibre properties is often mentioned in literature [49,50]. The properties of flax fibres depend on chemical composition and fibre structure, which are influenced by flax plant types, growing conditions, harvesting time, locations in the flax stem, fibre extracting methods and storage conditions [5,7,35]. In addition, testing methods, irregular fibre cross section [51], gauge length and the defects (e.g. kink bands) generated during mechanical processing [52] also attribute to the variation in fibre properties. However, the variation in flax fibre properties could be overcome if they are produced into flax fibre bundles due to the cooperative effect of a great number of fibres [53]. As a matter of fact, natural fibres are suggested to be spun into continuous yarns (fibre bundles composed of twisted fibres) in high performance natural fibres composites [54,55]. The influence of variation in fibre properties on the composites thus can be alleviated if flax yarns are used.

Tensile response

Similar to the tensile properties of flax fibres which show a large variation, the tensile response of flax fibres also displays a distinctive variation. Both linear and nonlinear response are reported and no consensus has been reached. C. Baley [30] studied the tensile behaviour of flax fibre and found that the fibre stiffness increased with strain due to the reorganization of cellulose fibrils in the fibre axis direction upon tension. Lefeuvre and Gourier et al. [49,56] studied the tensile properties of elementary flax fibres and divided the tensile response into three types of tensile behaviour, with two types exhibiting different nonlinear tensile responses. They emphasized one nonlinear type which displayed highest tensile properties. The type is featured by a nonlinear section at low strains with a decreasing tangent modulus, followed by another region where tangent modulus increases with strain. The nonlinearity was explained as the consequence of complex accommodation phenomena in S2 layer and the realignment of cellulose fibrils in flax fibres. M. Aslan et al. [57] also revealed that flax fibres could

behave either linearly or nonlinearly upon tension. However, it was found that flax fibres displaying linear behaviour had higher strength and modulus. They further suggested a correlation between the nonlinearity and the amount of defects, considering that low-processed green flax fibres exhibit only linear behaviour whilst the highly processed cottonized fibres show both the linear and the nonlinear behaviour.

Interestingly, the nonlinear tensile response of flax fibre is not reported in other researchers' studies. For instance, G. C. Davies et al. [42] reported that single flax fibres behaved linearly until fracture, and found no apparent creep on flax fibres upon constant loads. However, dynamic modulus of flax fibre was found to increase at a rate of 13 GPa/% with strain. N.E. Zafeiropoulos et al. [50] investigated untreated and chemically treated single flax fibres with 30 replicate tests for each sample. The results showed that all fibres exhibited essentially linear elastic behaviour.

Although the reported tensile response of single flax fibres varies from different studies, the variation in tensile behaviour is expected. On the one hand, flax fibre properties vary significantly due to several factors discussed above. On the other hand, single flax fibre tests are rather elaborate (conducted nearly in the limitation range of force and displacement measurement accuracy) and sensitive to manual operations. Test methods, test device, clamping system, loading conditions etc. can cause additional errors. Nevertheless, it is highly possible that the unique cellulose fibrils reinforced multilayer structure would result in a nonlinear response of single flax fibres under tensile loads, which if not apparent, would be pronounced when flax fibres are subjected to long term loads. This is evidenced by C. Baley, who found a stiffness increase in successive loading-unloading fatigue tests on single flax fibres [30]. The unique tensile behaviour would be translated into composites reinforced by flax fibres, which is important to their durability.

Influence of water absorption

Several studies reveal that the mechanical properties of flax fibres are strongly influenced by water absorption or drying process. G.C. Davies and

D. M. Bruce [58] investigated effects of relative humidity (five levels: 30%, 40%, 50%, 60%, 70% RH) on the tensile properties of single flax fibres. They took the effect of damage into account and found that the static modulus of flax fibre decreased with increasing RH at an average rate of 0.44 GPa/%RH. RH was found to have a small effect on tensile strength. However, they admitted that more data was required to draw precise conclusions on fibre strength considering the variation. A. Stamboulis et al. [42] studied tensile strength of two types of single flax fibres (Green and Duralin) at three RHs (30%, 66% 90% RH). Both types of fibres show higher tensile strength at high RHs (66% and 90% RH) compared to fibres at 30% RH. It was explained that absorbed water molecules can penetrate the cellulose network between cellulose fibrils and act as plasticiser, resulting in change in the fibre strength. Similar conclusion on fibre strength is reported by Baley et al. [28], who highlighted that dried single flax fibres (14 h at 105 °C) displayed a significant reduction in average tensile strength (-44%) and failure strain (-39%) compared to as received ones (contain about 7.1% of water content). They pointed out that the onset shear stress when cellulose fibrils slide in fibres decreased significantly after drying. In another study, they also reported that dried flax fibre were found to recover certain tensile strength after reabsorbing water [40].

The influence of water absorption on flax fibres has been also investigated at the scale of flax fibre bundles. A. Mustata et al. [59] compared tensile strength of flax yarns in dry and wet states and showed that wet flax yarns had a higher tensile strength than that of dry yarns, while force-elongation curves of wet yarns demonstrated a higher failure strain and a reduced stiffness than those of dry yarns. B. Masseteau et al. [53] also conducted tensile tests on dry flax yarns (water content: 1.5±0.35%) and wet flax yarns (water content: 7.6±0.3%). Compared to dry flax yarns, wet yarns exhibited a decreased modulus by 20.9%, while the ultimate tensile strength (UTS) increased by 19.9%.

These above-mentioned results suggest that properties of flax fibre composites could vary significantly for different amount of water present in flax fibres. Considering the fast water absorption behaviour of flax fibres, this

could also impose an issue of the mechanical durability of flax fibre composites used in moist or aqueous environments.

2.2 Bio-based polymers

Bio-based polymers are polymers synthesized by raw materials converted (at least partly) from biomass feedstocks. In non-food industries the most widely applied feedstocks are natural plant oils, polysaccharides (mainly cellulose, starch etc.), and proteins [60]. When reinforced with natural fibres, bio-based polymers can be used to produce all-natural green composites that have high environmental benefits. However, bio-based polymers are often considered to have inferior performance compared to their petroleum-based counterparts due to the chemical structure inherent from natural raw materials [6,60,61]. Thanks to the development from polymer industry in recent years, balances are achieved between the performance and the environmental benefits of the final products. More commercial bio-based polymers that have comparable mechanical properties to conventional petroleum-based polymers are available, e.g. high-performance bio-based epoxies derived from plant seed oils. Along with the growing awareness of depletion of fossil resources, the application of bio-based polymers in natural fibre reinforced composites is becoming prevail. The environmental benefit of bio-based polymers can be evaluated by the bio-based content calculated by contemporary carbon input (carbon 14) and that derived from fossil-based input (carbon 12 or 13). The method is given in detail in ASTM D6866 [62].

2.3 Durability of flax fibre sustainable composites

It has been proved by several works that composites reinforced with flax fibres have promising mechanical properties, whereas their extensive application in structural components is still hindered. One major concern rises from the lack of knowledge on the mechanical durability with regard to the long-term performance in service life.

Structural components are often exposed to humid atmosphere, rains or even aqueous environments in practical cases. Natural fibre composites would absorb certain amount of water in these cases in a long run and display a degradation in mechanical properties. Furthermore, structural components are often subjected to various load situations, including cyclic loads (fatigue), long term constant loads (creep), progressive loads and combinations of them. Properties e.g. stiffness and strength could evolve with time due to structural changes and inherent sensitivity of fibre reinforced composites to damage propagations under loads.

2.3.1 Environmental effects

Moisture/water absorption mechanism

The absorption of water molecules by polymeric composites is considered to be driven by several mechanisms: diffusion of water molecules into the bulk polymer matrix, capillary transport of water molecules through the gaps between fibres and matrix and the transport of water molecules through matrix cracks if damages exist during absorption [13,27]. In the case of natural fibre composites, the absorption mechanisms could be different. Unlike the conventional glass/carbon fibres which absorb much less water molecule than the matrix, natural fibres are prone to absorb water. The embedded natural fibres in the matrix can collect water molecules and act as transport paths. Furthermore, the swelling of natural fibres after absorbing water molecules is found being able to induce damages e.g. matrix cracks and fibre-matrix debondings [63–65], creating additional absorption sources.

The absorption process of water molecules by composites could be different depending on the environments (i.e. moist or aqueous) the composites are placed in. This is rarely discussed and emphasized in literature to the author's knowledge. Nevertheless, the main absorption mechanisms of FFCs should be similar in two abovementioned environments.

Moisture/water absorption behaviour

Moisture/water absorption behaviour of polymeric composites is normally analysed by performing gravimetric analysis, which is the measurement of

relatively weight increase of the conditioned specimens. The relative weight uptake of a composite specimen (in percent) during wet conditioning is evaluated by equation (2-1):

$$M_t = \frac{W_t - W_0}{W_0} \times 100 \quad \textbf{(2-1)}$$

Where M_t is the relative weight uptake at time t; W_t is the weight of wet specimen at time t; W_0 is the weight of dry specimen.

Despite the fact that the above mentioned absorption mechanisms are concurrently active, the diffusion laws are found applicable to model the global moisture/water absorption behaviour of polymeric composites [19]. According to diffusion theory, different categories of diffusion behaviour can be distinguished by Equation (2-2) [66]:

$$\frac{M_t}{M_m} = k \cdot t^n \quad \textbf{(2-2)}$$

Where M_m is the weight uptake at saturation state of specimens; k and n are kinetic parameters of diffusion. The exponent n indicates the categories of diffusion behaviour. That is to say, $n = 0.5$ represents a Fick's law; other cases at which $n \neq 0.5$ can be called non-Fickian diffusion. E.g. when n is less than 0.5 the behaviour is pseudo-Fickian, between 0.5 and 1 is defined as anomalous diffusion. For natural fibre reinforced polymer composites, several studies support the state that the moisture/water absorption behaviour of NFCs follows Fickian diffusion behaviour [15,17–19,67].

Fick's laws, in a one-dimensional diffusion case, shows that the water uptake increases linearly with the square root of time, and then gradually slows down until an equilibrium plateau is reached. The point distinguishing linear and nonlinear behavior on the absorption curve is mathematically defined as $0.6 \cdot M_m$. For a rectangular specimen, the linear part of curve is described as:

$$\frac{M_t}{M_m} = \frac{4}{h} \times \sqrt{\frac{Dt}{\pi}} \quad \textbf{(2-3)}$$

Where D is the diffusion coefficient; h is the specimen thickness.

The nonlinear part that has weight uptake higher than $0.6 \cdot C_m$ can be expressed by an approximation equation suggest by Shen and Springer [68]:

$$\frac{M_t}{M_m} = 1 - \exp\left[-7.3\left(\frac{Dt}{\pi}\right)^{0.75}\right] \quad \textbf{(2-4)}$$

Diffusion coefficient calculated by equation (2-4) from experiments might not reflect the true diffusion coefficient if a rectangular specimen is investigated. Therefore, a geometrical correction factor is applied.

$$D_c = D_m\left(1 + \frac{h}{w} + \frac{h}{l}\right)^{-2} \quad \textbf{(2-5)}$$

Where D_c is the corrected diffusion coefficient; D_m is the diffusion coefficient from measured data; l is the specimen length; w is the specimen width.

Influence of water absorption behaviour on mechanical properties

Since the mechanical properties of flax fibres are sensitive to water, the mechanical properties of FFCs are prone to be altered by moisture/water absorption. In many cases, the moisture/water uptake is found to induce a reduction in tensile and flexural properties of FFCs due to plasticization effect and the weakening of fibre-matrix interface [27]. However, the effects of water/moisture ageing on tensile strength and the fibre-matrix interface are controversial.

M. Assarar et al. [17] investigated the water ageing of UD FFCs by immersing specimens in water at room temperature. Water uptake at saturation (20 days) is 13.5%. Absorbed water caused a substantial decrease in tensile modulus and strength. Tensile strength decreased by 13% during the first day of immersion and loses 15% after 20 days. Tensile modulus decreased by about 30% during the first 10 days and by 39% after 20 days. Acoustic emission results revealed that matrix interface weakening was the main damage mechanism caused by water ageing. Similar trends were also found by D. Scida et al. for quasi UD FFCs aged at 90% RH 20°C [19]. Tensile strength declined by 10% and by 12%, respectively at 3 and 38 days, and E-modulus decreased by 33% during the first 3 days and by 55% after 38 days of ageing. Analysis of results showed that the ageing mainly damages the

matrix, which induced the earlier presence of fibre-matrix debonding and fibre breakage at lower loads than without the ageing process. K. Cheour et al. [15] highlighted significant loss of bending modulus of quasi UD FFCs after water ageing, attributing the loss to the damage of interface. The statement of weakened fibre-matrix bonding by water ageing was approved by L. Duigou et al. [69]. Interfacial shear strength was evaluated by debonding the single flax fibres embedded micro droplets of epoxy composites. It was found that the apparent interfacial shear strength decreased with immersion time in water, dropping by over 30% during the first 15 minutes of immersion then stabilizing. Z.N. Azwa et al. [63] pointed out the reason of weakened interface as: when a natural fibre/polymer composite is exposed to moisture, water penetrates and attaches onto hydroxyl groups of fibre, establishing intermolecular hydrogen bonding with fibres and reduces interfacial adhesion of fibre–matrix.

The degradation of tensile strength and fibre-matrix by moisture/water ageing is not always supported in literature. In some cases, an increase in tensile strength is reported. Note that such an increase in tensile strength is rarely reported for glass fibre reinforced plastics (GFRPs), possibly indicating unique water/moisture ageing mechanisms for FFCs. M. Berges et al. [67] conditioned UD FFCs at 70°C and 85% RH, and found the monotonic tensile strength was not degraded, but slightly increased. The slight increase in tensile strength in fibre direction was explained as 'a stronger interfacial fibre-matrix bonding' and 'the increased macromolecules mobility' introduced to the swelling of fibres. A. Moudood et al. [44] investigated water ageing of FFCs with balanced woven flax fabric. Composites with two fibre volume fractions (40% and 55%) showed an increase in tensile strength by 10% and 35%, respectively. The authors also stated that the fibre-matrix interface was improved because the gaps between the fibre and the matrix that appear during manufacturing process could be filled up due to fibre swelling.

The disagreement on the effects of water ageing on fibre-matrix interface can be attributed to many factors that influence the observed results, e.g. fibre types, matrix, porosity levels of specimens, and even manufacturing

methods. Apart from these factors, the water present in flax fibres prior to manufacturing (or infusion process) would also affect the obtained results.

D. Zhang et al. [41] investigated the influence of RH in composite fabrication on the interfacial shear strength and flexural properties of flax/unsaturated polyester composites. The interfacial shear strength of the flax/unsaturated polyester composite started to drop sharply at 70% RH and decreased by more than six-fold at 90% RH. However, an optimum RH level (40% RH) seems to exist to give the highest flexural strength. E. Munoz et al. [18] revealed the effects of water in flax fibres prior to manufacturing UD flax fibre/bio-based epoxy composites by a vacuum infusion process. Although a continuous decreasing trend was observed in term of flexural properties and tensile modulus, an optimum water content (fibres conditioned at 50% RH in prior to infusion process) was found to yield the highest tensile strength in fibre direction. That is to say, below and above that humidity level, the tensile strength of the composites would decrease.

Note that the optimum water content (prior to manufacturing) of flax fibre for composite strength, if existing, would differ and is not defined in most studies. Therefore, the current studies cannot assure a consensus with regard to the moisture/water ageing effects on composites strength, in particular the tensile strength of UD FFCs. Furthermore, current studies often focus on the mechanical properties of FFCs at saturation state, the evolution of mechanical properties during the whole water absorption process however get less attention, but is necessary knowledge for the usage of FFCs.

2.3.2 Fatigue properties

Evaluating the mechanical response of plant fibre composites subjected to cyclic loads is of vital importance to boost the confidence in their mechanical durability as structural components. Until the very recent years the fatigue properties of PFCs have been reported in a handful of publications. FFCs are found to offer better fatigue resistance than hemp fibre composites, and exhibit comparable performance to composites with sisal and jute fibres [21]. However, which plant fibre provides the best fatigue properties cannot

be answered due to the insufficient available data. This subchapter exclusively focuses on the results of fatigue properties of FFCs. Three interesting questions related to the fatigue properties of flax fibre composites will be answered through the review. The questions are:

1. What is the overall fatigue performance of flax fibre composites?
2. How is the fatigue performance compared to that of GFRPs?
3. Do flax fibre composites exhibit unique fatigue behaviour?

Overall fatigue performance of FFCs

To have an overview on the fatigue performance revealed in available publications, the fatigue strength at endurance limit (defined as 1 million cycles in this study) are summarized (Table 2-2). Composites with the most common configurations and fibre textile architectures are included. These studies are conducted on flax fibre reinforced epoxy at 5 Hz and loading ratio of R = 0.1, with the exception that [70] was conducted at a frequency of 10 Hz and the matrix is polyester.

It can be deduced that UD FFCs have the highest absolute fatigue strength at endurance limit due to their high static strength, followed by cross-ply [0°/90°], quasi-isotropic, twill-woven reinforced, [±45°], random-oriented flax mat reinforced, and transverse direction [90°] in a decreasing trend in fatigue endurance. Worth to mention that FE [0°/90°], twill fabric reinforced, and quasi-isotropic FFCs have comparable fatigue longevities and can be therefore interchanged. UD FFCs gained more attention than other configurations, and their fatigue strength for a high number of cycles (1 million) is between 40% -50% of the UTS. This indeed is a good sign of an encouraging property for structural applications in the long run.

Table 2-2: Overview of fatigue endurance of FFCs in literature

Work	Textile architectures / laminate configurations	UTS[1] (MPa)	Fibre volume fraction (%)	Fatigue strength at 10^6 cycles[2]
[70][3]	[0°]	164.3	27.7	(0.45,0.5) UTS
[70][3]	[±45°]	73.7	28.9	0.4 UTS
[71]	[0°/90°]	170±19.6	43.7	0.4 UTS
[71]	[±45°]	79±6.6	42.5	(0.5,0.6) UTS
[72]	Random mat	84	30	0.3 UTS
[72]	Low twist twill	120	40	0.35 UTS
[73]	Twill weave 1[4]	106±2.9	34.3	Ca. 0.4 UTS
[73]	Twill weave 2[4]	105.9±6.6	42.3	Ca. 0.4 UTS
[74]	Quasic isotropic	145.6±7.2	--	(0.5,0,6) UTS
[75]	[90°]	26.1±0.6	43.1	(0.4,0.5) UTS
[75]	[0°]	318±12	43.1	0.4 UTS or lower
[72]	[0°]	249	40	0.45 UTS
[67]	[0°]	311±13.9	45	0.42 UTS

[1] Static ultimate tensile strength (UTS) with or without standard deviation; [2] The most values were not given directly and were estimated via the S-N curves given by the authors; [3]matrix type: polyester, frequency: 10 Hz; [4] two different types of twill fabric whose details can be found in reference [73].

Comparison with GFRPs

FFCs are always compared to GFRPs. As introduced in subchapter 2.3.1, flax fibres (actually all plant fibres) composites cannot outperform glass fibre or carbon fibre composites in term of the static strength in fibre direction. FFCs are also expected to have an inferior fatigue strength in fibre direction than that of GFRPs due to the inferior static strength. However, FFCs do display better performances than GFRPs in some aspects of fatigue properties. Shah et al. [70] carried out tension-tension fatigue tests on UD flax fibre composites and revealed that damage development and fatigue strength degradation rate were slower in the case of FFCs. This was evidenced by the less steep S-N curve of FFCs than that of GFRPs. Similarly, Bensadoun [72] also found a slower fatigue strength degradation rate and a more stable stiffness evolution for composites reinforced with three types of flax fabrics (random mat, twill 2x2, and quasi-UD [0°,90°]) compared to composites with the same layout of glass fibres.

The advantage over GFRPs lies not only in fatigue strength degradation rate, but also could lie in the specific fatigue performance for composites with some fibre layouts. Liang et al. [71] compared fatigue properties of flax fibre composites and glass fibre composites with the two layouts: cross-ply [0°/90°] and angled cross-ply layout [±45°]. The results showed that $[0°/90°]_{3s}$ FFCs had lower but comparable specific fatigue performance than that of $[0°/90°]_{3s}$ GFRPs. $[±45°]_{3s}$ FFCs was found to have comparable absolute fatigue resistance than $[±45°]_{3s}$ GFRPs, while a higher specific fatigue performance at all tested stress levels (40% UTS to 80% UTS). The slower fatigue strength degradation rate over GFRPs was confirmed for both layouts as well.

Unique fatigue behaviour

Evaluating the fatigue endurance/strength is not sufficient to characterize fatigue properties of FFCs, because the fatigue behaviour (e.g. damage mechanisms, strength and stiffness evolutions, etc.) could differ even for composites having the same fatigue life and fatigue strength.

Damage mechanisms of FFCs during cyclic loading were found to be similar to those reported for static loads [21], i.e. matrix cracks, fibre-matrix debondings, fibre pull-outs, delamination, fibre breakages and so on. These mechanisms are also common in glass/carbon fibre reinforced composites. However, the damage evolution process of FFCs are found distinctly different from that of glass/carbon fibre composites.

It is commonly accepted that the stiffness reduction is a good indication of damage development during fatigue loading for the vast majority of fibre-reinforced composite materials. E.g., a typical stiffness reduction curve during fatigue cycling for a cross-ply laminate reinforced with continuous fibres can be divided by three stages, corresponding to different damage accumulating process (Figure 2-6). Interestingly, this three-stage stiffness decay evolution behaviour is found not applicable to UD FFCs. Several studies reveal that dynamic modulus of UD FFCs (matrix are all epoxy) increases progressively until reaching specific values [75–77], as shown in Figure 2-7. Such a unique stiffening effect at fatigue loads is ascribed to the

stiffening effects of flax fibres due to the progressive realignment of cellulose fibrils after each loading cycle. However, the stiffening behaviour of UD FFCs is still not clearly understood. El Sawi et al. [77] revealed that there is a linear relationship between stiffening degree and residual strain. With regard to the relationship between loading stress level and the stiffening degree, current studies give contradictory conclusions. Liang et al. [75] revealed that stiffening degree reduced with increasing loading levels, while El Sawi et al. [77] suggested an opposite trend. Y Ueki. et al. [76], on the other hand, stated that it was difficult to see a common trend with respect to the stress level and the stiffening degree. Nonetheless, more investigations are still required to better understand the unique fatigue behaviour of FFCs e.g. stiffness evolution.

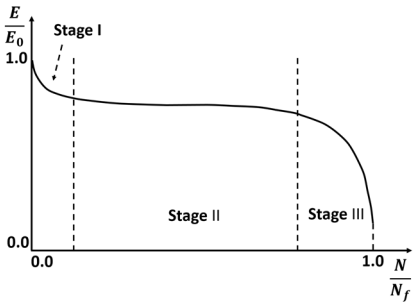


Figure 2-6: Typical stiffness degradation curve for a cross-ply laminate with continuous fibres (redrawn from [78])

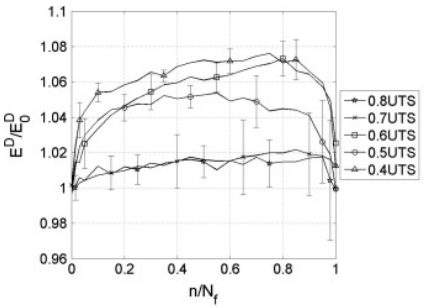


Figure 2-7a: Evolution of the normalized dynamic modulus [75]

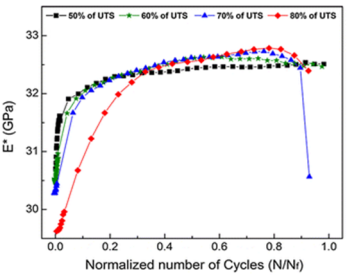


Figure 2-7b: Dynamic elastic modulus E* versus normalized number of cycles [77]

2.3.3 Creep properties

The time-dependent increase in stiffness of UD PFCs in fatigue tests suggests the necessity of investigating creep effects of PFCs for engineering design or analysis. Creep responses e.g. the time-dependent degradation in modulus and strength are among the vital material behaviours that determine the durability of structural components. However, to the author's knowledge, current available data from literature is insufficient for the assessment on creep behaviour of PFCs.

There are few studies focusing on the flexural creep behaviour of PFCs, in which the influence of fibre or matrix treatment and flexural creep deformation under low stress level were analysed. Acha et al. [79] investigated flexural creep response of bi-directional jute fibre reinforced polypropylene composites and found that creep deformation could be directly related to the interfacial properties. Composites with maleic anhydride modified polypropylene have an improved jute fibre-matrix bonding and consequently exhibited low creep deformation. Amiri et al. [80] applied time-temperature superposition principle (TTSP) to evaluate the long-term flexural creep compliance of flax/vinyl ester composites. The flax fibre orientation of the composites was however not mentioned. Smooth master curves of creep compliance were successfully generated using TTSP, although the validity was not proven by practical experiments. Jabbar [81] studied the flexural creep behaviour of woven jute fabric reinforced green epoxy composites and investigated the influence of fibre treatments on the creep behaviour of composites. Treatments that improved the tensile modulus resulted in improvements in flexural creep resistance. Findley's power law model gave satisfactory results in predicting the long-term flexural creep of jute fibre reinforced composites.

In terms of tensile creep behaviour of PFCs, especially in fibre direction, very few reports in literature can be found. Stochioiu et al. [82] reported that a pronounced creep deformation of PFCs was observed even for UD configuration. Plastic deformation was observed by performing creep-

recovery tests. A knowledge gap exists in a clear understanding of creep behaviour of UD PFCs, particularly under tensile loads.

2.4 Flax fibre treatments for the improvement of fibre-matrix bonding

Fibre-matrix interfacial bonding plays an important role in mechanical properties of fibre reinforced composites. Generally, a strong fibre-matrix bonding assures a high load transfer efficiency from matrix to fibres, consequently high mechanical properties. Interfacial bonding occurs by several means of mechanisms: mechanical interlocking, electrostatic bonding, chemical bonding and inter-diffusion bonding [83]. Mechanical interlocking occurs to a greater extent when the fibre surface is rough and increases the interfacial shear strength. Electrostatic bonding happens mainly to metallic interfaces. Chemical bonding occurs when there are chemical groups on the fibre surface and in the matrix that can react to form bonds. Inter-diffusion bonding occurs when atoms and molecules of the fibre and matrix interact at the interface. For fibre reinforced polymer composites, it is possible for multiple types of bonding to occur at the same interface at the same time [84].

Unlike synthetic glass fibres and carbon fibres which have commercially mature fibre sizing technologies to improve the bonding, plant fibres don't have such a well-developed fibre treatment technology up to date to the author's knowledge. Indeed, it is well accepted that interaction between the hydrophilic plant fibres and commonly hydrophobic matrices is limited, which leads to poor interfacial bonding that limits mechanical performance as well as long term properties (e.g. resistance of water ageing) [5]. Many methods are proposed to treat plant fibres in order to improve the fibre-matrix bonding properties. These methods can be divided into two categories: physical approaches and chemical approaches.

Proposed physical methods consist of corona [85,86], plasma [87], ultraviolet (UV) [85], electron radiation and fibre beating [88], which utilize physical energies to alter the fibre surface polarity, surface roughness and fibre structure. Although improvements are reported in different aspects of

mechanical properties, the disadvantages are obvious. E.g., it is difficult to apply radiation to three dimensional surfaces for corona, UV and plasma approach; fibre beating is only applicable to short fibres composites manufacturing. Proposed chemical methods cover a wide range e.g. alkaline, acetylation, silanization, benzoylation, acrylation, acrylonitrile grafting, and treatments with peroxide, fungal, isocyanate, etc. Detailed description on these chemical approaches is not introduced in this study and can be found in a review paper on chemical treatments on plant-based natural fibre reinforced polymer composites [20]. Fibre surface morphology, functional groups on the fibre surfaces and fibre structure are changed by these treatments. Consequently, hydrophilic nature of the fibres is reduced. The mechanical properties and the adhesion between flax and matrix are improved by these chemical approaches.

Nonetheless, most of these chemical treatments utilize synthesized chemical reactants derived from non-renewable resources, thus might comprise the environmental benefits of plant fibre composites. In addition, the durability of the claimed improvement under different conditions (e.g. humidity, high temperature, chemical abundance) has not gained much attention to the author's knowledge. Hence the applicability of these treatment in practical cases cannot be answered. Furthermore, the suitable fibre treatments that can assure a good improvement of fibre-matrix bonding for long term can differ with given environmental conditions and matrix types. Developing alternative effective fibre treatments in preparation for the possible upcoming expansion of applications of PFCs in structural components is beneficial.

3 Materials and methods

3.1 Materials

3.1.1 Flax fibres

A non-crimp unidirectional (UD) flax fabric (Bcomp Ltd., Fribourg, Switzerland) was used in this study. The fabric has a surface weight of 300 ± 5% g/m^2. Fibres that compose the fabric are twisted together into yarns and are stitched with textured polyester (Figure 3-1). The twisted angle of the fibres can reach 10° but varies from fibre to fibre depending on the location in the bundles (Figure 3-1).

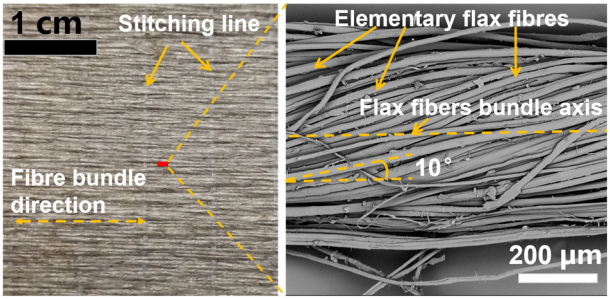


Figure 3-1. UD flax fibre fabric (left) and a SEM picture of an as received flax fibre bundle (right)

3.1.2 Matrix

This work originally chose a bio-based polyurethane system whose polyol is derived from rape seed oil. It has high bio-content (approx. 50 – 70% of polyol according to the supplier) and good moisture resistance. The curing agent (isocyanate) is also reported to treat plant fibres to improve fibre-matrix bonding. However, the manufacturing process was not successful after several attempts because it had a short optimized infusion time (ca. 20 minutes) after being mixed. This requires high pressure infusion which impairs the infusion quality and causes deformation of reinforcements in the mould.

Hence, a two-component green epoxy system (InfuGreen 810/SD 8822, mixing ratio in weight 100:31, from Sicomin, Châteauneuf les Martigues, France) is selected eventually. The resin (InfuGreen 810, Sicomin, Châteauneuf les Martigues, France) is derived from colza and has about 38% of carbon from plant origin. It is among the bio-based resin systems that have the best mechanical properties [61]. The allowed optimized infusion time is 67 minutes (at 30 °C), with a low initial mix viscosity of 120 mPa.s (at 30 °C). Curing cycle (30 °C for 8 h followed by 60 °C for 16 h) is chosen to obtain a high glass transition temperature.

3.2 Composites laminates manufacturing

3.2.1 Vacuum assisted resin transfer moulding

All laminates are manufactured through vacuum assisted resin transfer moulding (VARTM). Figure 3-2 schematically shows the VARTM system used in this study. The release agent that is applied on the inside mould surfaces is Mikon W-64, from Münch CHemie International GmbH, Weinheim, Germany. Fleece strips (1 cm wide) are paced surrounding flax fabrics to achieve an even resin flow. Before each resin transfer process, vacuum and pressure tests are performed to assure the system is compact. After resin transferring process, an excessive 2 bar air pressure is applied on the resource container during the whole curing process to reduce the effects of resin shrinkage and formation of pores as much as possible.

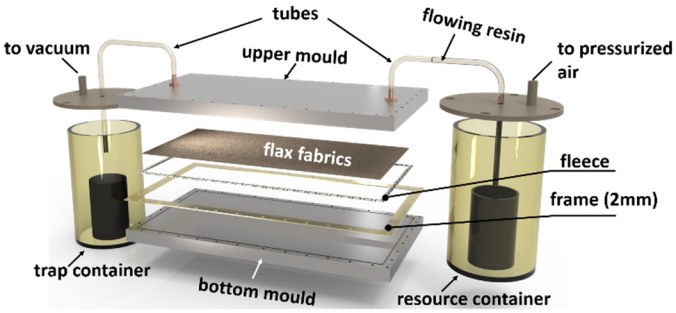


Figure 3-2: Schematic diagram of VARTM system

3.2.2 Stacking sequences of laminates

Laminates with three different layouts of flax fibres are investigated, i.e. $[0°]_4$, $[90°]_4$ and $[\pm45°]_s$. All specimens consist of 4 layers of UD flax fibre fabrics. $[0°]_4$ represent the layout of unidirectional laminates where the loading direction is aligned with the fibre bundle direction (Figure 3-1). Dimensions of tested specimens for different laminate layouts are listed in Table 3-1.

Table 3-1: Symbols and dimensions of tested specimens for different layouts (unit: mm).

	$[0°]_4$	$[90°]_4$	$[\pm45°]_s$
Symbols	UD	Tr	45
Dimensions	250×15×2	175×25×2	240×25×2

3.3 Physical properties of composite laminates

3.3.1 Density

Density of composite laminates is calculated in a simple way by formula 3-1. For each laminate's layout, densities of 6 specimens from 3 laminate plates are calculated. The density of laminate ('dry' state) is determined as 1.281±0.015 g/cm^3 from 18 specimens.

$$\rho_c = \frac{m_{c,dry}}{V_{c,dry}} \quad \textbf{(3-1)}$$

Where ρ_c is the density of flax fibre composite laminates; $m_{c,dry}$ is the weight of specimens at dry state; $V_{c,dry}$ is the correspondent volume of rectangular specimens.

3.3.2 Fibre volume fraction

The fibre volume fraction (40%) was calculated using the following formula:

$$V_f = \frac{\rho_{\mathrm{sf}} * \mathrm{n}}{\rho_f * t_l} \times 100 \quad \textbf{(3-2)}$$

Where ρ_{sf} is the surface density of flax fabric (300 ± 5% g/m^2); n is the layer number of fabric (4 layers); ρ_f is the flax fibre density (1.515g /10^{-6} m^3); t_l is the thickness of laminate. The density of flax fibres is provided by the supplier.

3.4 Mechanical tests

3.4.1 Specimens preparation

All specimens are cut dry (coolant: air) to desired dimensions. The edges of the specimens are carefully polished dry using a four-step process (grit sizes of sand paper: 320, 600, 1000 and 2500) to reduce the influence of edge roughness on mechanical properties. The dry state of specimens is achieved by drying them in a vacuum oven at 40°C for 24 hours and cooled down to room temperature in a desiccator. In most cases specimens from at least three different plates are prepared for each test condition to take the influence of different manufacture batches into consideration.

3.4.2 Monotonic tensile tests

Tests are conducted on a Zwick 100kN tensile testing machine according to ASTM 3039 [89]. A pair of hydraulic wedge grip is equipped on the machine. Specimens are loaded at a fixed crosshead speed of 2 mm/min until fracture. Strain analysed in this study refers to engineering strain and is measured by both the crosshead displacement and a class 0.5 clip-on extensometer. The gauge length of the clip-on extensometer is set as 80mm for [0°], [±45°] specimens, and 50 mm for [90°] specimens.

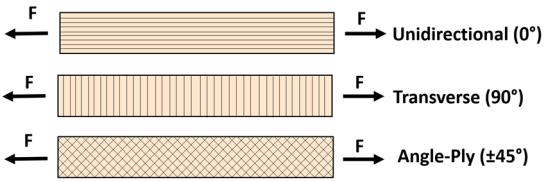


Figure 3-3: Schematic illustration of specimens in monotonic tensile tests

Load introduction

Load introduction to specimens is one primary concern for mechanical testing. A good load introduction should avoid premature failure of specimens at grips ends or in the gripping area. In the preliminary investigations several methods (aluminium tabbed specimens, glass fibre composites tabbed specimens, rubber tabbed specimens, flax fibre

composites tabbed specimens, dumbbell shaped specimens, and stream line shaped specimens) were evaluated to determine a suitable way to introduce load. It was found placing a sand paper (grit size: 320) between specimens and grips was the most effective one. Gripping pressure is also an important factor that would influence load introduction. Applied gripping pressure is 40 bar for UD specimens, while a pressure of 20 bar for [90°] and [±45°] specimens is applied.

3.4.3 Fatigue tests

Fatigue tests are conducted on an Instron 63 kN servo-hydraulic testing system. All fatigue tests are conducted under stress controlled mode. Loads are applied in sinusoidal wave form with a fixed stress ratio of 0.1 ($R = \sigma_{max}/\sigma_{min}$, tension - tension mode). Fatigue properties under five maximum stress levels (120 MPa, 150 MPa, 180 MPa, 210 MPa and 240 MPa) are investigated for UD specimens. For [±45°] specimens, three stress levels (60 MPa, 50 MPa and 40 MPa) are applied. The testing frequency is chosen to be 3 Hz to reduce self-heating effects. Load introduction with sand paper (grit size: 320) is again proved to be most effective after several tries. A gripping pressure of 60 bar is found optimal to avoid slippage without causing premature failures at the same time. For each stress level, specimens are chosen from at least two different laminates to reduce the influence of manufacturing quality.

Fatigue behaviour is investigated by analysing the evolution of dynamic modulus (E), hysteresis loop area (A), maximum and minimum strain (ε_{max} and ε_{min}) over the fatigue life at each test cases. Dynamic modulus is defined as the slope of the line connecting the maximum and minimum stress tips of a hysteresis loop. These parameters are illustrated in Figure 3-4.

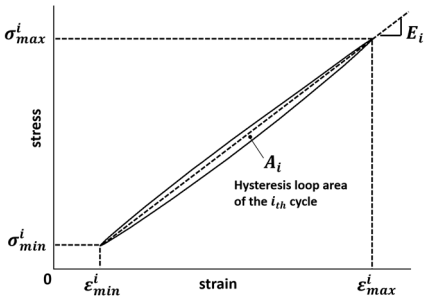


Figure 3-4: Illustration of investigated fatigue behaviour parameters of a i_{th} hysteresis loop

3.4.4 Tensile creep tests

The main features of the creep response of flax fibre composites in fibre direction are investigated at room temperature. All creep tests are conducted on a Zwick 100kN tensile testing machine as with monotonic tensile tests. Short term creep deformation at low tensile stress is analysed via 2 hours of tensile creep tests. For each stress, at least three specimens selected from three laminates are tested for each creep stress level. Strain measurement is the same with the case in monotonic tensile tests. Figure 3-5 depicts the loading sequence and a typical strain response. Specimens are loaded at a rate of 10 mm/min until the set creep stresses were reached. The creep phase then started by holding the load constant for 7200s. Creep rupture behaviour is analysed at high creep stresses. Load is held constant until the rupture of specimens. At least 5 specimens from three different laminates are tested for each creep stress, except that the creep rupture test at 180 MPa is performed on one specimen (4 days – creep run out test).

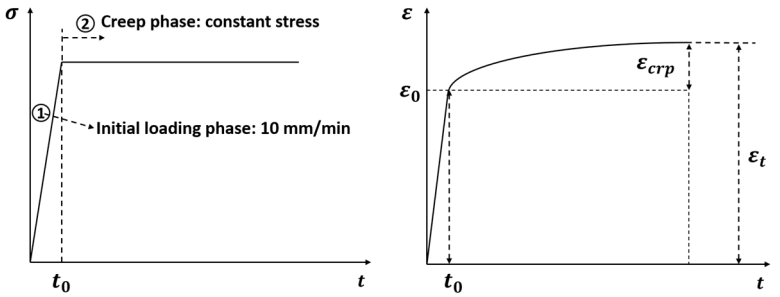


Figure 3-5: Illustration of loading sequence (left) and the typical strain response (right), where ε_{crp} is creep strain; σ is applied creep stress; t is time; t_0 is the time when creep phase starts; ε_t is the overall strain since the specimen is loaded.

To investigate the influence of water absorption on the long-term performance of FFCs, creep rupture tests were also conducted on wet conditioned UD specimens. In addition, the feasibility of a flax fibre pre-treatment (introduced in chapter 6) to reduce the creep of FFCs was verified.

3.5 Moisture/water ageing tests

3.5.1 Specimens preparation

Specimens are cut and polished in the same way with that is used in preparing specimens for mechanical tests. The dry state of specimens is achieved by drying them in a vacuum oven at 40°C for 24 hours and cooled down under vacuum (in vacuum bags). For each test case, at least 5 specimens (in most cases over 6 specimens) from 3 different laminates are tested to reduce the influence of manufacturing.

3.5.2 Water/moisture absorption tests

Water absorption is conducted according to ISO-62 [90]. Water absorption behaviour of specimens is investigated by analysing the weight increase over wet condition time, as has been introduced in chapter 2.3.1. Specimens' weight is measured on a precision balance with a tolerance of ±0.1 mg.

Two wet conditions are used, i.e. distilled water bath and a weathering chamber. The two wet conditions (Table 3-2) represent two common severe

wet conditions in practice. Home-made specimen holders are used to position the specimens, keeping each specimen at a distance of about 1-1.5 cm from each other.

Table 3-2: Wet conditions for water absorption tests

	Description	Symbol
Condition 1	Distilled water bath, 21±2 °C	W
Condition 2	80% relative humidity, 30°C	H

3.6 Control of water absorption during long term tests

It is believed that the dry FFCs specimens absorb certain amount of water and wet FFCs lose water relatively quickly in both cases. To reduce the influence of the change in water content of specimens during long term tests, the following measurements are taken. For dry specimens, the grips of the machine is wrapped with one piece of Teflon film, creating a space between the grips that is separated from the ambient environment. About 25 g desiccant beads is then placed inside the 'chamber' between the grips to keep the 'chamber' as dry as possible during tests. For wet specimens, the pure petroleum jelly (original Vaseline) is used to cover the specimen's surfaces after being taken out of wet conditions. It is found that water conditioned specimens that are covered by pure petroleum jelly lose only 0.4% of water after being placed in ambient environment for 17 hours.

3.7 Detection methods

3.7.1 Acoustic emission detection

Acoustic emission (AE) detection is an established technique to detect damage events within fibre reinforced composites under load. AE signal features e.g. maximum amplitude, accumulated energy, frequency and hits count can be correlated with specific damages (e.g. fibre breakages, fibre-matrix debonding, fibre pull out, etc.) [91]. To analyse damage development inside composites during loading, a Micro II multi-channel acquisition system from MISTRAS Group Inc. is used to record transient AE signals. Two wideband differential (WD) piezoelectric sensors are attached onto the

surface of the specimens with silicon grease as a coupling agent. The distance between the two sensors is 125 mm for UD and [±45°] specimens, while 70 mm for [90°] specimens. For the composites used in this study, AE time parameters are determined prior to tests through standard pencil breakage calibration process. The set-up parameters of AE system are listed in Table 3-3. Pencil lead breakage calibration procedure was performed before each tests to verify the accuracy of AE setup [92].

Table 3-3: Setting parameters of AE system used in this study

Parameter	Value
Sampling rate /MHz	5
Pre-amplification gain /dB	40
Threshold /dB	40
Hit definition time (HDT) /µs	250
Hit lockout time (HLT) /µs	500
Maximum hit duration /ms	100
Peak definition time (PDT) /µs	60

3.7.2 Microscopic observation

Scanning Electron Microscope (SEM) observation is conducted on a Phenom XL desktop SEM (Thermo Fisher Scientific, Phenom-World B.V., Eindhoven, Netherlands). Secondary Electron Detection (SED) is chosen under an acceleration voltage of 10 kV or 5kV for high quality pictures of composites fracture surfaces, while Backscatter electron detector (BSD) mode is used for observing the structure of fibre bundles. All samples are sputtered a thin layer of gold having a thickness of about 6.5 nm before observing.

3.8 Characterization of materials

3.8.1 Hydrophilic properties of flax fibres

The hydrophilic properties of flax fibres are investigated through a gravimetric analysis. Three pieces of flax fabric are cut at random positions of the fibre roll, having altogether a surface area of around 66000 mm^2. The fabric is then placed inside a vacuum oven and heated up to 102°C under vacuum to obtain a complete drying. The heating rate of the oven is around 7°C/min. A precise balance with a precision of 0.1 mg is used to measure the

weight of the fabrics every 10 minutes until no weight loss is observed. Afterwards the fabric is placed in the air and the change of weight is recorded to have an impression of how fast the flax fibres would reabsorb water from air. The weight loss during drying and regained water content are calculated through:

$$C_{drying} \text{ or } C_{reabsorption} = \frac{m_t - m_{dry}}{m_{dry}} \times 100 \quad \textbf{(3-3)}$$

Where m_t is the weight flax fabrics after an arbitrary time t being dried or the time that the fabric reabsorbs water in air; C_{drying} and $C_{reabsorption}$ are the weight loss and regained water content, respectively.

The results show that flax fabric loses water quickly in the first 10 minutes and reached to dry state within 1 hour (Figure 3-6 left). Note that the dry state might not be strictly 'dry' because certain amount of water might be also present in flax fibres. Figure 3-6 (right) shows that the 'dry' flax fibres reabsorbed water from air at a very fast rate. Within 25 minutes flax fibres reabsorb 4% of water. This means a strict control of the time that flax fibres are placed in air during manufacturing is needed to assure good reproducibility of composites.

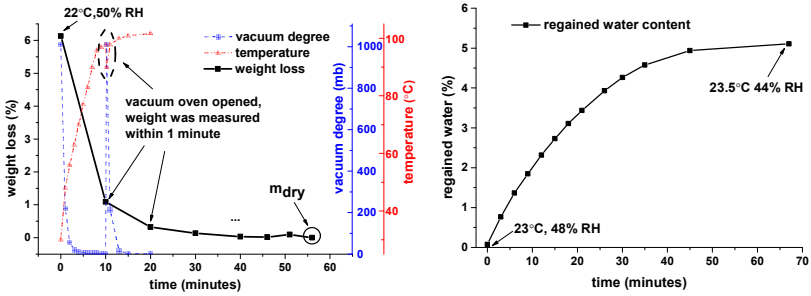


Figure 3-6: Weight loss of flax fibres during drying (left) and the weight increase of dry flax fibres in ambient environment (right)

3.8.2 Tensile properties of flax fibre bundles

As discussed, single flax fibres have a large variation in their tensile properties, making it difficult to draw reliable conclusions. However, the

variation can be reduced in the case of fibre bundles due to a cooperative effect of a great number of single fibres. Physically and mechanically, a continuous flax fibre bundle can be considered as a continuous fibre having a large diameter (200 – 500 μm), providing realistic information on composites properties. Therefore, the influence of drying/water on the tensile properties of flax fibre bundles is investigated. The flax fibre manufacturer suggests to dry the fibres (110°C for 15 minutes) before use to remove the absorbed humidity by fibres at ambient conditions. Same temperature is used in this study to obtain a 'dry' state of flax yarns. It is found that flax fibres dried at 110°C no longer lost weight after 30 minutes and are therefore considered as being in a 'dry' state.

Experimental

Tensile tests are conducted on a Zwick universal tensile testing machine with a load capacity of 10kN. Individual flax fibre bundles (yarns) are extracted randomly from the used flax fabrics. Paper tapes are wrapped at both ends of yarn for load introduction. It should be noted that the cross section area of yarns is not measured for each tested yarn because of the large scatter along with one individual yarn and the irregular shape of the cross section. Instead, the average cross section area was calculated by formula 3-4:

$$S_{yarn} = \frac{\rho_{linear}}{\rho_{fibres}} \quad \textbf{(3-4)}$$

Where S_{yarn} is the average cross section area of yarns; ρ_{linear} is the average linear density of yarns; ρ_{fibres} is the density of flax fibers. The calculated average cross section area of yarns was $6.931 \times 10^{-8}\ m^2$ ($\rho_{linear} = 105\ g/Km$, $\rho_{fibres} = 1515\ Kg/m^3$, data from the manufacturer).

Flax yarns are tested at a gauge length of 50 mm. They undergo different treatments to investigate the influence of drying /water absorption. As shown in Figure 3-7, yarns dried and tested within 2 minutes have low water contents of about 0.5% during tests, while yarns tested after 30 minutes reabsorbed about 3% water from ambient environment. Some yarns are also immersed into a water bath to obtain a higher water content of over 45%. All yarns are loaded at an elongation speed of $\varepsilon = 0.05/\text{min}$ until fracture.

Results of the yarns that broke very close to the clamp ends were discarded. At least 20 valid replicate tests are obtained for each test condition.

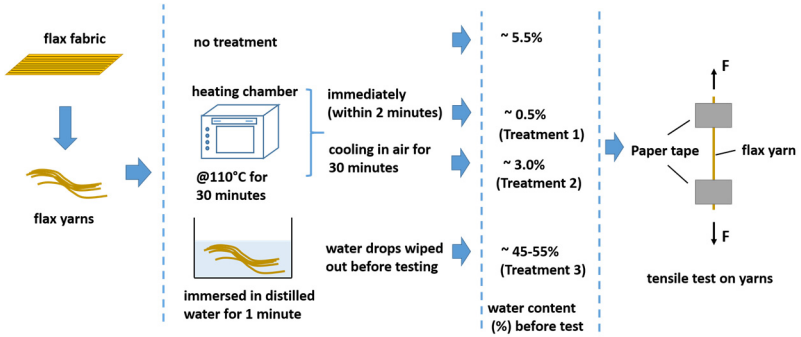


Figure 3-7: Schematic procedure to obtain different water contents

Results and discussion

Figure 3-8 shows representative tensile stress-strain curves of yarns underwent different treatments. A nonlinear region at initial loading stage was observed for all specimens, possibly due to the alignment of fibres in the beginning of loading. The initial nonlinear region is pronounced for yarns with highest water content (45% - 55%), showing much wider nonlinear region compared to yarns with lower water contents (lower than 5.5%). With the increase of load all yarns show an approximately linear response until fracture.

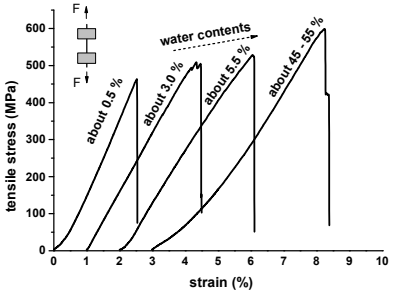


Figure 3-8: Representative tensile stress-strain curves of fibre bundles with different water contents (The three curves on the right have been offset on x-axis by 1% for clarity)

Table 3-4 lists the tensile properties of tested yarns. Drying imposes a significant influence on the tensile properties of flax yarns. Compared to as-received ones, yarns tested immediately after drying show a higher E-modulus (47.03%) and a decrease in tensile strength and failure strain by 10.7% and 39.6%, respectively. Water tends to have a positive effect on tensile strength and failure strain, while decreases the modulus. Dried yarns that reabsorb water for 30 minutes partially recover tensile strength and failure strain, showing mechanical properties between the 'oven dry' ones and as-received ones. Yarns having highest water content exhibit the highest tensile strength and failure strain, while showing the lowest modulus. Similar findings were also reported in studies on the tensile properties of flax yarns [93,94].

Table 3-4: Tensile properties of tested flax yarns

Water content (%)	Strength (MPa)	E-Modulus[1] (GPa)	Strain at maximum stress ε_m(%)
~ 0.5	485.99±74.86	21.09±2.90	2.49±0.23
~ 3	517.23±92.24	16.38±2.93	3.41±0.54
~ 5.5	544.06±81.23	14.35±1.89	4.11±0.42
~ 45-55	598.84±136.37	10.72±0.94	5.60±0.85

[1] E-modulus was calculated as the gradient of regression line between 100 MPa and 200 MPa.

The sensitivity of flax yarn to water could be a clear indication of flax fibre properties upon water absorption because yarn properties depend on intrinsic fibre properties and yarn structure [95]. Indeed, it has been reported that water absorbed single flax fibres exhibit higher tensile strength than dry ones [96], while tensile modulus decrease remarkably with water [58]. Whereas yarns that underwent treatment 3 (water content: 45-55%) could have a better realignment due to a lubricating effect of absorbed water between fibres, it is assumed that the lubricating effects on the other yarns having much lower water contents (below 5.5%) are negligible.

The sensitivity of tensile properties of flax fibre bundles to water would be translated to FFCs in terms of their mechanical properties. This will be introduced in detail in chapter 4.

3.8.3 Thermal properties of matrix

Glass transition temperature is a crucial parameter of composite matrices because it determines the maximum allowed application temperature for composites. There are several different methods to determine the glass transition temperature (T_g) of polymers. The results can differ depending on applied methods. This work utilized two common methods: differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA).

Differential scanning calorimetry (DSC)

DSC tests were conducted on a thermal analysis machine DSC 204 F1 Phoenix (Netzsch, Selb, Germany) according to ASTM E1356-08. Heating and cooling rate were 40 K/min and 20 K/min, respectively. Nitrogen was supplied at a rate of 20.0 ml/min during tests. The average T_g is 85.9 °C (onset) from three replicated tests.

Dynamic mechanical thermal analysis (DMTA)

DMTA tests are carried out on a DMA GABO Explorer 500N (Gabo Qualimeter Testanlagen GmbH, Ahlden, Germany) in tension-tension mode. Rectangular specimens of 50×4×2mm are tested at a fixed frequency of 1 Hz with a static strain of 0.2% and a dynamic strain of 0.1%. Temperature is swept from 20°C to 120°C at a heating rate of 2K/min. The average T_g (three replicated tests) determined by onset temperatures of storage modulus was 76.3°C, while the T_g determined by the peak of loss modulus was 82°C. The difference of identified T_g in different methods is expected.

3.8.4 Tensile tests of the matrix and its tensile properties

Tensile properties are analysed through monotonic tensile tests according to ISO 527-1 [97]. Specimens are fabricated via the same manufacturing method (vacuum assisted resin transfer moulding) for composites and cut into dumbbell-shaped specimens. The dimension of specimens is depicted in Figure 3-9 (1BA type specimen recommended by ISO 527-2 [98]). Loading rate is fixed at 1 mm/min (crosshead rate). Strain is measured by a video extensometer (Zwick/Roell VIDEO EXTENSOMETER ME 46) with two marks

attached on the specimens' surface at a distance of around 30 mm. E-modulus was determined by the gradient of regression line on a stress-strain curve between two strain points at 0.05% and 0.25%.

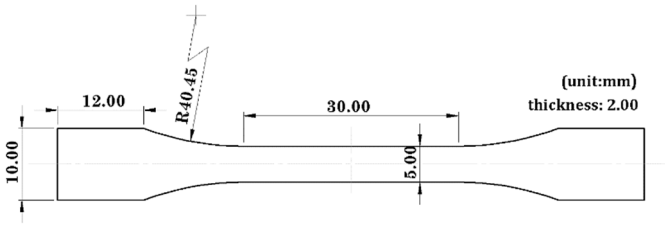


Figure 3-9: Dimension of matrix tensile specimens

Tensile properties of the matrix are summarized in Table 3-5. The matrix used in this study is among the currently available bio-based resin systems that have the best mechanical properties [61], which are also comparable to its petroleum-based counterparts.

Table 3-5: Tensile properties of the matrix[1]

E-modulus (GPa)	Maximum Strength (MPa)	Nominal strain[2] at failure ε_b (%)	Strain at maximum stress ε_m(%)
3.11±0.15	79.64±1.38	6.12±0.39	4.57±0.17

[1] Number of replicates: 8; [2] Nominal strain was calculated through method B in ISO 527-1 [97]

3.9 Defined manufacturing approach to reduce the variation

Variation in mechanical performance of laminates from different manufactured batches is expected for flax fibre composites. However, the variation should be reduced as much as possible to assure a good reproducibility. Considering the sensitivity of flax fibres properties on water absorption, a well-defined manufacturing approach that control the water contents of flax fibres during manufacturing is required.

3.9.1 Influence of fibre drying and fibre storage conditions

Since flax fibres are sensitive to water absorption, water present in the flax fibres prior to manufacturing plays an important role in the mechanical

properties of composites. As introduced in chapter 2, the water content of flax fibres varies a lot depending on the storage conditions, e.g. temperature and humidity. Composite laminates manufactured on a dry day and a wet day can exhibit a noticeable difference in mechanical performance even though a strict manufacturing procedure is followed. In addition, pre-drying of fibres and how long fibres are cooled down before resin transferring process also impose a substantial influence on the reproducibility.

To investigate the above mentioned two factors, two unidirectional laminates were manufactured on a 'wet' day and a 'dry' day, respectively. The corresponding fibre storage conditions and the tested tensile properties in fibres direction are listed in Table 3-6. Both laminates are manufactured following the same VARTM procedures, except that half of the fibres of laminate 2 are dried at 102°C for 1 hour in prior to manufacturing to investigate the influence of heating of flax fibres. Fabric are placed in the mould immediately. Closing mould takes around 20 minutes. Specimen preparation procedure and tensile test conditions are also the same.

Table 3-6: Tensile properties of unidirectional specimens manufactured at different fibre storage conditions (n=5)

Storage conditions[1]	Strength (MPa)	Modulus[1] (GPa)	Strain at maximum stress ε_m(%)
L1: 24°C, 60% RH	325.04±4.44	20.94±0.71	2.14±0.07
L2: 23°C, 32% RH	319.76±7.78	21.92±0.18	2.00±0.07
L2: 102°C, 1 hour	309.20±4.89	23.79±0.28	1.77±0.04

[1]L1 and L2 denote laminate 1 and laminate 2, respectively

The results demonstrate that fibre storage conditions and fibre drying have a noticeable influence on the tensile properties in fibre direction. The laminate with fibres stored at a dry condition tends to have a lower strength and higher E-modulus compared to that with fibres stored at wet conditions. Pre-drying of fibres introduces a more significant influence in tensile properties compared to specimens with as–received flax fibres. A remarkable increase in modulus and a decrease in strength and failure strain is found. Note that the change in tensile properties of UD composites is a clear indication of fibre properties, which is exactly the same with what the

author has observed for flax yarn tensile properties (Table 3.1). Therefore, the possible variations in tensile properties caused by manufacturing approach, fibre storage conditions and commonly adopted fibre pre-drying approach have to be highlighted.

3.9.2 Defined VARTM manufacturing approach

Although pre-drying of flax fibres is often recommended to reduce the influence of water in fibres, yet dried fibres still have the chance to absorb water fast from air because mould closing might take from 10 minutes to even 1 hour (normally caused by unexpected external factors) in practical cases. To address this issue, a VARTM manufacturing approach which involves pre-drying of fibres in the mould is defined to reduce the influence of water absorption. The temperature and pressure cycle during the whole manufacturing approach is depicted in Figure 3-10. Through this approach the fibres are considered as perfectly 'dry'.

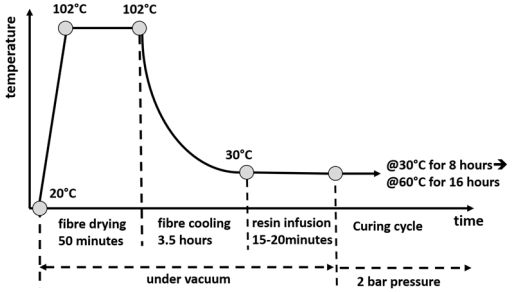


Figure 3-10: Heating and pressure cycles in the defined VARTM approach

Table 3-7 summarizes tensile properties of specimens from 4 separate laminates manufactured by the defined approach. A good reproducibility is obtained. The results show that the pre-drying procedure reduces the influence of storage conditions on composites properties.

Table 3-7: Tensile properties of unidirectional laminates using the defined approach

Laminate number[1]	Strength (MPa)	Modulus (GPa)	Strain at maximum stress ε_m(%)	Number of replicates
1	296.08±4.92	24.09±0.29	1.62±0.02	5
2	303.90±2.69	24.69±0.19	1.61±0.02	5
3	299.90±5.96	23.86±0.59	1.68±0.02	3
4	298.95±12.5	24.30±0.71	1.63±0.03	3

[1]Number are only used to distinguish the investigated laminates

3.10 Summary

This chapter provides details on the experimental setup in this study. In addition, the influence of water on the fibre bundle tensile properties and the influence of drying and fibre storage conditions on tensile properties of 0 ° FFCs are investigated.

The results reveal that flax fibre bundle strength increases with increasing water content while fibre modulus decreases with water content. Drying and storage conditions have a considerable influence on the tensile properties of composites. Hence, a standard manufacturing approach (involving fibre drying) is set up for the investigations in this study.

4 Moisture/water ageing effects

4.1 Water absorption behaviour

Figure 4-1 shows the percentage of water uptake of the composite specimens over the conditioning time. As would be expected, FFCs gain considerable amount of water in wet conditions. Specimens conditioned in the distilled water bath have a weight increase of 9-10% at equilibrium state, while specimens that are conditioned in humid environments absorb about 5.2-5.5% of water. A small discrepancy between the equilibrium water contents of different types of specimens is noticed, which could be caused by the deviation in manufacturing quality and the difference in the residual stress state of the specimens having different fibre orientations. All specimens display a water absorption behaviour characterized by a rapid weight increase in the initial stage with a decreasing rate, followed by a relatively steady state untill the equilibrium state.

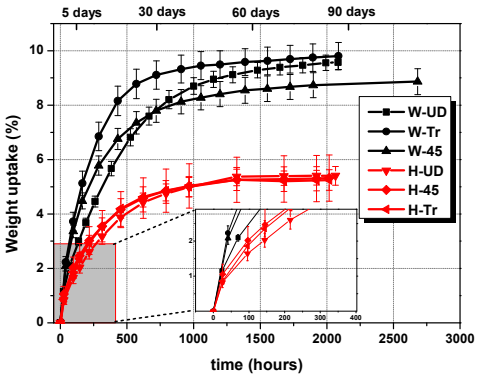


Figure 4-1: Weight uptake of composites specimens versus conditioning time

Swelling of composites after water absorption

Swelling of composites is also investigated since natural fibres tend to swell significantly upon water absorption. For each test case at least 2 specimens (in most cases three) are measured by a vernier calliper (precision: 0.01 mm)

before and after wet conditioning in terms of their thicknesses and widths at three marked locations. Note that the ultimate measurement accuracy is ±0.02 mm in the worst cases considering the operation error.

The averaged changes in specimens' thicknesses and widths are listed in Table 4.1. A pronounced change in specimens' dimension after conditioning is observed. Water conditioned specimens have an increase in thickness of about 6-9%. The swelling of natural fibre composites after water absorption is also reported by R. Masoodi et al [65]. Plain weaved jute fibre reinforced bio-based epoxy composites (40% of jute fibres) swelled by 22% in thickness direction. Higher water content tended to induce more severe swelling. Water conditioned specimens swell more than those in humid conditions, coincident with the higher water content for distilled water aged specimens.

The swelling of composites is anisotropic and depends on the fibre layouts. E.g., the pronounced increase in width is only observed for [0°] specimens, while [90°] specimens and [±45°] specimens showed negligible and marginal increase in width, respectively. Indeed, the dimensional change in fibre direction is negligible possibly due to the high stiffness of flax fibres, while swelling perpendicular to fibre length direction has less constraint, thus a pronounced dimensional change is observed. In addition, the twisted yarn structure also favour better swelling in the radial direction of a bundle than in bundle axis direction. A roughly measured length change by a ruler (precision: 1 mm) on specimens further evidenced this hypothesis. [90°] specimens' length is found to increase by about 5 mm and 3 mm, respectively after water ageing and humid ageing. On the contrary, [0°] and [±45°] specimens' length is found not changed.

Table 4.1: Increase in dimensions (unit:%) of wet conditioned specimens at equilibrium state

Specimens	Distilled water bath		Humid	
	Thickness	Width	Thickness	Width
[0°]	6.7	3.5	2.9	2.1
[90°]	5.7	0.0 (-0.03)	2.8	0.0 (0.01)
[±45°]	8.4	0.2	4.5	0.3

Fitting water absorption by Fickian's diffusion law

The absorption categories are firstly determined using Equation (2-2). Log (M_t/M_m) is plotted against log (time) in Figure 4-2. Linear parts in the initial stage are observed for all test cases. The linear slope, which is n in Equation 2-2, is analysed. The results indicate that the diffusion behaviour does not strictly follow Fickian's diffusion, because in most cases n is not equal to 0.5. This is in agreement with other studies' findings. E.g. D. Scida et al. [19] found that the quasi UD flax fibre epoxy composites conditioned at 90% RH/20 °C and 90% RH/40 °C had a n value of 0.59 and 0.55, respectively. The fact that water absorption does not strictly follow Fickian's diffusion law could be ascribed to many factors: superposition effects of absorption behaviour of matrix and flax fibres, absorption through specimens' edges and the possible change in absorption mechanisms caused by absorption-induced volume swelling or damages.

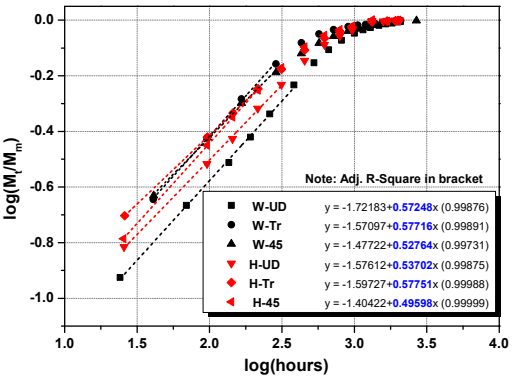


Figure 4-2: Diffusion case fitting plot for conditioned composites specimens

It is worth to mention that the n value is often not analysed by several authors. They draw the conclusion that water absorption of FFCs follows Fickian's diffusion by observing the fair fitting of experimental results by Fickian's law, which is inappropriate in the strict sense of the term. Nonetheless, the calculated n was close to 0.5, indicating that the water absorption of FFCs is close to Fickian's diffusion behaviour. In this regard, the second Fickian's diffusion law is also used to fit the water absorption of

FFCs. Figure 4-3 showed that Fickian's diffusion law is able to characterize the absorption curve with fair accuracy. The used diffusion parameters are listed in Table 4-2. Discrepancy between diffusion coefficients of composites at both wet conditions are small, possibly because that the diffusion coefficient is a material property that is relatively independent of exposure moisture levels [99]. The obtained diffusion coefficients are in the same order of magnitude that have been reported by other authors, and are actually among the lowest values [27].

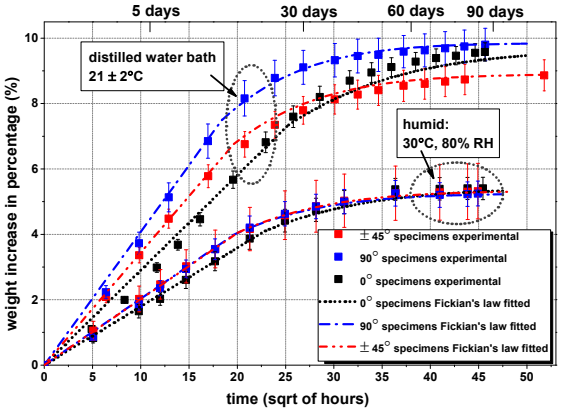


Figure 4-3: Experimental and Fickian's law fitted weight uptake curves of composites in wet conditions

Table 4.2: Diffusion parameters used for fitting experimental results in Figure 4-3

Specimens	Distilled water bath			Humid		
	D_m*	D_c*	M_m**	D_m	D_c	M_m
[0°]	1.98	1.52	9.65	2.40	1.84	5.41
[90°]	3.73	3.13	9.85	3.27	2.74	5.25
[±45°]	3.26	2.76	8.90	3.13	2.65	5.33

*unit: 10^{-7} mm2/s; **unit: %

The amount of absorbed water is useful but may not be an infallible indication of the magnitude of the change in mechanical properties. Therefore, the retention of mechanical properties of FFCs during water absorption process is investigated in detail in the next subchapter.

4.2 Influence of water absorption on mechanical properties

4.2.1 Matrix

Mechanical behaviour of FFCs is affected by the matrix properties. Hence, the change in matrix properties caused by water absorption would have an influence on the retention properties of FFCs upon water absorption. In this regard, the influence of water absorption on the mechanical properties of the matrix is investigated. Tensile specimens of the matrix are conditioned in distilled water bath and humid condition (30°C, 80% RH) like the composite specimens. Their tensile properties are analysed. Note that the equilibrium water contents of tensile specimens are not measured but are estimated due to the slow diffusion especially at final stages. In a preliminary investigation, the measured equilibrium water content of the matrix in distilled water bath is around 2.65% (by extrapolating water absorption curve at final investigation stage). Similarly, the equilibrium water content of the matrix in humid condition is estimated to be around 1.62%.

Figure 4-4 displays the representative tensile stress-strain curves of the matrix at dry and wet states. All specimens showed typical yield phenomena in which the elongation increase continuously after yield point with a decreasing stress. The tensile properties of the matrix at dry state are 79.64±1.38 MPa, 3.11±0.15 GPa and 6.12±0.39%, respectively in terms of their maximum tensile stress, E-modulus, and nominal fracture strain. Clearly, tensile properties of the matrix are severely changed by water absorption.

Figure 4-5 shows the evolution of the tensile properties of matrix with regard to the water contents of the matrix. The maximum tensile strength and the modulus degrade continuously with increasing water content. Specimens conditioned in water bath (94 days) and humid conditions (86 days) show a degradation of 28.7% and 19.2% in tensile strength on average, respectively. As for the modulus, an averaged deterioration of 9.3% and 7.7% is observed, respectively. However, the ductility increases with water content as expected, due to the plasticization effect caused by absorbed

water molecules. The considerable deterioration in tensile strength and modulus with water absorption is in agreement with the findings for conventional epoxy matrices in composites manufacturing [100–102]. The reasons of deterioration in tensile strength are explained by the plasticization effect [101,102] and the reduced intersegmental attractions when preferential hydrogen bonding to water occurs [100]. Mechanisms e.g. leaching of additives, polymer relaxation, swelling-induced micro cracking etc. are also reported [101].

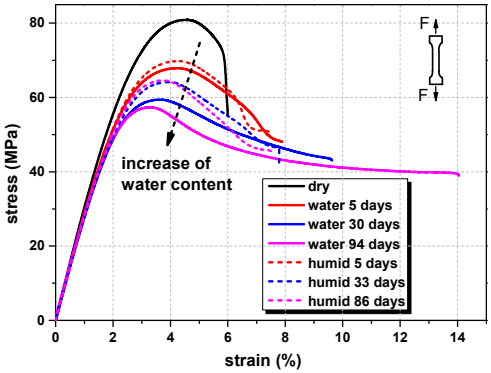


Figure 4-4: Representative tensile stress-strain curves of the neat matrix at different conditions

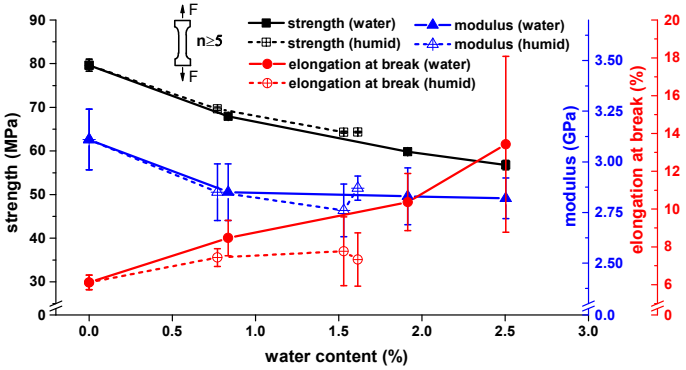


Figure 4-5: Tensile properties of the matrix plotted against the water contents (refer to averaged water contents of specimens which were conditioned for different times, shown in Figure 4-3)

4.2.2 Transverse [90°] laminates

Transverse properties of composites are the properties perpendicular to the fibre direction of the composites. They are directly related to the matrix properties and fibre-matrix bonding properties. Generally, a reduced fibre-matrix bonding would result in a decrease in the transverse strength [103,104]. A unidirectional laminate loaded perpendicular ([90°]) to the fibre direction can be used to investigate the transverse properties of composites.

Figure 4-6 compares representative tensile stress-strain curves of dry and wet conditioned [90°] specimens. Specimens at dry state exhibit the highest strength and modulus (29.36±1.42 MPa and 4.25±0.14 GPa, respectively). They show linear stress-strain relationship till the vicinity of the fracture, followed by a narrow region where a pronounced stiffness decrease is observed. Wet conditioned ones tend to have narrower linear regions possibly due to the plasticization effect and the change in fibre-matrix bonding properties. Furthermore, the transverse strength and modulus are adversely changed by the water absorption.

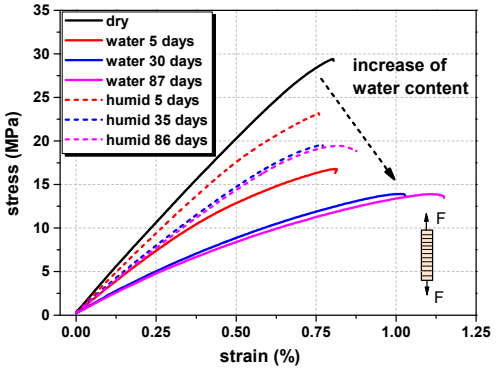


Figure 4-6: Representative tensile stress-strain curves of [90°] specimens at different conditions (Note: The trend line of the water content in this figure has an exception. Specimens conditioned in water for 5 days have a slightly lower averaged water content than that of specimens conditioned at humid for 35 days)

Figure 4-7 illustrates the transverse properties of specimens with different water contents after being wet conditioned for different times. Similar to the change of matrix properties, the transverse strength and modulus decrease continuously with the increase of water content at both wet conditions. Specimens conditioned in water bath (87 days) and humid conditions (86 days) show a reduction of 52.8% and 32.3% in the tensile strength on average, respectively. Correspondently, the decrease in modulus is 58.1% and 28.9% on average. The fracture strain however displays a distinct trend with water content. Fracture strain does not change significantly for specimens having a water content lower than 5%, but increases considerably thereafter. This could be ascribed to two competing effects: an increasing trend caused by plasticization and a possible decreasing trend due to the change in fibre-matrix bonding properties, which is analysed further in the following paragraphs.

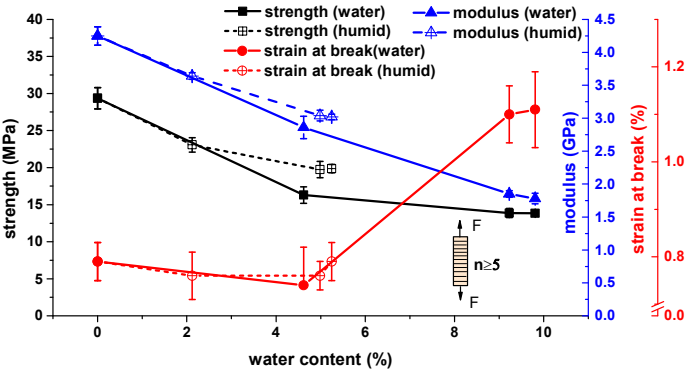


Figure 4-7: Tensile properties of [90°] specimens plotted over the water content (refer to averaged water contents of specimens which were conditioned for different times, shown in Figure 4-5)

As discussed above, the transverse tensile strength of composites is a good indication of fibre-matrix bonding properties but it also depends on the strength of the matrix. To evaluate the change in fibre-matrix bonding properties, two main assumptions are made. Firstly, it is assumed that any change in matrix strength or fibre-matrix bonding strength would result in the same proportion of change in the transverse strength. Secondly, for a

conditioned composite specimen, the ratio between the water contents of matrix and flax fibres at any conditioning time are assumed to be constant up to the equilibrium state. Based on the two assumptions, the matrix strength and the transverse strength are then normalized to the values at dry states and plotted against the correspondent water contents that are normalized to the values at equilibrium states. As shown in Figure 4-8, the degradation in transverse strength at a given water content is always more severe than the degradation of matrix strength for both wet conditions, indicating that the fibre-matrix bonding strength is also degraded and played an important role in the reduction of transverse strength. Based on the assumptions, it can be also roughly deduced that the degradation of fibre-matrix bonding is rapid in the first stage and then reach a relatively stabilized state.

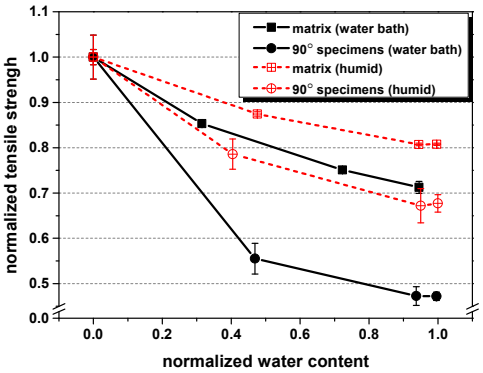


Figure 4-8: Normalized transverse strength and matrix tensile strength over their respective normalized water contents

Fracture morphology (SEM observations)

On the whole, the fracture morphology of [90°] specimens at both dry and wet conditions display similar failure modes, e.g. fibre fractures, debondings of single fibres, sub fibre bundles and whole fibre bundles etc. The fracture surfaces are to some extent chaotic due to the large variability of fibre properties (diameters, defects, etc.), misalignment of fibres in a bundle (Figure 3-1), etc. However, distinctions are found in the presence of splitted

fibres for dry and wet specimens. As shown in Figure 4-9, flax fibres that show micro fibrils and peeling of fibre layers are often found on the fracture surfaces of dry specimens, indicating good fibre-matrix or inter-fibre bonding properties. For the wet ones on the other hand, the vast majority of flax fibres display smooth surfaces with no indication of collapse of hierarchal fibre structure and less peelings of fibre layers, revealing a weakened fibre-matrix interface or inter fibre bonding properties compared to the dry ones.

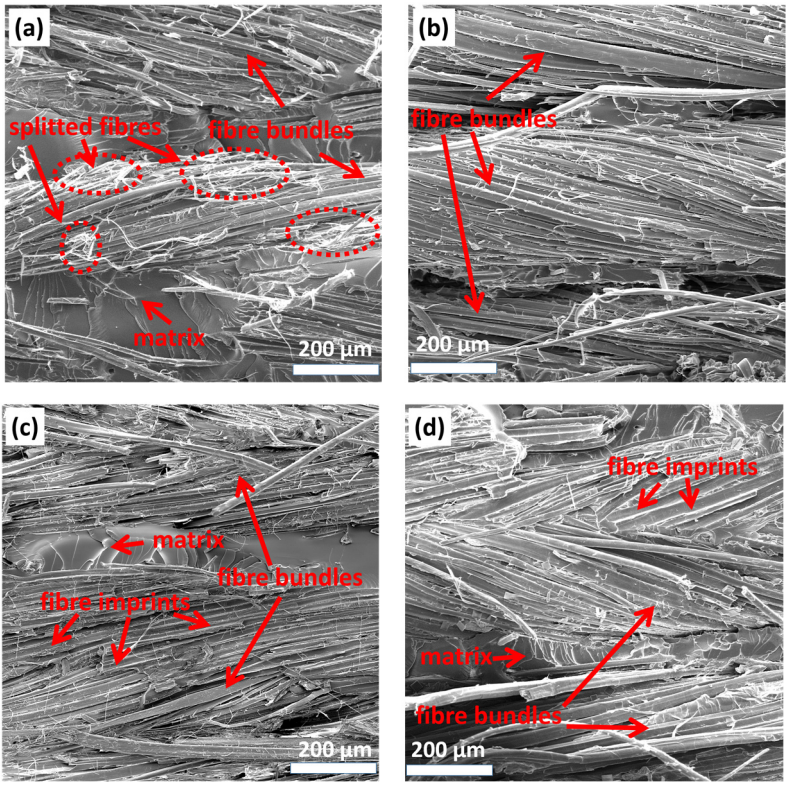


Figure 4-9: Fracture morphology of 90° specimens at both dry and wet conditions (a – dry state; b – in water bath for 5 days; c – in humid for 35 days; d – in humid for 86 days)

4.2.3 Angle ply [±45°] laminates

Angle ply that has fibre orientation of [±45°] is an important fundamental layout configuration of fibre reinforced polymers. It is ideal for carrying shear loads but is also extensively used in multidirectional laminates to control the stress concentrations of laminates [105]. E.g. the popular quasi-isotropic laminate contains 50% of [±45°] plies, as much as [0°] and [90°] plies together. For flax fibre reinforced composites, there would also be cases in which [±45°] plies reinforced with flax fibres are used to build up composites carrying tensile or compressive loads. Hence, the intrinsic mechanical properties of [±45°] plies, together with their mechanical durability is of interest. This subchapter analyses tensile properties of [±45°] flax fibre composites and the influence of water absorption on the tensile properties. In addition, tensile tests on [±45°] laminates can reveal the in-plane shear response of fibre reinforced composites [106], thus could give indications on the influence of water absorption on fibre-matrix bonding properties.

Figure 4-10 displays representative tensile stress-strain curves of [±45°] specimens at dry and wet states. Tensile behaviour was significantly changed by the absorption of water. Dry specimens break at a relatively small elongation of around 2.7% and show no phenomena of stiffness increase during tension. In fact, the stiffness drops drastically after attainment of the maximum tensile stress until fracture. On the contrary, wet conditioned specimens resist several times higher deformation before facture than the dry ones do, exhibiting a ductile tensile behaviour. Furthermore, a pronounced stiffness increase during tension is observed for all wet specimens. Indeed, the stiffness evolution of [±45°] laminates under tensile loads involves two main competing effects: increasing stiffness due to fibre rotation in the load direction and decreasing stiffness due to the shearing of the matrix and damages [107]. Apparently, the stiffness increase observed for wet specimens indicates a much more significant fibre rotation effect after water absorption. This could be ascribed to an increased ductility of the matrix and a reduced fibre modulus, as well as a weakened fibre-matrix bonding that favours fibre rotation.

Figure 4-11 shows the tensile properties of [±45°] specimens at dry and wet states. Plasticization effect after absorption is pronounced. The tensile modulus decreases with water content, while the strain at break exhibits an increasing trend. The maximum tensile stress decreases continuously with water absorption. After conditioning in a water bath for 30 days the maximum tensile strength decreases by 30% on average, and does not change significantly thereafter until the end of conditioning (112 days). Specimens conditioned in the environment of 30°C, 80% RH show a decline of 17.9% in the maximum tensile stress after 35 days, and 19.9% after 84 days. ASTM 3518 [106] proposes a method to calculate the in-plane shear strength of composites as the half of tensile strength of [±45°] laminates for low failure strains or the tensile stress at 5% of shear strain for high failure strains. Although the shear strain is not measured in this work, it still can be deduced from the tensile curves (Figure 4-10) and tensile properties (Figure 4-11) that the in-plane shear strength is degraded after water absorption, and changed with water absorption in a similar trend as the maximum tensile stress.

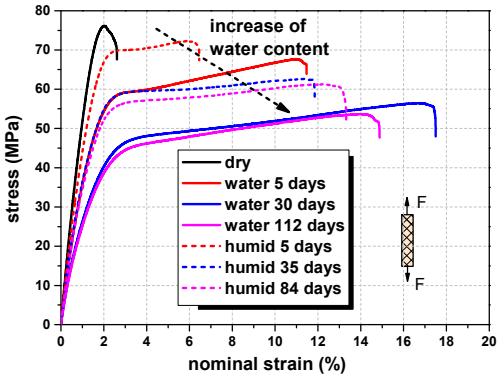


Figure 4-10: Representative tensile stress-strain curves of ± 45° specimens at different conditions (nominal strain is obtained not from the clip-on extensometer but from the displacement of crosshead due to the presence of necking)

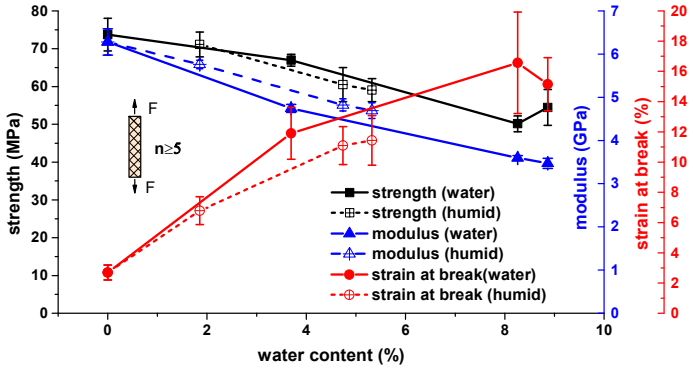


Figure 4-11: Tensile properties of ± 45° specimens plotted over the water contents (refer to averaged water contents of specimens which are conditioned for different times, shown in Figure 4-9. Tensile modulus is calculated using strain data from clip-on extensometer, while strain at break is obtained from the displacement of crosshead.)

4.2.4 Unidirectional [0°] laminates

Influence on the tensile behaviour

To analyse the influence of water absorption on the tensile behaviour, stress-strain curves of dry and wet specimens are compared. As shown in Figure 4-12, tensile response of dry specimens exhibited a brittle behaviour. The stress-strain relationship is not ideally linear and exhibits a perceivable nonlinearity. The nonlinearity of dry UD FFCs has been reported by other researchers [108,109]. Wet specimens also show a nonlinear tensile response but seem to have a distinct nonlinearity compared to the dry ones. In addition, the strain at break increases considerably with water absorption due to plasticization effect.

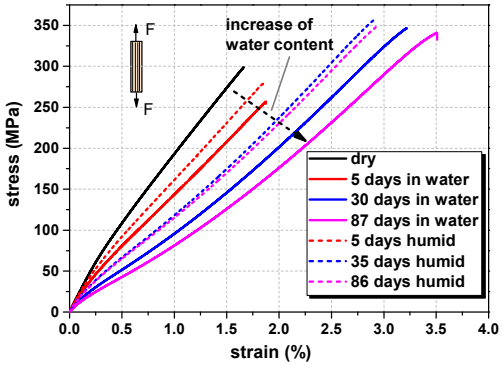


Figure 4-12: Representative tensile stress-strain curves of [0°] specimens at different conditions

To further analyse the change in the tensile behaviour, stiffness evolution of dry and wet specimens is compared. As can be seen in Figure 4-13, distinct stiffness evolution processes are found for dry and wet specimens. The stiffness evolution of dry specimens could be divided into three main regions. The first region is featured by a drastical drop in stiffness up to around 0.5% of strain, followed by a second region where the stiffness decreases moderately. The third region is relatively narrow, where stiffness decreases drastically again up to fracture. The stiffness evolution of wet specimens is also composed of three regions. However, a stiffening trend is found in the second region, which is opposite with that of dry ones. The increase in stiffness is minor for specimens that are conditioned in water bath and in humid environment for 5 days, and becomes more remarkable with the increase of water absorption. Furthermore, the third region becomes wider after water absorption, especially for the ones conditioned over 30 days in water and over 35 days in humid environment.

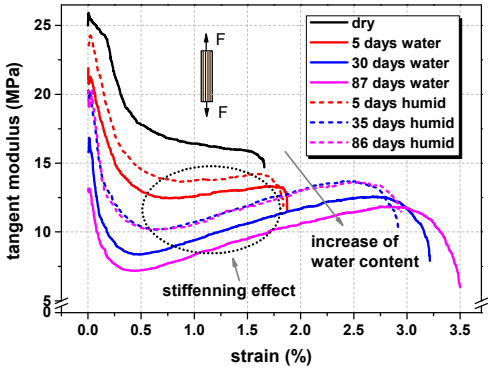


Figure 4-13: Stiffness evolution of [0°] specimens during tension (tangent modulus was smoothed by median filtering to eliminate short noises featured with localized spikes)

Analysing the reasons for the change in the tensile behaviour

It is believed that the degradation in stiffness of UD FFCs in the first region can be attributed to the intrinsic changes in the stiffness of flax fibres [108,109], as flax fibre are found to have an initial loss in stiffness as well [109]. Lefeuvre and Gourier et al. [49,49,56,56] also reported that flax fibres could exhibit a nonlinear behaviour which the fibre stiffness decreases firstly due to the complex accommodation of micro fibrils in S2 layer of flax fibre, and then increases due to the realignment of micro fibrils after exceeding a certain stress. Indeed, at a larger scale of twisted flax fibre yarns, off-axis aligned flax fibres would also have relative movements in the matrix (accommodation effect) that are able to result in an initial softening. Furthermore, the development of damages in composites would result in reduction of stiffness as well. However, it is questionable whether significant damages development exist in the first region. AE detection is then applied to detect the damage events during tensile tests for dry specimens and wet specimens.

Figure 4-14 and Figure 4-15 show the AE detection results of a dry UD specimen and a wet specimen (in humid environment for 35 days) during tensile tests. No extensive AE hits are found in the first region for both dry and wet specimens, revealing that the damage development is not significant

in the first region. Hence it is clear that the stiffness loss in the first region is not caused by the damage development. A drastical increase in detected AE hits is found from the beginning of the second region onwards. The majority of AE hits had amplitudes below 60 dB and distributed along the second and third regions. They can be correlated to damage events of matrix cracks and fibre –matrix debonding [110]. At the end of the second region AE hits having amplitudes between 60 -80 dB are detected, indicating the presence of damage events of fibre pull-outs [110]. In third region more severe fibre breakages (AE hits having amplitude larger than 80 dB) is expected to happen but is not recorded due to the limited capacity of AE detection system used in this study.

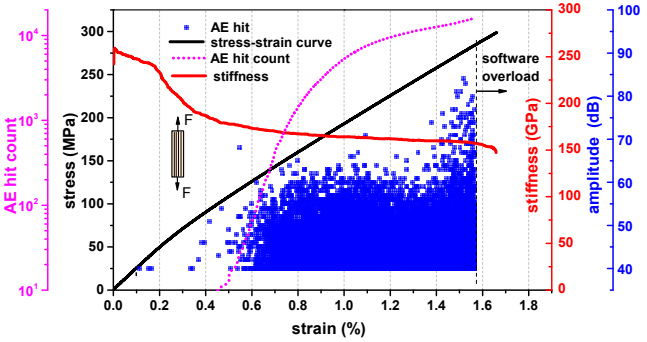


Figure 4-14: AE results, stress, and stiffness plotted against strain for a dry UD specimen

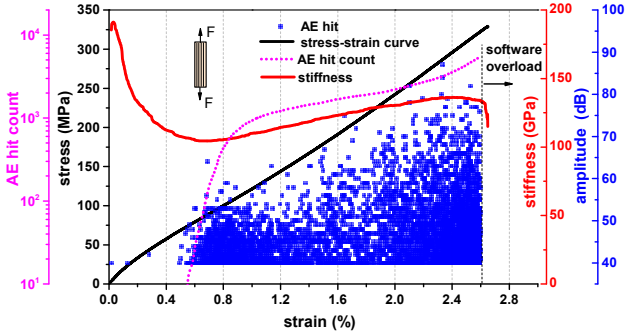


Figure 4-15: AE results, tensile stress, and stiffness plotted against tensile strain for a dry UD specimen that was conditioned in humid environment for 35 days

In accordance to the proved extensive damage events in the second region, the composite stiffness at dry state does not show an increasing trend as the single flax fibre did. However, specimens start to show a stiffening effect of after 5 days in wet environments even with the presence of damage development. The larger the water content, the more pronounced the stiffening effect. This phenomenon can be explained by two counterbalancing effects in the second region: the softening trend due to damages (e.g. matrix cracks, fibre-matrix debonding, etc.), and the stiffening trend due to realignment of flax fibres as well as the rotation of micro fibrils in flax fibres. It is reasonable to believe that damage development plays comparable role in stiffness degradation for dry and wet composites, as seen in Figure 4-14 and Figure 4-15. However, compared to wet specimens, dry specimens have stronger fibre-matrix interfacial bonding and a higher modulus of matrix, which impeded the realignment of fibres. After water absorption, the modulus of matrix and fibre-matrix bonding degrades, which favours the realignment of flax fibres. In a similar way with the twisted flax fibres, realignment of micro fibrils is assumed to be also favoured by the water absorption due to the analogous structure with twisted flax fibre yarns.

Influence on tensile properties

Apart from the tensile behaviour, tensile properties of UD FFCs are also changed significantly by water absorption. In fact, the tensile strength initially decreases with water absorption and then increases with further water absorption to higher values than that at the dry state, which has been rarely reported in literature. As seen in Figure 4-16, specimens that are conditioned in water bath and in humid environment for 5 days display a remarkable decrease in strength by 14.3% and 8.8% on average, respectively. Further conditioning for about 30 days induces a recovery of the tensile strength and actually increases the strength by over 15% on average for both wet conditioning cases. The increase in tensile strength is able to be maintained till the end of conditioning (87 days in water and 86 days in humid environment), with only a slight decrease being observed. Unlike the tensile strength, the strain at fracture increases continuously with water absorption. Specimens conditioned in water for 87 days have a strain to

failure, nearly twice as that at dry state. As expected, the modulus decreases continuously mainly due to the decrease in modulus of fibre and matrix modulus with water absorption.

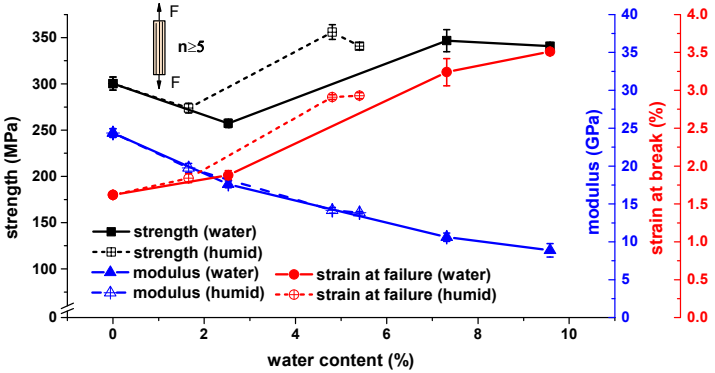


Figure 4-16: Tensile properties of [0°] specimens plotted against the water contents (refer to averaged water contents of specimens which were conditioned for different times, shown in Figure 4-12.)

Generally, the strength of composites depends on fibre properties, fibre orientations, fibre-matrix interfacial properties and other factors e.g. damage development, matrix properties and fibre swelling. To explain the changing trend of tensile strength with water absorption, the effects of water absorption on the abovementioned factors are analysed in Figure 4-17 schematically. It should however be noted that the trend lines in Figure 4-17 only roughly reflect the separate trends of the factors for the convenience of interpretation.

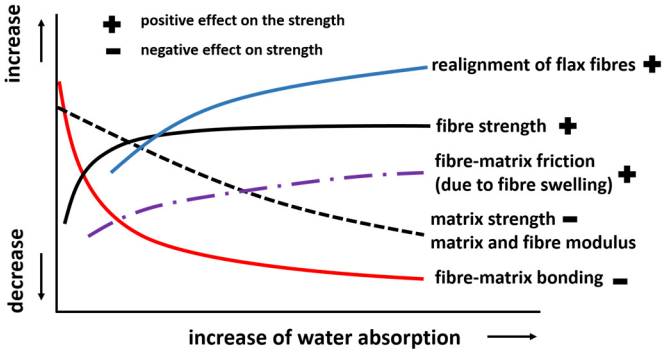


Figure 4-17: Trend lines of factors that would influence the tensile strength of UD FFCs

The decrease in tensile strength in the first stage of water absorption (before around 3% of water absorption) can be mainly ascribed to the averaging effect of the rapid degradation in fibre-matrix bonding and an increase in fibre strength. It seems the increase in fibre strength cannot compensate the effects of degradation in fibre-matrix bonding at this stage. In addition, the inhomogeneous water distribution in the beginning of water absorption would probably cause a degradation in tensile strength. Fibres near specimen's surfaces have lowered modulus and carried less load than the fibres which are relatively 'dry' inside the specimens, resulting in additional shear stress inside composites. However, this effect could be minor at least for the specimens conditioned in humid environment for 5 days, because no distinction of fracture morphology is observed compared to that of dry specimens. As more water is absorbed, the effects of realignment of flax fibres in load direction become pronounced due to the increased ductility of fibres and matrix and the decreased fibre-matrix bonding, resulting in an improved fibre stiffness and a better utilization of fibre strength. Another positive effect is the increasing friction at fibre-matrix interface, which arises from the compression force at interface induced by swelling of flax fibre because flax fibre swells more than the matrix. The increased friction assures a load transfer at interfaces when fibre-matrix debonding occurs during realignment. Consequently, the overall effect after about 3% of water absorption is a considerable increase of tensile strength until reaching a

stabilized state. The realignment is evidenced by the stiffness increase shown in Figure 4-13 and is favoured by the increased ductility of composites (remarkably increased strain to failure).

The fracture morphologies of specimens with different conditioning times in the humid environment give further hints on the change of tensile strength. As seen in Figure 4-18, extensive long longitudinal matrix cracks along fibres are found for specimens having increased strengths, while less and shorter longitudinal matrix cracks are observed for dry and 5 days conditioned specimens. The increased long matrix crack could result from the decreased fibre-matrix bonding and the increased composites ductility. The more and longer the matrix cracks, the more energy is absorbed. Therefore, the increased longitudinal matrix cracks would be an important mechanism of the improvement in tensile strength of [0°] specimens.

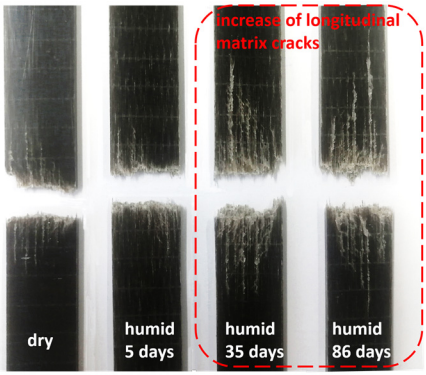


Figure 4-18: Fracture morphology of dry and wet UD specimens

4.3 Summary

This chapter introduces the mechanical durability of FFCs upon long term of water absorption in two severe wet conditions. Water absorption and the evolution of mechanical properties of composites having three different stacking sequences ($[0°]_4$, $[90°]_4$ and $[\pm45°]_s$) are analysed. The major findings are:

- Tensile modulus of matrix and composites decreases with water absorption due to plasticization effect. On the contrary, their strain to failure is significantly increased at high water contents.
- The fibre-matrix bonding properties and tensile properties of matrix properties continuously decrease with water absorption, which results in a continuous decrease in tensile strength of FFCs having stacking sequences of $[90°]_4$ and $[\pm45°]_s$. It is worth to note that the evolution of the tensile properties of 90° and [±45°] FFCs have not been reported in literature to the author's knowledge so far. The results in this chapter can improve the understanding of the environmental degradation in the mechanical properties of FFCs caused by water absorption.
- Tensile strength of [0°] specimens shows a distinct trend upon water absorption which has not been reported in literature. The strength firstly decreases and then increases up to over 15% higher than the strength at dry state. This distinct changing trend is believed to be ascribed to the competing effects of degradation of fibre-matrix bonding, increased fibre strength and strengthening effects due to realignment of flax fibres.

5 An alternative flax fibre pre-treatment

5.1 Defining the furfuryl alcohol pre-treatment approach

5.1.1 Furfuryl alcohol

Furfuryl alcohol (FA) is an organic compound containing a furan substituted with a hydroxymethyl group. It is a colourless liquid with a faint burning odour. FA is considered as a green chemical because it can be cheaply mass produced from furfural, which is obtained from hydrolysis of pentosan-rich biomass renewable agricultural wastes (e.g. corn, sugarcane, wheat, oat, cottonseed hulls, rice hulls, birch wood, and hazelnut shells) [111–113]. The commercial available FA with a minimum purity of 98% can be lower than 2 $ per kilogramme (Alibaba.com).

FA has many applications and producing furan resins is a major one. E.g., FA can be used as a precursor and polymerized into a solid organic hydrophobic polymerized furfuryl alcohol (PFA). The polymerization mechanism of FA is rather complex involving acid-catalysed polycondensation (Figure 5-1). The mechanistic complexity arises from the fact that two inevitable side reactions alter the ‘‘normal’’ course of the linear growth profoundly, generating unsaturated sequences, which undergo intermolecular Diels–Alder (DA) reactions leading to black cross-linked polymers [114].

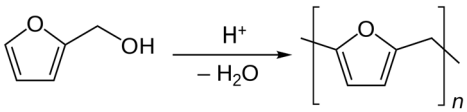


Figure 5-1: A highly simplified mechanism of acid-catalysed polycondensation of FA

Owing to the fact that FA has a low viscosity and low molecular weight, FA molecules can penetrate into cell walls and undergo the above mentioned in-situ polymerization process. This makes FA very promising for treating natural fibres to reduce the hydrophilicity. Recently, applications of furfuryl alcohol are found in wood preservation to enhance the moisture resistance

and dimensional stability of cellulosic woods [115–117]. Nordstierna et al. [117] revealed that polymerising furfuryl alcohol can covalently bind to hydroxyl groups of lignin units which are present in natural fibres, indicating a possibility of improving the natural fibre-matrix interfacial bonding. For natural fibre reinforced composites, a few studies have tried to manufacture full bio-composites with polymerized furfuryl alcohol (PFA) as the matrix, while problems of compatibility and solvent removal remained to be addressed [112,118,119]. As for fibre pre-treatment with FA, Saw et al. [120] conducted a study in which luffa cylindrical fibre was grafted with FA followed by oxidation. Thermal and mechanical properties of composites were reported to be improved. However, to the author's knowledge, very few studies have investigated treating flax fibres with FA.

5.1.2 Pre-defined FA treatment approach

The polymerization process of FA into PFA is assumed to involve a series of complex reactions [111]. It is sensitive to several parameters such as type of catalysts, catalyst content, applied temperature histories, FA solvent contents of treated fibres, etc. These parameters could significantly affect the influence of FA treatment on flax fibre composites. In this regard, the type of catalysts, catalyst contents, and FA solvent contents of treated fibres were firstly defined in a preliminary work.

Pre-defined treatment parameters and approach

Applied catalyst is p-Toluenesulfonic acid (PTSA), purchased from Sigma-Aldrich Chemie GmbH, Steinheim, Germany. FA solution is prepared by dissolving PTSA in distilled water and then mixed with furfuryl alcohol (weight ratio: 0.3 PTSA, 10 water, and 100 FA). Flax fabrics (280 mm × 270 mm) are then impregnated with FA solvent by carefully dipping the FA solvent evenly onto every fabric layer. The fabrics absorb FA solution very fast. Slight pressure is evenly applied to improve the impregnation quality. Content of FA absorbed by flax fabrics is carefully controlled at 40% ± 1% by using paper towels to absorb excessive FA solution. Afterwards the impregnated fabrics are wrapped with aluminium foils and placed into a heating chamber. The pre-treatment procedure is illustrated in Figure 5-2.

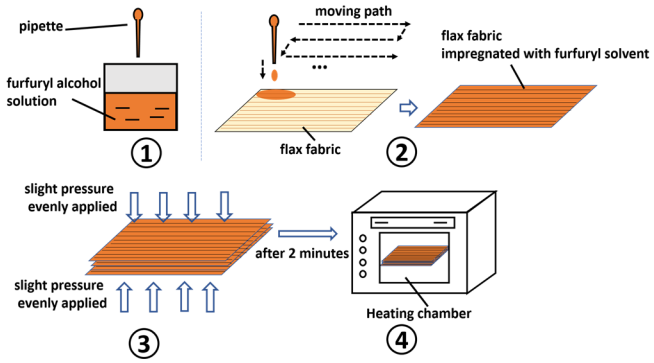


Figure 5-2: Procedures of FA treatment on flax fibres. Step 1: prepare the FA solvent; step 2: impregnate flax fabrics with FA solvent; step 3: apply pressure for a good impregnation; step 4: impregnated flax fabrics (wrapped with aluminium foils) are placed into heating chamber.

Heating cycles of FA treatments

Firstly, two different heating cycles are used to investigate the effects of temperature on the treatments (Table 5-1). The selected temperatures of TI and T2 are determined in preliminary investigations.

Table 5-1: Two heating cycles of FA treatment in preliminary investigation

Treatments	Heating cycles
T1	120 °C for 6h➔150 °C for 4.5 h
T2	120 °C for 2 h ➔150 °C for 7 h

5.2 Verify the feasibility of FA treatment

5.2.1 Composites manufacturing and methods

Composites with untreated flax fibres and FA treated fibres (T1 and T2) are manufactured via VARTM. Their mechanical properties and water ageing effects are analysed and compared to verify the feasibility of FA treatment.

It is worth to note that experiment procedures (e.g. manufacturing, specimen's dimensions and tests) are slightly different with what have introduced in chapter 3. Nonetheless, reliable results can be obtained at this preliminary investigation stage, since the same procedures are strictly

performed on untreated and FA treated composites. The differences are detailed as follows.

1. In manufacturing, both treated and untreated fibres are not pre-dried in the mould. Furthermore, a different mould and frame are used which yield composites with a thickness of 2.2 mm. The fibre volume fraction is then around 36%.
2. [0°] and [90°] specimens have dimension of 2 × 18 × 250 (mm) and 2 × 20 × 110 (mm), respectively. Tensile tests on [90°] specimens are conducted on Zwick 2.5 kN with a scissor grip to assure a valid breakage (testing speed: 1 mm/min). However, the measured transverse modulus does not reflect the intrinsic modulus of the composites due to the high compliance of the scissor grip. Therefore, only the transverse strength is analysed. Fracture morphologies of treated and untreated [90°] specimens are compared to analyse the fibre-matrix and inter-fibre bonding properties.

To characterize the FA treatment on flax fibres, tensile properties of yarns are also compared. Individual flax yarns are extracted directly from flax fabrics at random location. The distance between paper tape ends is 100 mm. All yarns are loaded at a constant speed of 5 mm/min. The tensile strength is not measured because of the large scatter in the cross-section area along one individual yarn and the irregular shape of the yarn cross section. At least 10 yarns are tested for each type of fabrics and their break forces are analysed.

In addition, SEM observation and Fourier Transform Infrared Spectroscopy (FTIR) are used to characterize influence of FA treatment on flax fibres. FTIR tests are performed on Bruker TENSOR II (Bruker Corporation, Billerica, USA) with an ATR-unit (Attenuated Total Reflection). The chosen wave number range is from 500 cm^{-1} to 4000 cm^{-1}. The resolution is 4 cm^{-1} and the spectra are averaged over 16 scans. Spectra at 5 different locations on each treated or untreated flax fabric are measured and then averaged.

Preliminary water absorption tests are also performed. Specimens with T2 fibres are immersed in distilled water bath for 40h, 115 h. Five replicate specimens are tested for each condition.

5.2.2 Characterization on FA treatment

Impregnated FA in the flax fabrics polymerizes into PFA after the heating procedure. The colour of flax fabric turns from light brown to yellow-red (Figure 5-3) after FA treatment. Such change of colour is ascribed to the formation of chromophores during polymerization process of FA [111,118]. Weight of fabric is found increased after the FA treatment. T2 flax fabric' weight increased by about 10%, slightly lower than that of T1 flax fabrics (about 11%). The weight increase can be ascribed to the PFA on flax fibres.

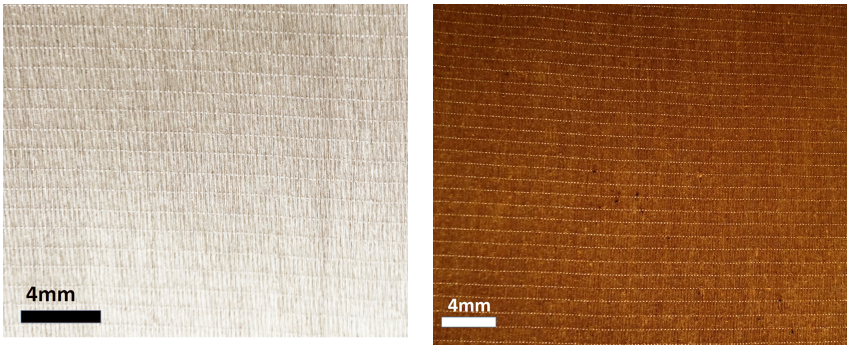


Figure 5-3: Untreated flax fiber fabric (left); and FA treated flax fiber fabric (right).

Figure 5-4 shows the changes in fibre surface morphology after FA treatment. Most untreated flax fibres have smooth surfaces, with some degraded substances that probably are residues of lammea. In contrast, parts of FA treated flax fibre have surfaces partly covered by thin layers of wrinkled materials, which can be recognized as PFA.

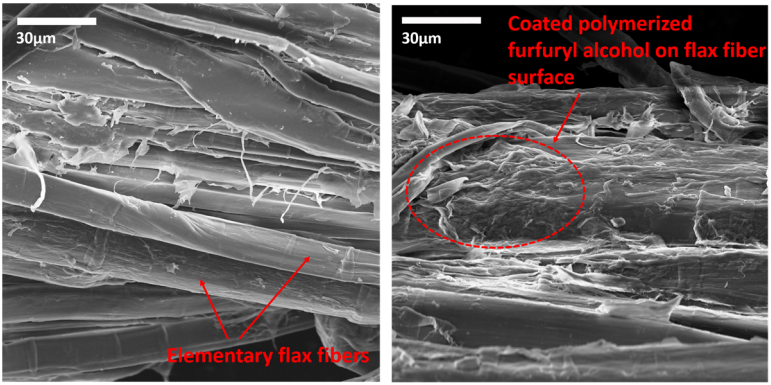


Figure 5-4: Representative morphology of untreated flax fibres (left), and FA treated flax fibres (right).

FTIR observation on treated flax fabric also gives indication of presence of PFA (Figure 5-5). The broad band from 3000 cm–1 to 3600 cm–1 fades after the FA treatment, indicating reduced hydroxyl groups on the flax fibre surfaces which are covered by PFA coating. Peaks at 1714 cm^{-1} and 1504 cm^{-1}, which are the feature peaks of the furan rings [112,119], reveal the presence of PFA. No significant difference was observed between spectra of T1 and T2 flax fabrics.

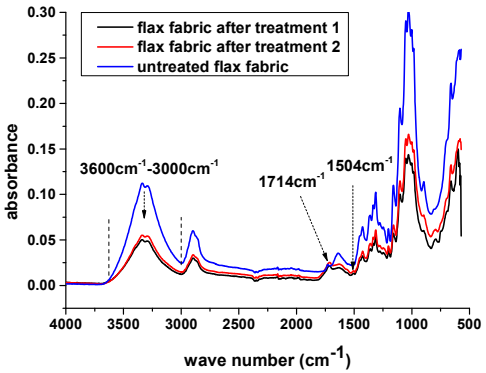


Figure 5-5: Infrared spectrum of untreated and FA treated flax fibres.

Figure 5-6 shows representative force-elongation curves of flax fibre yarns. All types of yarns exhibit brittle tensile behaviour. FA treated yarns have a

considerably stiffer tensile response compared to untreated ones. However, a reduction in break force is observed for treated yarns. As listed in Table 5-2, the strength of yarns is significantly degraded by FA treatment. Treated yarns break at lower load levels and have much lower elongation to fracture compared to untreated yarns. No significant difference is observed between two treatments. The decrease in breaking force is indeed the side effect of FA treatment. It has been reported that hemicellulose could be degraded under acid conditions at high temperatures [121]. The treatments applied a maximum temperature of 150 °C under acid condition, thus could be an attributing factor to the decrease of break force. Nonetheless, the reduced hydroxyl groups on fibre surfaces and the coated PFA could introduce improved moisture resistance and fibre-matrix bonding to composites with FA treated fibres. The assumption is confirmed in the following subchapters.

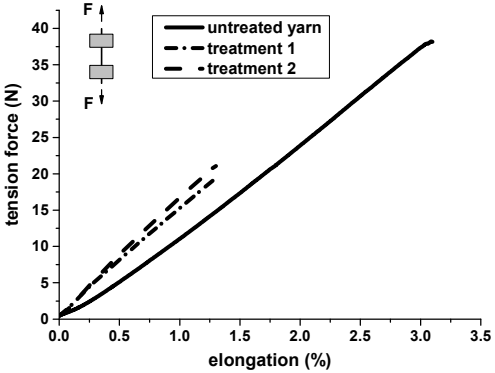


Figure 5-6: Representative tensile force-elongation curves of treated and untreated yarns.

Table 5-2: Tensile test results of untreated and FA treated yarns

Treatments	Break force (N)	Strain at breakage (%)
untreated	37.16± 2.94	2.94± 0.43
T1	19.76± 6.75	1.11± 0.36
T2	20.17± 5.49	1.17± 0.36

5.2.3 Influence on the Mechanical Properties of Composites

The tensile properties of composites are substantially changed by the FA treatment. As can be seen in Figure 5-7, tensile strength in fibre direction degrades by about 30% after FA treatments. The degradation can be attributed to the decrease of fibres strength (by over 45%, shown in table 5-2). However, the modulus in fibres direction are considerably improved by both FA treatment approaches. Investigation on the tensile tests of [90°] composites allows evaluating the effects of treatment on fiber-matrix interfacial bonding properties. A slight increase in transverse tensile strength is observed for treated composites. SEM observations on the fracture surface of [90°] composites prove a good fibre-matrix bonding and inter-fibre bonding for treated composites. Split fibres showing micro-fibrils and peeled fibre layers are observed for both treated and untreated specimen surfaces. The PFA at interfaces on fibres is found adhering flax fibres and the matrix intimately, showing no clearance between each other (Figure 5-8). In comparison, the inter-fibre bonding for untreated composites seems not as intimate as of treated ones since clearance between fibres are often observed, indicating an inferior fibre-matrix bonding and inter-fibre bonding (Figure 5-8).

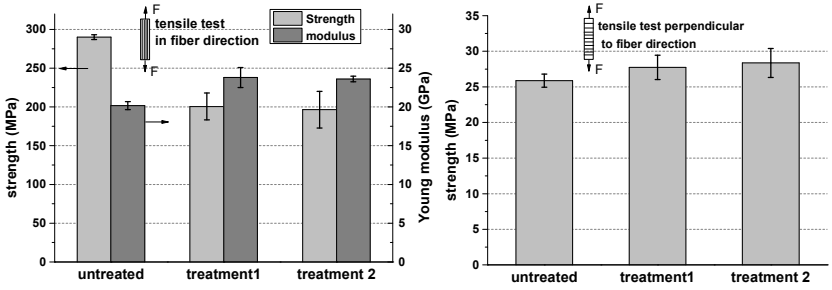


Figure 5-7: Influence of FA treatments on the tensile properties of composites: in fibres direction (left); perpendicular to fibres direction (right)

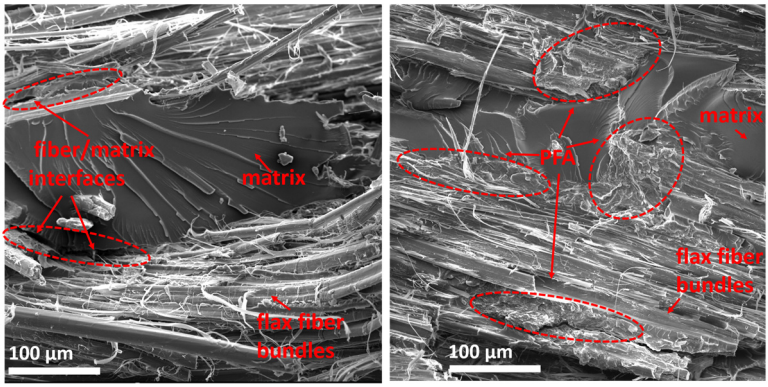


Figure 5-8: Morphology of fracture surface of [90°] specimens: untreated (left); FA treated (right)

The improved fibre-matrix bonding could result from three-fold mechanisms. Firstly, the treated yarns surfaces are more hydrophobic due to the coated PFA on the fibre surfaces. Hence, they could be more compatible with the hydrophobic matrix than untreated flax fibres. Secondly, as already shown in Figure 5-4, treated fibre surfaces have rough areas where PFA is coated, providing a larger surface area for mechanical interlocking with the matrix. Lastly, there could be chemical bonds generated between PFA and the matrix, although no conclusive evidence is given in this study.

5.2.4 Influence on moisture absorption of composites

The preliminary 5 days water absorption test shows an expected improvement in water absorption rate for FA treated composites. Compared with untreated composites, [0°] specimens that underwent FA Treatment 2 display reduced amount of water uptake after 40 h, 115 h by 34% and 39%, respectively (Figure 5-9). The improvement of moisture resistance can be ascribed to the better fibre-matrix bonding which impede the propagation of water molecules along with the fiber-matrix interfaces, and the hydrophobic PFA on the flax fibers or possibly inside flax fiber cells. In fact, PFA is reported to have an excellent water resistance property. Water uptake of PFA at

saturation is reported to have a value of 1.12% [112], which is lower than of the used bio-epoxy matrix in this work (over 2.5% at saturation).

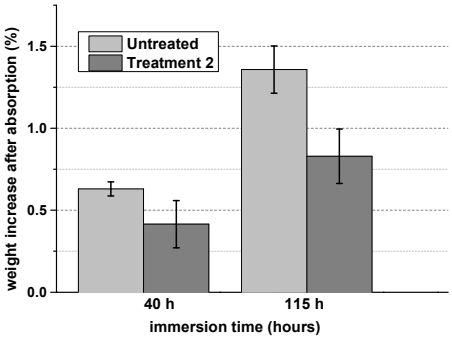


Figure 5-9: Influence of FA treatments on the water uptake of [0°] specimen (error bars indicate standard deviation).

5.2.5 Influence on retention properties upon water absorption

Figure 5-10 compares the tensile strength of FA treated specimens (T2) and untreated specimens after water absorption. Tensile strengths of treated and untreated specimens both show a decreasing trend with ageing time. However, the tensile properties of treated composites are better maintained compared to the untreated ones at the same immersion duration. Longitudinal tensile strength of treated composites decreases by 5.3% after 115 hours of immersion, while the untreated ones drop by 15.5%. For transverse strength, FA treated specimens also show a better retention compared to untreated composites. This could indicate a slower degradation in fibre-matrix bonding, testified by SEM observations on [90°] specimen fracture surfaces. As displayed in figure 5-11, there is an evident difference in the fractographic features for untreated composites before and after water absorption, while no obvious change is observed for FA treated composites. Figure 5-11a shows fracture morphology of untreated [90°] specimens. Flax fibres are bunched up together in the original form of yarns, revealing a loose fibre bundles/matrix bonding. After absorbing water for 115 h, inter-fibre splitting inside fibre bundles is noticed (Figure 5-11b),

indicating that inter-fibre bonding is weakened after water ageing. In contrast, FA treated composites show similar fractographic features before and after 115 h of ageing, revealing a better resistance of fibre-matrix and inter-fibre bonding after water uptake. Intimate flax fibre-matrix bonding and broken fibres bundles are observed.

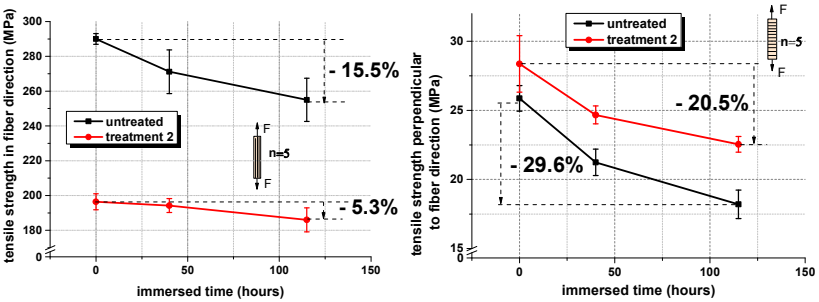
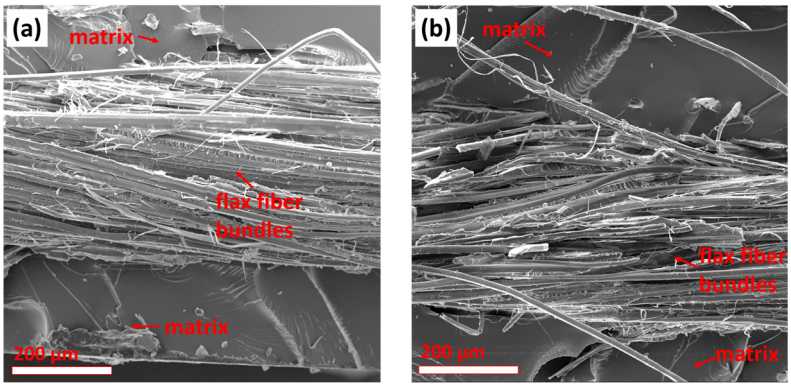


Figure 5-10: Influence of FA treatments on the water ageing effects on tensile strength of composites: in fibres direction (left); perpendicular to fibres direction (right).



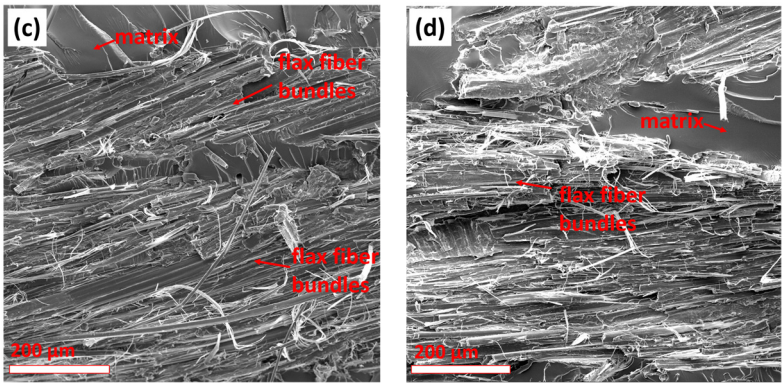


Figure 5-11: Morphology of fracture surfaces of [90°] specimens: (**a, b**) untreated, 0 h and 115 h in water, respectively; (**c, d**) T2, 0 h and 115 h in water, respectively.

The Young's modulus of [0°] composites indicates the efficiency of load transfer at fiber-matrix interfaces and the intrinsic fiber tensile modulus. It is clearly revealed that FA treated composites show not only a higher modulus than the untreated composites (Figure 5-12), but also reserve larger extent of Young's modulus. Stronger fiber-matrix bonding again explains the better resistance against degradation at fiber-matrix interfaces. Meanwhile, the PFA also impedes the plasticizing effect on flax fibers caused by water absorption, which could be partly responsible for the superiority of FA treatment.

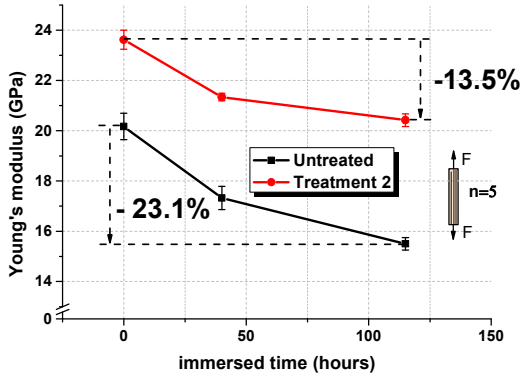


Figure 5-12: Changes in Young's modulus in fiber direction after water absorption

5.2.6 Defined FA treatment approach

The two investigated heating cycles do not have significant difference in FA treatment effects, which is revealed by single yarns tensile tests, FTIR observation on treated flax fabrics and tensile tests on treated composites (results above). It is worth to mention that both heating cycles were determined to assure a high polymerization degree of FA (Figure 5-5). Therefore, it is assumed that FA treatment might not be sensitive to temperature histories, as long as the polymerization degree of FA is similar when other parameters are held constant. Since T2 takes shorter time than T1, it is then decided to use T2 for the further investigations.

The investigation on the feasibility of FA treatment is performed at early stage of this study. Composites that are manufactured for preliminary investigation on the feasibility of FA treatment do not involve the defined pre-drying process. To compare with the composites with pre-dried fibres, the heating cycles of FA treatment is eventually modified to 120 °C for 2 h ➔150 °C for 6 h, followed by the same pre-drying procedure under vacuum as has been descripted in subchapter 3.9.2 (The same mould and frame are also used). The other procedures are kept the same with what has been introduced in subchapter 5.1.2. Besides this subchapter, the FA treatment in this work refer to the defined FA treatment approach except in the context of subchapter 5.2.

5.3 Influence of defined FA treatment approach on mechanical durability

5.3.1 Mechanical properties of composites

Mechanical properties of FA treated composites using the defined treatment approach are listed in Table 5-3. With no surprise, similar effects on the mechanical properties are found as those discussed in preliminary investigations. Tensile strength in fibre direction is degraded by 21% due to degradation of fibre strength, while the modulus and transverse strength are increased due to the enhanced inter-fibre and fibre-matrix bonding. The extensive micro-fibrils observed on the fracture surfaces of the specimens

(Figure 5-13) again evidences the improvement of FA treatment on the inter-fibre and fibre-matrix bonding properties.

Table 5-3: Tensile properties of untreated and FA treated composites at dry state

Composites	Strength (MPa)		Modulus (GPa)	
	[0°]	[90°]	[0°]	[90°]
untreated	300.25±7.09	29.36±1.42	24.36±0.57	4.25±0.14
FA treated	237.27±8.30	31.03±0.16	27.26±0.34	4.62±0.04

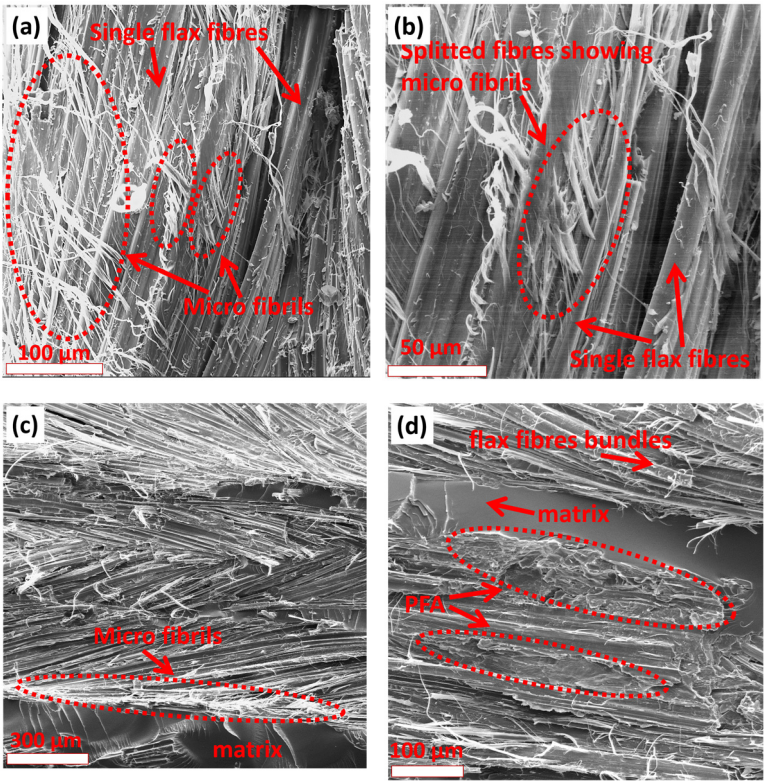


Figure 5-13: Fracture morphology of FA treated [0°] and [90°] specimens at both dry conditions (a, b – [0°] specimens; c, d – [90°] specimens)

5.3.2 Water absorption at long term

Although the preliminary investigation shows that the water absorption resistance of FA treated FFCs is improved in short term (115 hours in water

bath), it might not guarantee a reduced water absorption at long term. To clarify this point, FA treated [0°] specimens are conditioned for about 3 months at the same wet conditions with those being used for untreated ones. Figure 5-14 compares the water absorption of FA treated [0°] specimens and untreated ones. It turns out that FA treated composites absorb nearly as much water as the untreated ones in both wet conditions, showing only slightly less water contents after 3 months conditioning. However, the water absorption rate of FA treated specimens is considerably lower than untreated ones at short time.

Indeed, an improved fibre-matrix bonding and inter-fibre bonding impedes the absorption of water, resulting in a slower water absorption rate. Whereas, the water content at equilibrium absorption state will not be changed by the bonding properties, because the fibre constituents (cellulose, hemicellulose and pectin) are mainly responsible for the amount of absorbed water. FA treatment does not reduce the main fibre constituents (except for a certain amount of degradation of hemicellulose). Hence, it has no significant improvement in water absorption at equilibrium state.

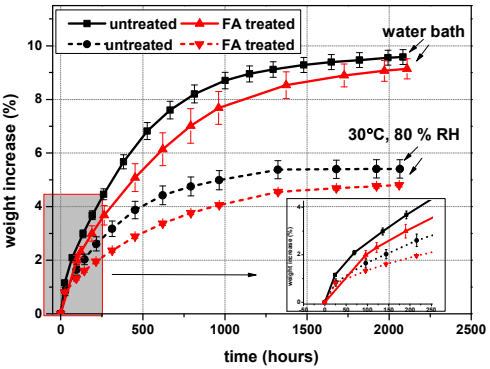


Figure 5-14: Water absorption curves of FA treated and untreated [0°] specimens

5.3.3 Retention in mechanical properties upon water absorption

Tensile behaviour

Figure 5-15 gives an overview on the change of the tensile behaviour with water absorption by plotting the representative tensile stress-strain curves at dry and wet states. Similar to the untreated [0°] specimens, FA treated specimens exhibit a pronounced plasticization effect due to water absorption. The modulus of wet specimens reduces significantly, corresponding with the remarkably increased strain to failure. However, the tensile strength does not show the same trend as for untreated specimens. No increase in tensile strength upon water absorption is observed. The reduction in modulus and increase in stain to failure is expected because the fibre and matrix modulus are reduced and by water absorption. The distinct changing trend of tensile strength with water absorption, on the other hand, might be related to the improved fibre-matrix bonding resulting from FA treatment. The reasons are analysed in detail in the following text.

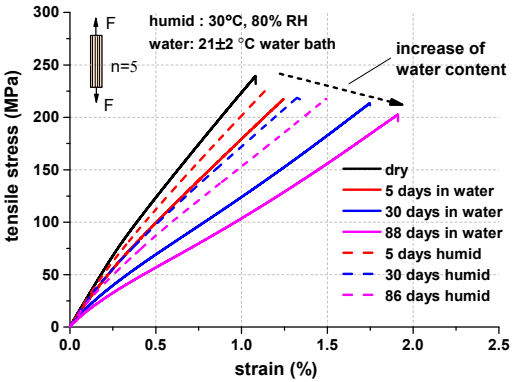


Figure 5-15: Representative tensile stress-strain curves of FA treated [0°] specimens at different conditions

Retention in tensile properties: comparison of FA treated and untreated [0°] specimens

Figure 5-16 (left) clearly shows the distinct changing trends of tensile strength with absorption. FA treated specimens exhibit a continuous decrease in strength with water absorption. After conditioning in water bath and in humid environment for 5 days, the strength decreases by 8.9% and 3.0% on average, respectively. Unlike the untreated specimens, further conditioning induces a continuous but slow reduction in strength for FA treated ones. Specimens conditioned in water bath for 88 days displays the highest degradation in strength by 12.3%, followed by the specimens conditioned in humid environment for 86 days (degradation by 8.9%).

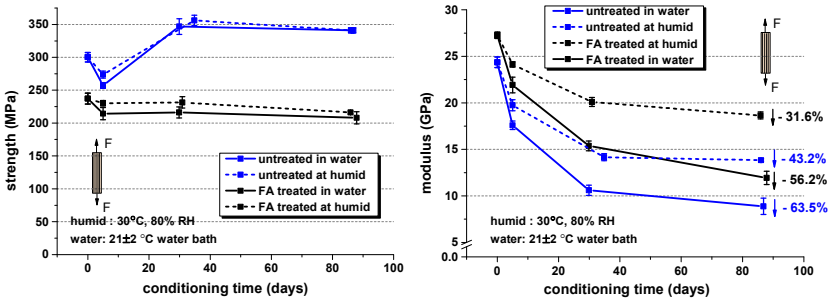


Figure 5-16: Tensile properties of FA treated and untreated [0°] specimens at dry and wet states (left: tensile strength; right: tensile modulus)

Tensile modulus decreases with water absorption for both treated and untreated ones (Figure 5-16, right). However, it is worth to mention that the superiority in modulus of FA treated specimens is maintained over the whole conditioning time span. One can assume that the fibre modulus and matrix modulus have the same, if not, nearly the same degradation degree for FA treated and untreated specimens due to their similar water contents at equilibrium absorption state. Therefore, the superior modulus of FA treated specimens, conditioned either 88 days in water bath or 86 days in humid environment, is attributed to a better inter-fibre and fibre-matrix bonding than that of untreated ones. In other words, the inter-fibre and fibre-matrix

bonding of FA treated composites are less degraded by water absorption than their untreated counterparts.

Analysing the distinct changing trend in tensile strength of FA treated [0°] specimens

As discussed above, the increase in tensile strength upon water absorption can be attributed to the realignment of fibres in load direction. To analyse the realignment of fibres for FA treated specimens, Figure 5-17 compares the tensile stress-strain curves and the correspondent tangent modulus evolution of FA treated with those of untreated specimens at equilibrium absorption states. As seen, the strain to failure of FA treated specimens is much lower than untreated specimens at the same water contents (Figure 5-14). From the shape of curves, one can also notice a less pronounced stiffening effect for the FA treated ones. This is evidenced by the tangent modulus curves depicted in Figure 5-17 (right). FA treated ones conditioned in humid environment for 86 days exhibit no noticeable increase in tangent modulus, while their untreated counterparts displayed a remarkable increase. Likewise, the FA treated specimens in water bath for 88 days show a less pronounced increase in tangent modulus compared to their untreated counterparts conditioned in water for 87 days. Since the stiffening effect is directly related to the fibre realignment in load direction, one can deduce that the realignment of fibres is less pronounced for FA treated specimens than for untreated ones.

Indeed, the realignment of fibres is favoured by the decreased bonding and the increase in the ductility of fibre and matrix. For FA treated and untreated specimens (at least at equilibrium absorption states), the increase in ductility of fibre and matrix can be assumed similar (considering the similar water contents). Hence, it is highly possible that less degraded inter-fibre and fibre-matrix bonding is the main reason for the less pronounced realignment effect of FA treated specimens. Furthermore, no apparent increase in longitudinal matrix cracks are observed for wet FA treated specimens (Figure 5-18), opposite with what is seen in the case of untreated ones (Figure 4-17). This could also be an indication of a less pronounced

realignment effect and a sign of a good bonding properties for FA treated composites upon water absorption. Cracks tend to propagate through flax fibres due to the good fibre-matrix bonding, instead of opening fibre-matrix interfaces.

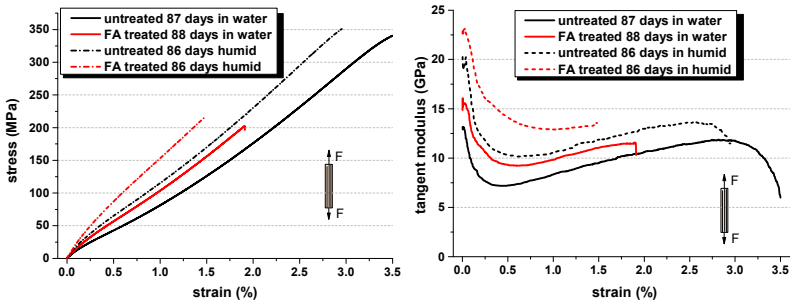


Figure 5-17: Comparison of the tensile behavior of FA treated and untreated [0°] specimens at wet conditions: tensile stress-strain curves (left) and the corresponding stiffness evolution with strain (right)

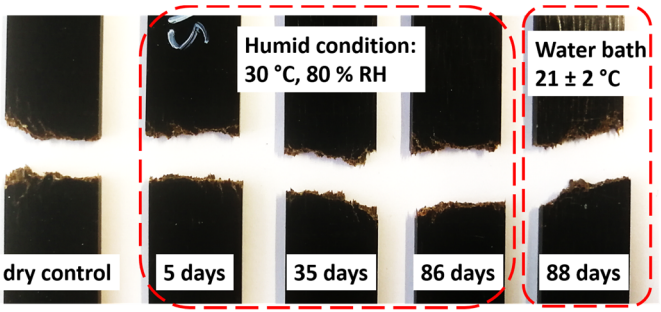


Figure 5-18: Fracture morphology of dry and wet FA treated [0°] specimens

5.4 Summary

This chapter introduces an alternative flax fibre pre-treatment approach developed by the author. The aim of the treatment is to improve the fibre-matrix bonding using a green chemical. Influences of the treatment on the mechanical properties, as well as the durability of treated FFCs are investigated. Main results and conclusions are as follows:

- The fibre pre-treatment using FA significantly improves the inter-fibre and fibre-matrix bonding as expected. During the FA treatment however, the acid catalyst reduces the strength of the flax fibres.
- The FA treatment can significantly reduce the water absorption rate of FFCs due to the improved inter-fibre and fibre-matrix bonding properties. A nearly 3-months water absorption test shows that of FA treated composites better resist the degradation in the fibre-matrix interface and inter-fibre bonding properties caused by water absorption in the long term compared to untreated counterparts.
- Due to the better bonding properties of FA treated FFCs at wet states, the realignment of flax fibres in load direction is found less pronounced for FA treated [0°] FFCs (compared to untreated [0°] FFCs. FA treated FFCs show a continuous but slow degradation of tensile strength upon water absorption.

6 Mechanical durability under long term loads

6.1 Tensile creep behaviour of composites at dry state

The creep responses of UD FFCs at dry state and the influence of water absorption on the creep properties of UD FFCs are investigated. In addition, the feasibility of the defined flax fibre pre-treatment approach to reduce the creep of FFCs is verified. Detailed information on the test setups is summarized in Table 6-1. For each test cases (except for the run out creep rupture test at 180 MPa), specimens are selected from three manufactured laminates to reduce the influence of the manufacturing quality.

Table 6-1: Applied creep stress levels

Creep stress	Fibre type/Composite	Creep time	Number of replicates
66 MPa	Untreated/dry	2 hours	3
132 MPa	Untreated/dry	2 hours	4
180 MPa	Untreated/dry	96 hours (run out)	1
210 MPa	Untreated/dry	until rupture	5
240 MPa	Untreated/dry	until rupture	6
240 MPa	1Untreated/W 88d	until rupture	5
270 MPa	1Untreated/W 88d	until rupture	5
240 MPa	2Untreated/H 87d	until rupture	5
270 MPa	2Untreated/H 87d	until rupture	5
132 MPa	Treated/dry	2 hours	4
188 MPa	Treated/dry	until rupture	4

[1]Untreated UD conditioned in water bath for 88 days; [2]Untreated UD conditioned in humid for 87 days

6.1.1 Creep properties at low stresses

Tensile creep curves at 66 MPa and 132 MPa

Figure 6-1 shows representative creep-deformation curves of untreated composites at 66 MPa and 132 MPa. UD FFCs exhibit perceivable creep deformation in fibre direction at 66 MPa (22% of UTS). Higher creep stress

results in a higher initial strain and creep deformation. Strain curve shapes at both creep stresses follow a typical creep response of viscoelastic material which could be divided by distinct deformation regions [122]. In the first region, creep deformation increases rapidly with a decreasing creep rate. The second region is steady, where creep strain increases at a low rate in an approximately linear regime. A two-term parameter power function of time, which has the same form as Findley's power law [81,122,123], can successfully model the short term creep deformation with high accuracy.

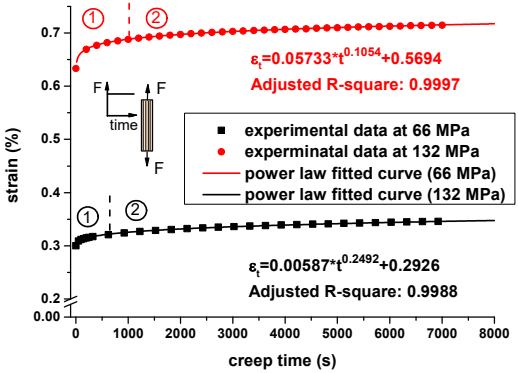


Figure 6-1: Creep deformation of UD flax fibre composites in fibre direction at 66 MPa and 132 MPa. The creep curves were divided into two regions by a dashed line.

Analysing the tensile creep mechanism at low stresses

To analyse the contribution of damage development during creep at 66 MPa and 132 MPa, AE detection results are analysed. It is found that very few AE signals (less than 5) are detected for specimens tested at 66 MPa, indicating that the damage development during creep at 66 MPa is negligible. On the contrary, considerable AE events are found in the case of creep at 132 MPa. As seen in Figure 6-2, AE hits below 60 dB are detected along the creep process, indicating a continuous presence of fibre-matrix debonding and matrix cracks (correlated with AE hits having amplitudes below 60 dB [110]) inside the composites.

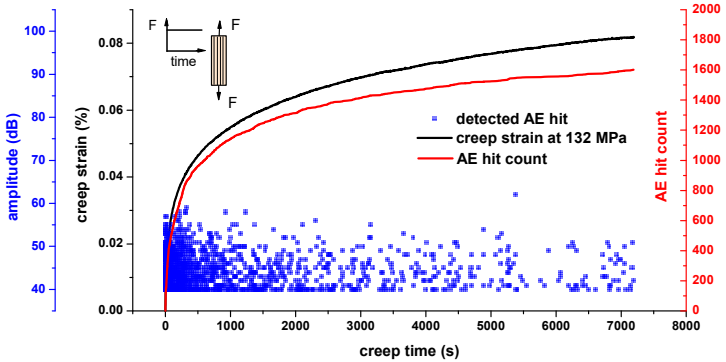


Figure 6-2: AE signals detected during creep at 132 MPa (44% of UTS)

It is worth to note that UD flax fibre composites has an appreciable creep deformation in fibre direction at 66 MPa without the contribution of damage development. Such perceivable creep deformation at low creep stress is not seen often for UD glass/carbon fibre composites loaded in fibre direction, but is only seen when load is applied in off fibre-axis direction [123–126]. The mechanisms that can contribute to the perceivable creep at 66 MPa are analysed as follows.

Firstly, a single flax fibre can exhibit creep at tensile loading. A loaded flax fibre in fibre direction is analogous to an off-axis loaded UD FRPs. As introduced before, flax fibres themselves are composites having cellulose micro-fibrils embedded in a hemicellulose/pectin matrix (Figure 2-2). In S2 layer, the micro fibrils are helically wound around the second layers of cell wall, having off-fibre axis angles of 10° [30]. Due to off-axis loaded fibrils, time-dependent shear deformation of hemicellulose/pectin matrix can occur at low stress, because polymers show viscoelastic and viscoplastic response to load regardless of the magnitude of stress and strain [127]. Likewise, flax fibres are also off-axis aligned in a fibre bundles (Figure 3-1). This twisted fibre bundle structure can favour the time-dependent shear deformation of the epoxy matrix at fibre interface at low load, resulting in creep of composites. Nedjar [128] simulated creep deformation of a carbon fibre epoxy UD composites, and found that a slight off axis tensile load angle

(θ =5°) can result in an appreciable creep deformation in load direction, whereas creep deformation in fibre direction upon 0° tensile load is negligible. Considering the off-axis angle (10°) of the micro fibrils in S2 layer (Figure 2-2) and the off-axis aligned flax fibres in a bundle (Figure 3-1), it can be concluded that time-dependent shear deformation of the matrices (hemicellulose/pectin matrix in flax fibres and the epoxy matrix) plays a major role in the creep of UD FFCs in fibre direction at low stress.

It is reasonable to assume that the abovementioned shear deformation of the matrices become more significant with the increasing creep stress, hence are important creep sources at all stress levels. However, creep at high stresses can be influenced by the presence of the damage development. The damage development at high creep stresses can even lead to substantial change in material properties because fibre reinforced composites are sensitive to damages. This assumption is confirmed in the next subchapter.

6.1.2 Creep properties at high stresses

Tensile creep curves and rupture life at high stresses

Figure 6-3 shows tensile creep behaviour of flax fibre composites at 180 MPa, 210 MPa and 240 MPa. Creep curves exhibit similar shape with those tested under lower stresses until the rupture of specimens. A tertiary stage featured by a rapid increase in creep deformation before rupture point is not observed. Overall strain at rupture was listed in Table 6-2. Higher stress leads to a higher creep rupture strain. It is worth to note that creep ruptured specimens have a relatively smaller strain to rupture compared to that from monotonic tensile tests (1.62±0.04%).

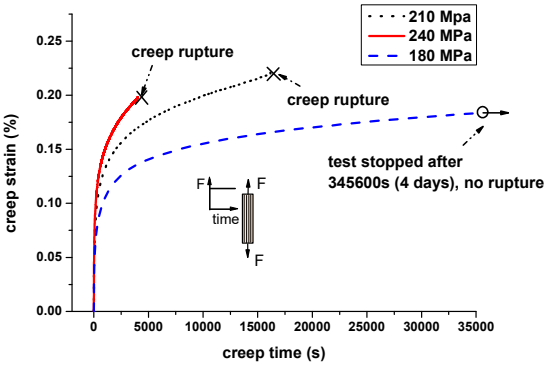


Figure 6-3. Representative creep strain curve at different stress levels

Creep rupture life is strongly dependent on the creep stress. The majority of specimens loaded at 240 MPa (80% of UTS) break within one hour. Specimens loaded at 210 MPa (70% of UTS) withstand longer up to a few hours. With further reduction of stress to 180 MPa (60% of UTS), the specimen could survive over 96 hours.

Table 6-2: Tensile creep rupture life and the overall strain at rupture

Creep stress	Creep rupture life (s)	* Overall strain at rupture (%)
180 MPa	> 345600	-
210 MPa	17104 ± 6630	1.34±0.06
240 MPa	1406 ± 1308	1.46±0.05

*Strain at break from monotonic tensile tests is 1.62±0.04%

AE detection results

Flax fibre composites exhibit a relatively short rupture life upon high constant tensile loads. The short creep rupture life correlates well with the short tension-tension fatigue duration at high stresses. E.g. Liang et al. tested fatigue duration of UD flax fibre epoxy composites. The fatigue life is around 4000 cycles (ca. 1000s) at maximum stress level of 70% UTS [12]. Therefore, it can be concluded that creep damage effects played an important role in fatigue properties.

Intense damage development during creep is observed for the ruptured ones as expected. Figure 6-4 and Figure 6-5 show the detected AE signals during

creep at 210 MPa and 240 MPa, respectively. Extensive AE signals are detected over the creep time span in both creep stresses. The vast majority of AE signals are below 60 dB and distribute along the creep phase. They can be correlated with damage events of matrix cracking, fibre-matrix debonding [25]. AE signals larger than 60 dB are mainly detected in the last creep stage before rupture. These AE signals could be correlated to more severe damage events of fibre pull outs, or even fibre breakages [25]. The detected AE hits clearly reveal that intensive damage events occur along the creep process.

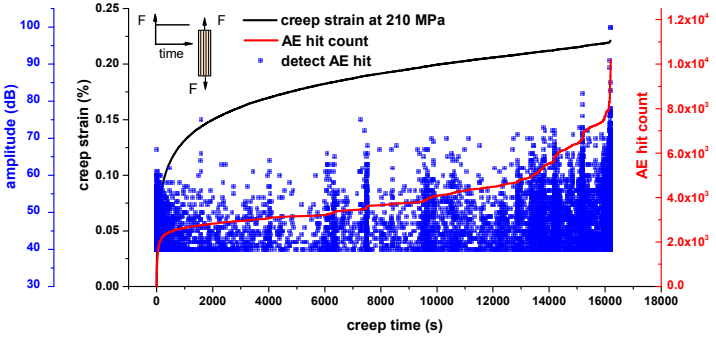


Figure 6-4: AE signals detected during creep at 210 MPa (70% UTS)

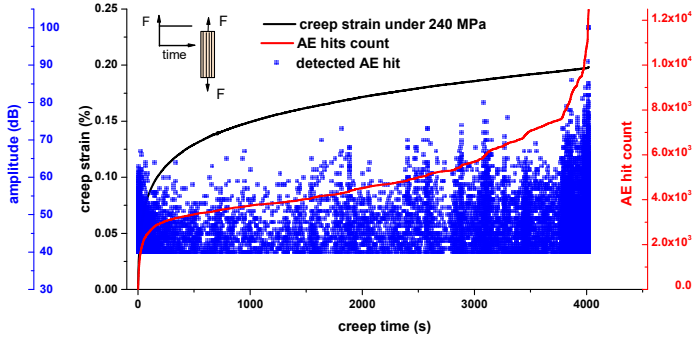


Figure 6-5: AE signals detected during creep at 240 MPa (80% UTS)

Figure 6-6 shows the creep strain at 180 MPa and AE signals development along creep deformation. AE hit counts and AE hits larger than 60 dB are

much less than those recorded at 210 MPa and 240 MPa, indicating less severe damage events (fibre pull out and fibre breakages) during creep at 180 MPa even for 96 hours.

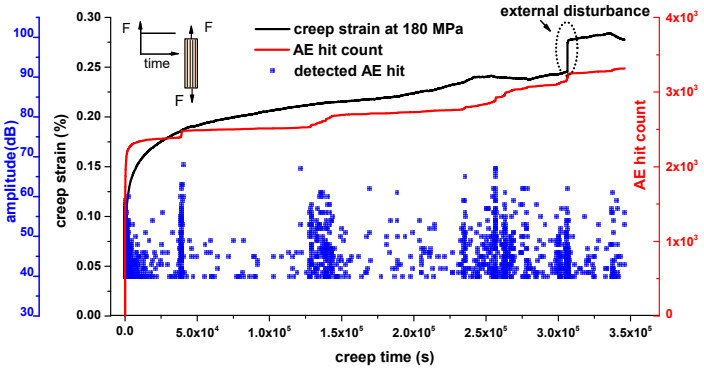


Figure 6-6: AE signals detected during creep at 180 MPa (60% UTS)

Overall strain at rupture

It is interesting to observe that the strain at failure is larger for a monotonic tensile test than for a high stress creep test. This is counter intuitive because high creep stress is expected to yield a larger strain at failure than monotonic tensile load due to accumulated creep deformation. To understand this phenomenon, the representative stress-strain curves at monotonic tensile load and creep loads are compared in Figure 6-7. As seen, creep curves at 210 MPa and 240 MPa can be divided into two distinct phases, corresponding to the load increasing phase and the creep phase. The load increasing phases of creep curves show nearly no difference with monotonic tensile curve and almost coincide with it. In creep phases, strain increases continuously at constant stress showing remarkable creep. The accumulated creep deformation does not yield larger strains to failure, but terminates at smaller strains (ε_{cr210} and ε_{cr240} in Figure 6-7) compared to the strain to failure from monotonic tensile tests ($\varepsilon_{mo-break}$ in Figure 6-7). The termination of creep deformation is ascribed to the 'early' ruptures of composites. As have discussed above, intensive damage events occur during creep. The damage development will result in a continuous decrease of the

residual strength of composites during creep, until rupture happens when the residual strength of composites equals to the applied creep stress. Hence, the accumulated intensive damage development is responsible for the 'early' rupture at high creep stress, resulting 'insufficient' accumulated creep deformation before rupture. In addition, the intensive damage development also accounts for the absence of typical tertiary stage in creep-time curve at which creep rate increase considerably leading to a large amount of deformation.

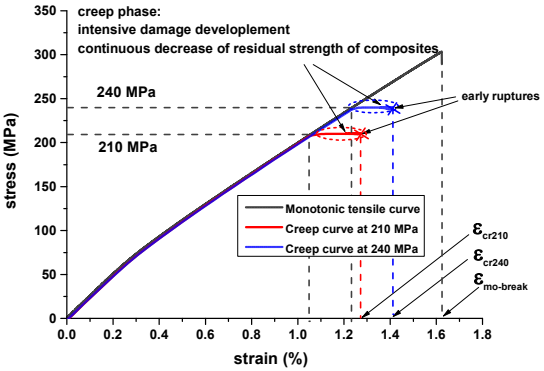


Figure 6-7: Representative stress-strain curves of monotonic tensile test and creep rupture tests

Analysing the creep rupture surfaces

The failure mechanisms analysed above are confirmed by the SEM observations on creep rupture surfaces. Failure mechanisms, e.g. damages like matrix cracks, fibre-matrix deboning, and fibre pull outs are observed (Figure 6-8). These failure mechanisms are indeed similar to those seen in monotonic tensile tests, as displayed in Figure 5-8. Mahboob et al. [21] also found that the failure mechanism of FFCs under long term fatigue tests were similar to those identified in static tensile tests. It is worth to note that extensive matrix cusps at fibre interfacial area are observed in both monotonic tensile tests and creep rupture tests, indicating a high shear strain in fibre interfacial regions which is favoured by off- axis aligned flax fibres.

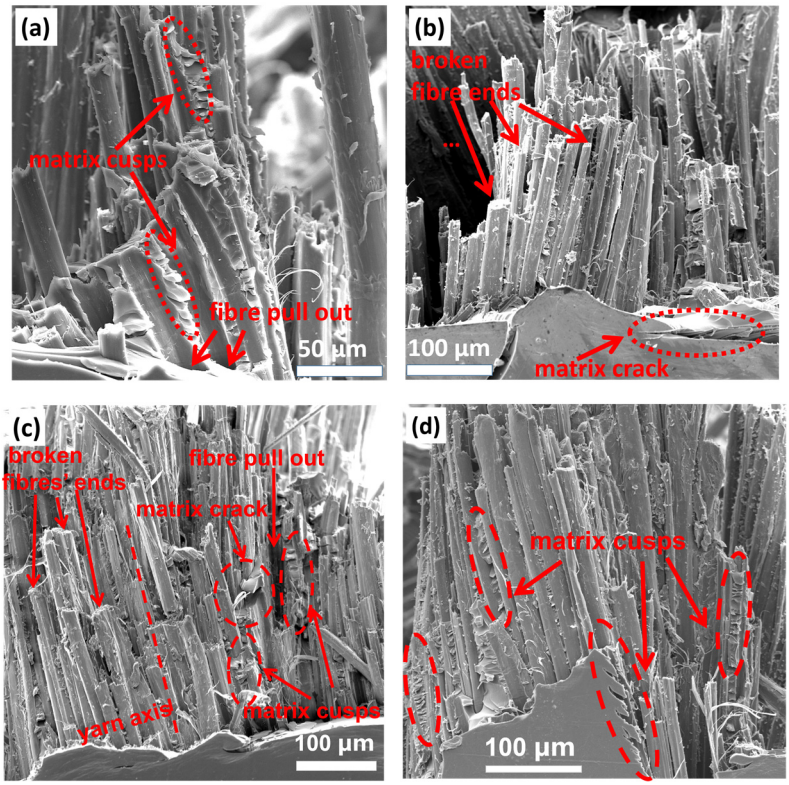


Figure 6-8: Fracture morphology of [0°] specimens under monotonic tensile loads and creep loads (**a, b** – monotonic tensile loads; **c, d** –creep load of 210 MPa)

6.2 Influence of water absorption on creep

It is interesting to investigate the influence of water absorption on tensile creep properties of FFCs since no available data is found in literature. Creep deformation is expected to increase significantly because the tensile modulus is remarkably degraded by water absorption. It is however not sure whether the creep rupture life would be improved by water absorption.

Two high stress levels (240 MPa and 270 MPa) are chosen to investigate the creep rupture properties of FFCs at wet states (Table 6-1). The increased creep deformation is confirmed by the high rupture strains listed in Table 6-

3. The strain at rupture of wet conditioned specimens is significantly higher than that of dry specimens. Similar to the dry composites, wet conditioned specimens resist less deformation under creep loads than under monotonic tensile loads. Furthermore, no apparent tertiary stage (featured by a rapid increase in creep deformation before rupture point) is observed. The reasons would be the development of extensive damages during creep, same with what have been analysed for dry specimens.

Table 6-3. Overall strain (%) before failure of specimens

Tests	Water[1]	Humid[2]
Monotonic tensile	3.51±0.04	2.93±0.05
Creep at 240 MPa	3.09±0.04	2.40±0.04
Creep at 270 MPa	3.16±0.03	2.55±0.03

[1]Conditioned in water bath for 87 days for monotonic tensile specimens, 88 days for creep rupture specimens; [2]Conditioned in 30°C, 80% for 86 days for monotonic tensile specimens, 87 days for creep rupture specimens

It is found that the creep rupture life of FFCs is indeed extended by water absorption. Figure 6-9 compares the creep rupture life of FFCs at dry and wet states. At the same creep stress of 240 MPa, the averaged creep rupture life increases by 281% and 745% for specimens conditioned in water bath (88 days) and humid environment (87 days), respectively. The increase in the duration before rupture can be directly correlated to the increase in monotonic tensile strength after water absorption, where the tensile strengths for dry, water conditioned (87 days) and humid conditioned (86 days) composites are 300.25±7.09 MPa, 340.91±3.82 MPa and 351.15±6.12 MPa, respectively. The improvement in creep rupture life and tensile strength reveals that water absorption, not as often expressed as 'water ageing', does have some positive effect on the mechanical properties and the durability of FFCs.

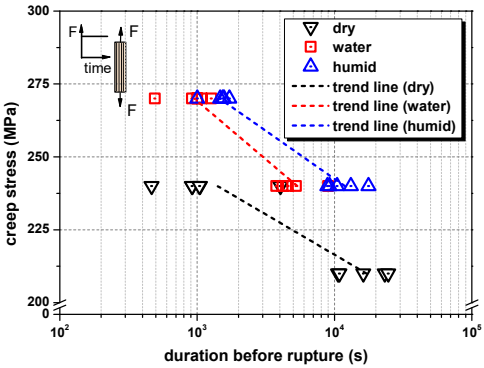


Figure 6-9: Duration before creep rupture of FFCs at dry and wet state at different creep stress levels (water: conditioned in water bath for 88 days, humid: conditioned in 30°C, 80% RH for 87 days)

6.3 Influence of defined FA treatment approach on the creep resistance

The influence of FA treatment on creep resistance of FFCs is investigated at one low stress level and one high stress level, as shown in Table 6-1. Similar to untreated UD FFCs, FA treated ones exhibit a relatively short rupture life of 985.4 ± 347 s at 188 MPa (about 80% of their UTS), showing no significant influence on the creep rupture life after treatment. However, the creep deformation is significantly reduced compared to untreated ones. In the case of creep at 132 MPa, the initial strain and overall creep strain of FA treated composites are on average 19% and 34% lower than those of untreated ones, respectively. The reduced creep after FA treatment can be ascribed to the improved inter-fibre and fibre-matrix bonding, which constraints the shear deformation of matrix at fibre interface. Furthermore, much less damages (mainly refering to matrix cracks and fibre-matrix debondings) are found for FA treated composites than untreated ones, as evidenced by AE detection results (Figure 6-11).

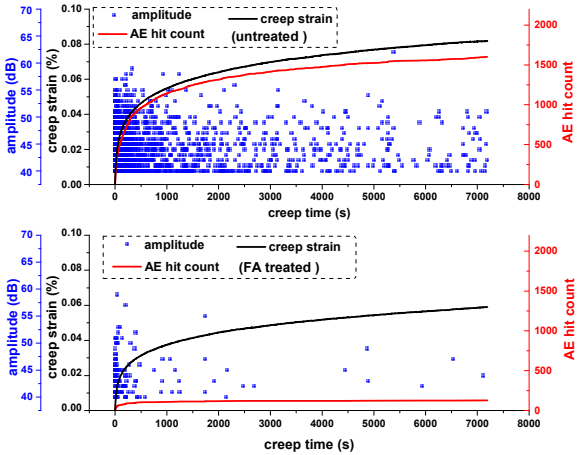


Figure 6-10: Representative creep strain curves of untreated and FA treated composites at 132 MPa and the detected AE hits

The good inter-fibre and fibre-matrix bonding is evidenced by observing the rupture surfaces of FA treated specimens at 188 MPa (Figure 6-11). Flax fibres are strongly bonded with matrix (some part could be polymerized FA) and even splitted showing the micro fibrils. Furthermore, residual matrix adhered to the fibre surfaces, indicating a strong fibre-matrix bonding as well.

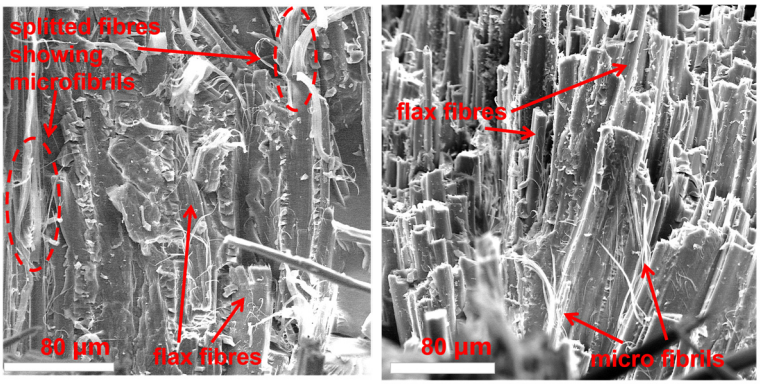


Figure 6-11: Morphology of fracture surfaces of FA treated composites at creep stress of 188 MPa

6.4 Fatigue properties of composites

6.4.1 Fatigue performance

Figure 6-12 illustrates the fatigue life of [0°] and [±45°] specimens, plotted in log scale against the maximum stress (σ_{max}). The fatigue performance strongly depends on the layout of fibre reinforcement as expected, with [0°] specimens showing superior fatigue properties than that of [±45°] specimens. The fatigue strength for a high number of cycles (1 million) is approximatively 120 MPa (0.4 UTS) for [0°] specimens, and is approximately 40 MPa (0.55 UTS) for [±45°] specimens, in agreement with results reported in literature (Table 2-2). The Wöhler law appears to be a good fit to the experimental fatigue performance of [0°] specimens within in the investigated stress span. This is consistent with the findings in literature, where a linear S-N model relationship is found applicable to FFCs [21]. In this regard, a linear fit is also applied to [±45°] specimens using data at two stress levels. The fitted linear functions are shown in Figure 6-12.

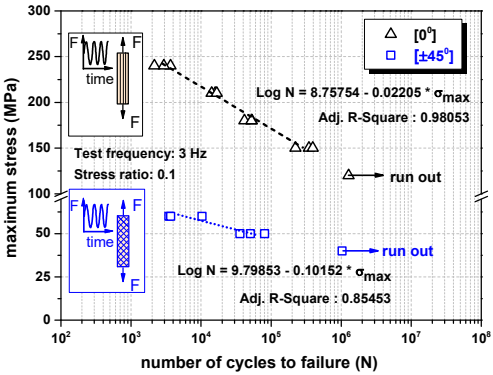


Figure 6-12: S-N curves of [0°] and [±45°] specimens under cyclic tensile loading

6.4.2 Fatigue behaviour

The changes in fatigue behaviour of [0°] and [±45°] specimens are identified by the representative hysteresis loops of load cycles at different fatigue phases. As seen in Figure 6-13, hysteresis loops are found to shift to higher strains with the increase of load cycles, indicating the presence of permanent

deformation during fatigue for both [0°] and [±45°] specimens. The slope of hysteresis loop also evolves with the fatigue cycles but shows different trends depending on the fibres layout. [0°] specimens exhibit an increasing trend of hysteresis slope, while [±45°] specimens displays an opposite trend. In addition, the hysteresis loops of [0°] and [±45°] specimens possess different tendencies with regard to the loop areas.

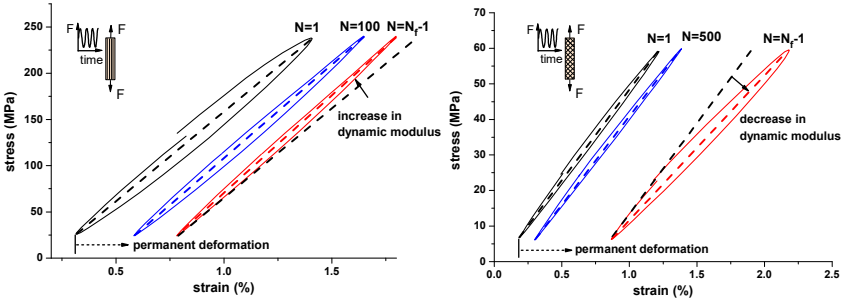


Figure 6-13: Illustrations of hysteresis loops of a [0°] specimen (left, N_f=3662 cycles) and a [±45°] specimen (right, N_f=3473 cycles) at cyclic loads

Stiffness evolution

The dynamic modulus of a loading cycle, defined as the slope of the hysteresis stress-strain loop, is used to analyse the stiffness evolution during cyclic loading. Figure 6-14 illustrates the evolution of dynamic modulus over the fatigue life for [0°] specimens (left) and [±45°] specimens (right).

[0°] specimens exhibit a remarkable increase in dynamic modulus over fatigue life at all investigated stress levels (from 0.5 UTS to 0.8 UTS). The increase can be roughly divided into two stages: a first stage featured by a rapid rise followed by a relatively stable stage where the dynamic modulus increases much more slowly. The overall increase in dynamic modulus, regardless of the stress levels, is around 9%. The stiffening phenomenon of [0°] composites over fatigue life is opposite with what have been observed for glass and carbon fibre composites as introduced in chapter 2, and is in agreement with the findings reported by Liang et al. [75] and EI Sawi et al. [77], recently. The reason can be attributed to the reorientation of micro fibrils in load direction and the global realignment of flax fibres in the matrix

at each cycle of load. Influence of stress levels on the stiffening degree however couldn't be derived from the results of this study due to the variation. Y. Ueki et al. [76] stated that it was difficult to see a common trend with respect to the stress level and the stiffening degree. Nonetheless, the influence, if exists, could be small and would be within the intrinsic variation of material properties and the measuring error of experiments.

On the contrary, dynamic modulus of [±45°] specimens possess no increase over fatigue and the evolution process matches the typical three-stage trend (Figure 2-6) that is expected for conventional fibre reinforced composites. A rapid decrease is found in the beginning (the first stage) and at the end of the fatigue life (the third stage), with a relatively moderate decreasing stage between them. The drop in dynamic modulus is mainly ascribed to the damage activity during fatigue loading, which is analysed by the integrated hysteresis loop area below.

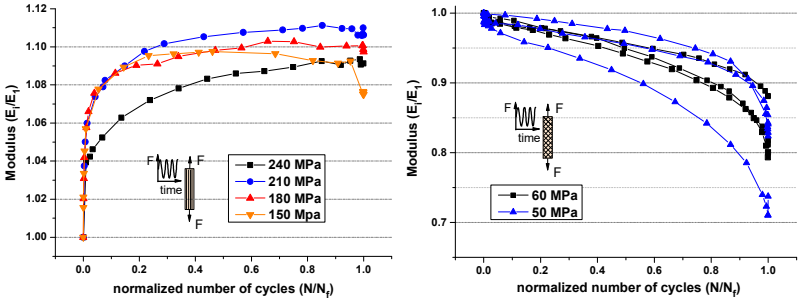


Figure 6-14: Evolution of dynamic modulus of [0°] specimens (left) and ±45° specimens (right) over fatigue life at different maximum stress levels

Hysteresis energy

The magnitude of dissipated energy is an indication of the internal damage activity [74], and can be calculated as the area enclosed by a hysteresis stress-strain loop. The integrated loop area is depicted in Figure 6-15 to analyse the damage activity over the fatigue life. In general, the higher the maximum stress (or the stress amplitude), the higher the magnitude of dissipated energy. [0°] specimens exhibit a decreasing trend in hysteresis energy over fatigue life at all stress levels. The most energy is dissipated in

the beginning of fatigue life. This decreasing trend in dissipated energy is again different with the trend for glass fibre composites [129], where an increase in loop area is normally found at the end of the fatigue life. Notice that the decreasing trend of dissipated energy is similar to that of stiffening trend (Figure 5-12, left), which indicates a correlation between the decrease in dissipated energy and the realignment of flax fibres in load direction. The correlation is also found for [±45°] specimens, where the hysteresis energy increases slowly after a drop in the beginning of the fatigue life, and displays a sharp rise at the end of the fatigue life. The rapid rise in dissipated energy reveals an increase of intensive damage activity at the end of the fatigue life, which results in the drop of dynamic modulus correspondently.

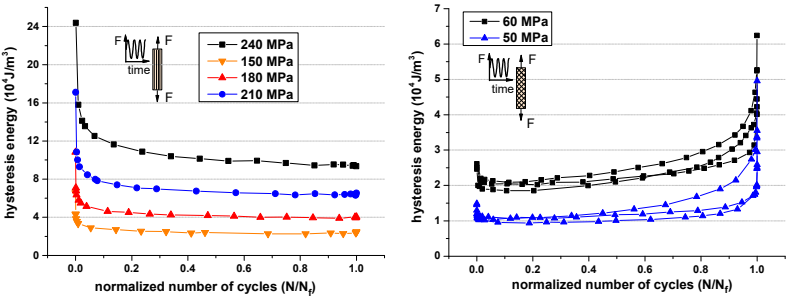


Figure 6-15: Evolution of dissipated energy of [0°] specimens (left) and [±45°] specimens (right) over fatigue life at different maximum stress levels

Permanent deformation

The permanent strain during fatigue loading is analysed by evaluating the increment of minimum strain from the first loading cycle ($\varepsilon^{i}_{min} - \varepsilon^{1}_{min}$). As seen in Figure 6-16, remarkable permanent deformation is found for both [0°] specimens and [±45°] specimens over the fatigue life. The increment strain curves of [0°] specimens evolves with fatigue life in a similar way as the creep deformation with time (Figure 6-1, 6-3). Permanent deformation increases rapidly with a decreasing rate in the beginning of fatigue life, followed by a second region where deformation increases at a slow rate in an approximately linear regime. Indeed, the permanent deformation during fatigue can be considered as creep at an effective creep load, because the

fatigue load effect consists of effects of a non-zero static load superimposed with sinusoidal variations for a loading ratio of 0.1. Generally, the higher the maximum stress, the larger the deformation. Permanent deformation of [±45°] specimens exhibits a similar trend as [0°] specimens for the most of their fatigue life, except that a tertiary stage where a drastical rise at the end of fatigue life is observed. This correlates with the increase in damage activity at the final stage discussed above.

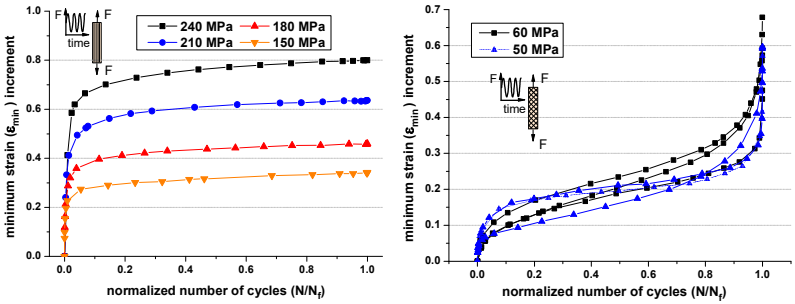


Figure 6-16: Evolution of the increment in minimum strain of [0°] specimens (left) and [±45°] specimens (right) over fatigue life at different maximum stress levels

6.5 Summary

This chapter investigates mechanical properties of FFCs at two fundamental forms of long-term loads: constant load and cyclic fatigue load. The main results and conclusions are as follows:

- Perceivable creep at low stress (22% of UTS) at room temperature is observed for [0°] FFCs without detecting evident damage development during creep. The creep is favoured by the structure that micro-fibrils in S2 layer of flax fibres and the fibres in bundles are off-axis aligned. Upon off-axis loading, time-dependent shear deformation of the matrices (hemicellulose/pectin matrix in flax fibres and the epoxy matrix) occurs and plays a major role in the creep at low stress. The creep deformation of FFCs can be significantly improved by FA treatment, because the improved inter-fibre and fibre-matrix bonding properties better constraints

the shear deformation of the matrix at fibre interface and reduces damages e.g. fibre-matrix debonding during creep loading.

- Creep under high stress shows a relatively short creep rupture life without the presence of a typical tertiary stage before rupture due to the accumulation of intensive damage events. Long term water absorption can extend the creep rupture life of [0°] FFCs due to the enhanced static strength by water absorption.
- The fatigue life of FFCs can be well fitted by the Wöhler law. The fatigue strength for a high number of cycles (1 million) is approximatively 120 MPa (0.4 UTS) for [0°] specimens, and is approximately 40 MPa (0.55 UTS) for [±45°] specimens.
- A continuous increase in dynamic modulus over fatigue life is observed for [0°] FFCs due to the realignment of flax fibres. The realignment of flax fibres over fatigue loading life also leads to a distinct decreasing trend of hysteresis energy for [0°] FFCs compared to that of [0°] glass fibre composites and [±45°] FFCs. Considerable permanent deformation over fatigue life is found for both [0°] FFCs and [±45°] FFCs.

7 Conclusions and outlook

7.1 Conclusions

This work investigates the durability of the mechanical performance of a bio-composite reinforced by flax fibres, i.e. the mechanical properties upon long term water absorption and the mechanical properties at long term constant loads and fatigue loads. In addition, an alternative flax fibre pre-treatment that can improve the fibre-matrix bonding and maintain the improvement upon long term water absorption is introduced. The results yield a better understanding of the durability of bio-composites, which can boost the confidence in wider application of bio-composites in structural components. Based on the obtained results and discussions, the main conclusions are summarised below.

Sensitivity of FFCs in their mechanical properties upon water absorption

The mechanical properties of FFCs are sensitive to water absorption. The sensitivity is reflected in three aspects.

Prior to manufacturing, the flax fibre storage condition has a noticeable influence on the tensile properties of FFCs in fibre direction. The laminate with fibres stored at a dry condition tends to have a lower strength and higher E-modulus compared to that with fibres stored at wet conditions. During manufacturing, pre-drying of fibres introduces a noticeable increase in E-modulus and a slight decrease in strength compared to those manufactured without pre-drying of fibres. The sensitivity in above-mentioned two aspects is mainly ascribed to the sensitivity of flax fibre properties on water absorption. To reduce the variation of mechanical properties of FFCs, attention on fibre storage should be paid and a well-defined manufacturing approach should be applied to control the water content of flax fibres.

Water absorption in the service life of FFCs can have significant influences on the mechanical properties. E-modulus of FFCs decreases continuously with water absorption regardless of the fibre layouts due to the plasticization effect on both matrix and fibres. On the contrary, composite strength shows distinct trends upon water absorption depending on the layout of fibres. Composites having layouts of [90°] and [±45°] exhibit a continuous decreasing trend in strength with water absorption. The decrease is ascribed to the degradation in matrix strength and the fibre-matrix bonding strength. [0°] composites however demonstrate a decrease of strength in the beginning of the water absorption and a subsequent increase of up to 15% higher than the strength at dry state. This distinct changing trend is believed to be related to the competing effects of degradation of fibre-matrix bonding, increased fibre strength and strengthening effects due to realignment of flax fibres in load direction. The realignment of flax fibres is favoured by the increased matrix and fibre ductility and a weakened fibre-matrix bonding after water absorption. The results can help clarifying the contradictory findings on the effects of water absorption on the strength of [0°] PFCs.

With better understanding of the effects of water absorption on the mechanical performance of PFCs, it is possible to prevent or even utilize the sensitivity of PFCs to water absorption in specific application cases.

An alternative fibre pre-treatment to improve the fibre-matrix bonding

The flax fibre pre-treatment approach (referring to the eventually defined one) proposed in this study is very effective. Inter-fibre bonding and the fibre-matrix interface is improved by the FA treatment. This is evidenced by the enhanced modulus of [0°] and [90°] FFCs, and by observing fracture surfaces of specimens via SEM. Creep deformation is significantly reduced by FA treatment due to the improved inter-fibre bonding and the fibre-matrix bonding. The improved bondings result from three-fold mechanisms. Firstly, the treated fibre surfaces are more hydrophobic due to the coated PFA on the fibre surfaces. Hence, they are more compatible with the hydrophobic matrix than untreated flax fibres. Secondly, treated fibre surfaces have rough

areas where PFA is coated, providing a larger surface area for mechanical interlocking with matrix. Lastly, there could be chemical bonds generated between PFA and matrix, although none conclusive evidences are given in this study.

The improvement in bonding properties is also well maintained upon long term water absorption. This is indicated by the superior modulus of FA treated [0°] FFCs than untreated counterparts over the water absorption process and the morphology of fracture surfaces of wet [0°] FFCs. Owing to this fact, the realignment effects of flax fibres of wet [0°] FFCs is less pronounced than that of untreated ones. The strength of FA treated [0°] composites show a slow decrease with water absorption but is more stable than that of untreated [0°] FFCs.

In addition, the FA is a green chemical that is cheaply derived from the agricultural wastes which retains the environmental benefits and cost effectiveness of plant fibres. One disadvantage of the current FA treatment approach is the degradation of fibre strength caused by the acid catalyst. This can be however overcome by further optimizing.

In general, the proposed treatment using FA is a very promising alternative in preparation for the industry.

Mechanical properties of PFCs under long term constant loads and fatigue loads

Attention on the creep deformation of FFCs should be raised. [0°] FFCs display appreciable creep deformation at low stress without detecting significant damage development during creep. The creep is not seen for [0°] UD glass or carbon fibre composites and is believed to be favoured by the unique structure that micro-fibrils in S2 layer of flax fibres and the fibres in yarns are off-axis aligned. Upon off-axis loading, time-dependent shear deformation of the matrices (hemicellulose/pectin matrix in flax fibres and the epoxy matrix) can be pronounced at low stress, thus plays a major role in the creep of [0°] FFCs at low stress. The short creep rupture life of FFCs (few hours at creep stress of 70% of their UTS) is consistent with the short fatigue life of FFCs at high stress. Intensive damage development during high

stress creep is found, evidenced by the AE detection. Water absorption can extend the creep rupture life of FFCs at high stress, in accordance with the enhanced static strength of wet specimens at equilibrium absorption state.

The fatigue life of FFCs under cyclic loads can be well fitted by Wöhler's law. The fatigue strength for a high number of cycles (1 million) is approximatively 120 MPa (0.4 UTS) for [0°] FFCs, and is approximately 40 MPa (0.55 UTS) for [±45°] FFCs. In this regard, the absolute fatigue strength of [0°] FFCs is comparable to that of aluminium, with a lower density than aluminium at the same time. It is interesting to confirm that the fatigue dynamic modulus of [0°] FFCs is found to increase over the fatigue life, evidenced by the increased slope of the hysteresis loop with the increasing number of load cycles. The stiffening effect is attributed to the realignment of flax fibres due to the above-mentioned off-axis structure over fatigue life.

7.2 Outlook

The structure that cellulose fibrils are off-axis aligned in fibres and flax fibres are off-axis aligned in yarns lead to several unique mechanical responses of FFCs, e.g. perceivable tensile creep of [0°] FFCs at low stress, strengthening effect due to pronounced realignment of flax fibres of wet [0°] FFCs and the increase in dynamic modulus of [0°] FFCs over tension-tension fatigue life. In this study, explanation on these unique mechanical responses does not distinguish the contribution of the off-axis cellulose fibrils and the off-axis flax fibres. However, their contribution degree might be different at specific load cases. Further investigation on the distinguished contribution is of necessity to get deeper understand the mechanical response of PFCs.

Mechanical performance of FFCs could be influenced by several environmental factors which brings possible concerns on the durability. This work investigates on the mechanical performance of PFCs upon water absorption at short and long term. Influence of other environmental factors e.g. UV light, temperature, fungi, etc. (or the combination of them) would also be of great interest for the research and industry. E.g. the impact of fungi on damaged PFCs in humid environment can be completely unique with the research on glass/carbon fibre composites. In addition, the influence of

water absorption on the fatigue performance of PFCs is worth to study, considering the improvement on the creep rupture life by water absorption that is found in this study.

The fibre-pre-treatment approach using FA is promising, however the approach still needs to be optimized to overcome the side effects of the degradation in fibre strength. Possible ways would be: varying the reaction conditions and changing the type of catalysts. On one hand, the acid concentration, temperature, and amount of FA solution for impregnation can be optimized to reduce the fibre strength degradation and maintain the improvement in fibre-matrix and inter-fibre bonding at the same time. On the other hand, the acid used for catalysing the polycondensation of FA can be changed to avoid the degradation of hemicellulose at high temperature with acid. E.g., γ – alumina or UV light could be used as catalyst sources [113].

8 References

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Publications

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